In order to make rough estimates of the M–P stretching force constants, we have calculated the frequencies of the tetrahedral MR_4 ($R = P(OC_2H_5)_3$) molecules using the Urey–Bradley force field.[18] Assuming that H (bending force constant) is 0.05 mdyn/Å and F (repulsive force constant) is 0.4 mdyn/Å, all of the calculated frequencies can be fitted to those observed within an error of 25 cm^{-1} if K (the M–P stretching force constant) is taