

Detailed comparison of the kinetic data for the present system with those for oxidation of other dimeric halo-(amine)copper(I) complexes by dioxygen¹³ is not straightforward because k_D is regarded as a composite parameter. This amounts to saying that variation in k_D for oxidation of a series of dimeric $L_4Cu_2X_2$ (L monodentate) or $(L-L)_2Cu_2X_2$ (L-L bidentate) complexes can be ascribed to variations in K_6 and k_7 or both if the suggested mechanism is general.

There are two major differences between the present system and those referring to tetrameric $[L_4CuX]_4$ and dimeric $[L_2CuCl]_2$ copper(I) oxidation.^{6,13} First, the product of oxidation of $(TEED)_2Cu_2Br_2$ is dimeric, whereas monodentate pyridine ligand systems give tetrameric $[L_4Cu_4X_4]O_2$ products.^{6,13} Second, ΔH_D^\ddagger and ΔS_D^\ddagger for $(TEED)_2Cu_2Br$ oxidation (Table VII) are substantially more positive than those observed in the monodentate pyridine ligand systems (where $\Delta H_T^\ddagger =$

$2.1-5.9$ kcal mol⁻¹; $\Delta S_T^\ddagger = -(35-48)$ cal deg⁻¹ mol⁻¹; $\Delta H_D^\ddagger = 0-1.4$ kcal mol⁻¹; $\Delta S_D^\ddagger = -(38-39)$ cal deg⁻¹ mol⁻¹).^{6,13}

Acknowledgment. We gratefully acknowledge financial support for this work through Biomedical Research Support Grant RR07143 from the Department of Health and Human Services and Faculty Research Grant 7590 from Northeastern University (G.D.).

Registry No. $(TEED)_2Cu_2Br_2$, 88510-91-2; $(TEED)_2Cu_2Br_2O$, 88510-92-3; $(TEED)_2Cu_2Br_2CO_3$, 72029-99-3; TCFH, 88-06-2; Cu, 7440-50-8.

Supplementary Material Available: Positional and isotropic thermal parameters for hydrogen atoms in the independent molecules of $(TEED)_2Cu_2Br_2$ (Table IIa), anisotropic thermal parameters (Table III), and a listing of observed and calculated structure factors for $(TEED)_2Cu_2Br_2$ (20 pages). Ordering information is given on any current masthead page.

Notes

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Preparation of Activated Cobalt and Its Use for the Preparation of Octacarbonylcobalt

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Received March 16, 1983

Transition-metal carbonyl complexes have played a very important role in the development of modern organometallic chemistry and have continued to attract attention because of their diverse chemistry and their potential value as stoichiometric and catalytic reagents for synthesis.¹ Among the many preparative methods that exist for metal carbonyls, only a very limited number of transition metals have been demonstrated to react directly with carbon monoxide to give reasonable quantities of metal carbonyl complexes. Nickel and iron are the prototypic examples of the direct reaction of transition metals with carbon monoxide to give $Ni(CO)_4$ and $Fe(CO)_5$, respectively.² Finely divided chromium prepared by the reduction of $CrCl_3 \cdot 3THF$ with potassium in benzene has been found to be sufficiently activated to react with carbon monoxide at 280 atm and 220 °C to form $Cr(CO)_6$ in 51% yield.³

The method first used to prepare $Co_2(CO)_8$ ⁴ was the reaction of carbon monoxide in the absence of solvent at 30–40 atm and 150 °C with finely divided cobalt prepared by the high-temperature hydrogen reduction of cobalt oxalate. Since that time other workers have also succeeded in preparing the carbonyl from elemental cobalt. For example, when cobalt carbonate containing sulfur was impregnated on infusorial earth, reduced with hydrogen at 400 °C, and then carbonylated at 120 °C and 100 atm, yields of $Co_2(CO)_8$ up to 97% were obtained.⁵ A pelletized reduced cobalt oxide was reported

to give good yields of $Co_2(CO)_8$ at 170 °C and very high pressures of carbon monoxide (700–1000 atm).⁶

More commonly used methods for the preparation of $Co_2(CO)_8$ involve reduction of cobalt(II) salts with high-pressure hydrogen-carbon monoxide mixtures at elevated temperatures. For example, hydrated cobalt(II) acetate in acetic anhydride at 160–180 °C under 40 atm of hydrogen and 160 atm of carbon monoxide gave a 60% yield of $Co_2(CO)_8$.⁷ Hydrated cobalt carbonate reacts with 1:1 hydrogen-carbon monoxide at 238 atm and 150–160 °C in petroleum ether to give $Co_2(CO)_8$ in a 53% yield.⁸ An indirect preparation of $Co_2(CO)_8$ used $Co(NO_3)_2$, KCN, and KOH under 1 atm of carbon monoxide to give potassium tetracarbonylcobaltate.⁹ This material was then acidified to give the hydride, $HCo(CO)_4$, which was decomposed at 100 °C to produce hydrogen and $Co_2(CO)_8$.

As part of our continuing program of preparing highly reactive metal powders and utilizing them for synthetic purposes,¹⁰ we wish to report here the preparation of $Co_2(CO)_8$ from cobalt metal in good yields under relatively mild conditions. The reduction of anhydrous cobalt halides with alkali metals in ethereal solvents in the presence of a catalytic amount of naphthalene has previously been reported to give a very reactive form of cobalt.^{10b,c}

A more reactive form of cobalt resulted however when the cobalt halide was added to a cold solution of preformed lithium naphthalide. It is not clear whether the reaction was actually a homogeneous reduction of dissolved and solvated cobalt

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halide by soluble naphthalene radical anions or a heterogeneous reduction. A heterogeneous reduction was a reasonable possibility because of the low solubility of cobalt halides in ethereal solvents, especially at low temperature.

The cobalt powders prepared by this method were extremely finely divided, as shown by their slow sedimentation rate without the use of a centrifuge. The brown supernatant liquids after centrifugation contained the bulk of the naphthalene as well as the more finely divided cobalt particles and a fraction of the alkali metal halide byproducts. In one reaction, employing a stoichiometric amount of naphthalene, it was possible to remove nearly all the naphthalene (97%) by centrifugation followed by washing with several portions of fresh solvents. It has not proven possible to remove all of the alkali metal halide, even with repeated washings, owing to its limited solubility and slow rate of dissolution in ethers. The alkali metal halide may be trapped in the cobalt microparticles and therefore not accessible to the solvent.

We are attempting to define the nature of the cobalt metal powders with the aid of surface area measurements, particle size determination, and various surface analysis techniques that will be described in future communications.

Cobalt, prepared in this way from lithium naphthalide and cobalt chloride in glyme, reacted with carbon monoxide under comparatively mild conditions (100 °C, 95 atm) to give dicobalt octacarbonyl, $\text{Co}_2(\text{CO})_8$, in good yields. In one experiment a 79% yield was obtained after 7 days under these conditions. Reactions run for shorter times at the same or lower temperatures gave poorer yields of isolated metal carbonyl. Surprisingly, however, a carbonylation run carried out on an incompletely reduced sample of cobalt chloride gave a 73% yield of product after 16 h at 100 °C. Carbonylation of cobalt powders prepared in diglyme gave slightly poorer results. When cobalt powder prepared in glyme at -22 °C by reacting lithium, naphthalene, and cobalt chloride was treated with carbon monoxide at 95 atm and 100 °C, a 56% yield of $\text{Co}_2(\text{CO})_8$ was isolated.

The cobalt powders sometimes showed impressive reactivity even when nonoptimum conditions were used for their preparation. For example, when lithium was used to reduce cobalt chloride, at room temperature in THF in the presence of a catalytic quantity (6 mol % naphthalene based on lithium) of naphthalene, a cobalt powder was obtained that was sufficiently reactive to give a 26% yield of $\text{Co}_2(\text{CO})_8$ when treated with 78 atm of CO at 120 °C in an unstirred reactor. Even at 14 atm and 78 °C, cobalt powder from lithium, cobalt iodide, and 20 mol % naphthalene in THF at room temperature could be converted to $\text{Co}_2(\text{CO})_8$ in a 16% yield. The use of THF as a solvent for the reduction of cobalt halides offers no advantages, and it may, in fact, be detrimental since THF is known to react with electrophiles as well as with the naphthalene radical ion.

Reductions of cobalt iodide by potassium in THF or glyme produced a cobalt powder of significantly decreased reactivity. In these cases, the yield of $\text{Co}_2(\text{CO})_8$ obtained was low, even though a stirred bomb and more forcing conditions (95 atm, 120 °C) were used for the carbonylation.

Finally, we note that the carbonylations of cobalt powders dispersed on alumina to avoid sintering of fine cobalt particles into larger less reactive conglomerates failed to provide any useful quantity of $\text{Co}_2(\text{CO})_8$ at all.

Conclusion

A method of preparing highly reactive cobalt powder and its use in the preparation of dicobalt octacarbonyl have been described.

The cobalt powder is very easily prepared from readily available starting materials with simple equipment. It reacts quickly and smoothly under relatively mild conditions to

provide a good yield of cobalt carbonyl.

Work is in progress to determine the usefulness of these cobalt powders for the preparation of other complexes with small molecule ligands as well as to determine the catalytic activity of such powders.

Experimental Section

A. General Procedures and Equipment. All manipulations of air- or moisture-sensitive materials were performed in a Vacuum Atmospheres Corp. drybox, in a glovebag, or on a utility vacuum line using standard procedures.¹¹ Argon was freed of oxygen and moisture by passing it through 1-m-long columns of activated BTS catalyst, P_2O_5 , and KOH. Tetrahydrofuran (THF, Aldrich Gold Label), glyme (Aldrich), and diglyme (Aldrich) were distilled from sodium-potassium alloy under argon while hexanes were distilled from blue solutions of potassium benzophenone. Anhydrous cobalt chloride and cobalt iodide were purchased and used as received from Cerac. Naphthalene, lithium, and potassium were reagent grade and used as received. Carbonylations were performed in unstirred (125-mL) or stirred (600-mL) Parr reactors constructed of type 316 stainless steel and equipped with glass liners. Linde C.P. grade carbon monoxide was used without further treatment. Infrared solution spectra in hexanes were obtained in 0.1-mm amalgam sealed cells on a Perkin-Elmer 283 spectrophotometer calibrated with polystyrene.

B. Preparation of $\text{Co}_2(\text{CO})_8$ from Activated Cobalt. Method 1. In a 100-mL round-bottom flask equipped with an argon inlet and a Teflon-clad stir bar were placed 0.691 g (108.0 mmol) of lithium and 14.085 g (109.9 mmol) of naphthalene. Attached to this flask via one of its side arms was a bent glass tube terminating in a 50-mL flask containing 6.754 g (52.64 mmol) of cobalt chloride.

Glyme (70 mL) was added to the lithium-naphthalene mixture and the dark green solution allowed to stir overnight at -22 °C to ensure complete dissolution of all the lithium. The solution was then chilled to -50 °C and the cobalt chloride added by tipping the apparatus and rotating the side-arm tube.

The solution thickened immediately and had to be warmed to -15 °C to allow stirring. After stirring overnight, at -15 °C, the gray-black mixture was warmed to room temperature where it became sufficiently mobile to be transferred via an 18-gauge cannula to a prepurged centrifuge tube capped with a rubber septum. The solids were then separated from an opaque brown solution by centrifugation at 1200–1800 rpm. The solids were washed by centrifugation with three 25-mL portions of fresh glyme and six 25-mL portions of hexanes before being transferred to the stirred Parr bomb with 200 mL of hexanes. The hexanes washing was found to be necessary to remove the ethereal solvent, which was found to be detrimental to the high yield preparation of $\text{Co}_2(\text{CO})_8$. The washing also serves to remove most of the naphthalene, simplifying the isolation of the pure metal carbonyl. The bomb was pressurized to 95 atm with carbon monoxide and allowed to stir (400 rpm) at room temperature (ca. 18 °C), while the pressure drop vs. time was monitored. After 2 h the pressure had dropped to approximately 90% of the theoretical amount and had ceased to drop as precipitously as in the early stages of the reaction. The reaction mixture was heated to 100 °C and a rapid decrease in carbon monoxide pressure was observed over a period of ca. 14 h, after which time the pressure continued to drop but at a much slower rate. The drop was monitored for 7 days and found to be linearly decreasing with time, suggesting slow leakage around the stirrer shaft. The reaction mixture was now cooled and vented and the soluble components isolated from a gray residue by filtration. The solution was concentrated to a small volume in vacuo and 7.093 g of reddish brown crystals were isolated from the mother liquor by filtration. These crystals were identified as $\text{Co}_2(\text{CO})_8$ (79%) by comparison of their infrared solution spectrum to that reported in the literature;¹² IR (literature values shown in parentheses) 2076 s (2075), 2065 wsh (2064) 2048 vs (2047), 2034 msh (2035), 2028 s (2028), 1869 m (1867), 1860 m (1858) cm^{-1} . A small amount of $\text{Co}_4(\text{CO})_{12}$ is apparently present in this sample as revealed by an extra peak at 2060 cm^{-1} . Other bands expected for this species are either too weak to observe in this sample or are obscured by those of $\text{Co}_2(\text{CO})_8$.

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In separate experiments using similar quantities of the same starting materials and the same procedures, a 17% yield of $\text{Co}_2(\text{CO})_8$ was obtained after 1.7 h and 95 atm and 20 °C and a 47% yield of $\text{Co}_2(\text{CO})_8$ after 16 h at 95 atm and 107 °C.

Method 2. In a separate preparation, 0.441 g (63.54 mmol) of lithium, 6.881 g (53.69 mmol) of naphthalene, and 4.018 g (30.95 mmol) of cobalt chloride were placed in a 100-mL flask and 50 mL of diglyme was added to the mixture at -35 °C. After stirring overnight at that temperature there was little evidence of reaction. It was necessary to stir the mixture at -20 °C for an additional 72 h. When the gray-black slurry was then transferred to a centrifuge tube as previously described (vide supra), a scrap of unreacted lithium (0.060 g, 8.62 mmol) was recovered from the reaction flask.

The cobalt powder was washed by centrifugation with six 30-mL portions of hexanes and loaded into the stirred bomb with 150 mL of hexanes. The bomb was pressurized with carbon monoxide to 95 atm and allowed to stir overnight. In this experiment, the pressure drop with time was not monitored as closely as in the preceding experiment. After 8 h the theoretical pressure drop was observed. Heating to 100 °C overnight and cooling to room temperature failed to cause an appreciable change in the pressure of the remaining carbon monoxide. The bomb was then vented and the contents filtered to give a clear brown solution from which 3.856 g of $\text{Co}_2(\text{CO})_8$ were isolated by concentration of the solution in vacuo. The yield, based on cobalt chloride, was therefore 73%.

Method 3. Lithium (0.506 g, 72.85 mmol), 9.138 g (71.39 mmol) of naphthalene, and 4.608 g (35.49 mmol) of cobalt chloride were placed in a 250-mL flask. Glyme (140 mL) was added to this mixture and the resulting slurry allowed to stir at -22 °C for 3 days. The gray-black product slurry was centrifuged and washed with hexanes at room temperature as described previously and placed in a stirred bomb with 300 mL of hexanes. After treatment with 95 atm of carbon monoxide for 4 days at 100 °C, a brown solution was obtained which when concentrated to small volume gave 3.400 g (56%) of orange-red $\text{Co}_2(\text{CO})_8$.

Acknowledgment. We thank Professor T. A. George for the loan of the stirred high-pressure bomb used in this work. Funding for this work was provided by the U.S. Army Research Office.

Registry No. $\text{Co}_2(\text{CO})_8$, 10210-68-1; CO, 630-08-0; cobalt chloride, 7646-79-9; cobalt iodide, 15238-00-3; lithium naphthalide, 27939-69-1; cobalt, 7440-48-4.

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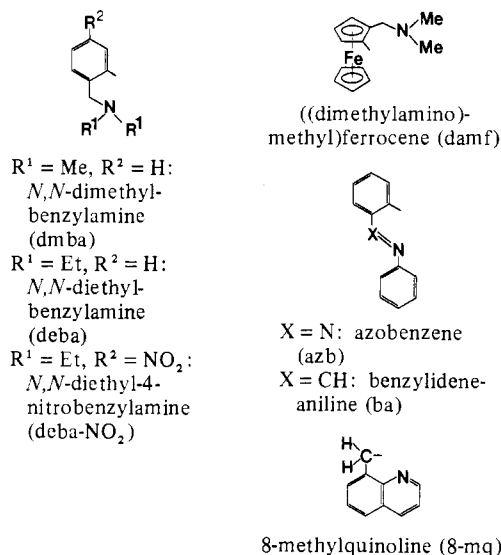
Exchange of Cyclopalladated Ligands in Chloro-Bridged Palladium(II) Complexes

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Received April 29, 1983

Cyclometalated complexes of transition metals have been intensively studied and a variety of their reactions reported.¹ In particular two types of substitution reactions are known, namely the exchange or substitution of ancillary nonmetalated ligands¹ and transmetalation reactions between cyclometalated complexes and free metal salts forming new metalocycles.² We report here a novel ligand-exchange reaction between a cyclopalladated complex and a free ligand to afford a new metalocycle. We have recently obtained evidence³ that such a reaction could occur in the case of ortho-palladated *N,N*-

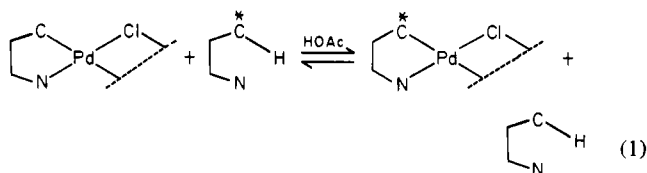
Chart I



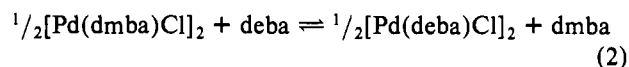
dialkylbenzylamines in acetic acid solvent.

Results and Discussion

This work deals with reaction 1, employing the ligands listed in Chart I.



The results obtained are summarized in the Table I. Entries 1 and 2 show that $[\text{Pd}(\text{dmdba})\text{Cl}]_2$ reacts smoothly with azobenzene at 50 °C in binary acetic acid (HOAc)-benzene or chloroform mixtures affording excellent crystals of $[\text{Pd}(\text{azb})\text{Cl}]_2$ in good yields. Other N donor ligands such as *N,N*-diethylbenzylamine, *N,N*-diethyl-4-nitrobenzylamine, benzylideneaniline, and 8-methylquinoline also undergo this ligand-exchange reaction, giving the respective chloro-bridged dimers, eq 2 and entries 4-6, Table I. On the other hand, a



ligand with an O donor atom, namely acetanilide, which is known to form an ortho-palladated complex,⁴ does not react, entry 7, Table I. No ligand exchange is observed without acetic acid as co-solvent, entries 8 and 9, Table I. Adding benzene or chloroform to a reaction mixture is necessary to increase solubility of the starting complexes. The low solubility of a majority of chloro-bridged cyclopalladated compounds restricts the number of those that can be tested in reaction 1. As a result, only $[\text{Pd}(\text{dmdba})\text{Cl}]_2$ (mentioned above) and $[\text{Pd}(\text{damf})\text{Cl}]_2$ have been successfully used in the reaction, entries 10-12, Table I. The latter proceeds under milder conditions compared to the former.

The ligand exchange between $[\text{Pd}(\text{dmdba})\text{Cl}]_2$ and 8-methylquinoline has been used to confirm the reaction stoichiometry, entry 6, Table I. GLC analysis of the reaction products has shown the presence of 0.091 and 0.042 mmol of free dmdba and 8-mq, respectively. This means that 0.11 mmol of the incoming ligand is consumed when 0.09 mmol of the initially metalated ligand is liberated, in accord with the metal to ligand 1:1 stoichiometry of reaction 1 (within experimental uncertainties).

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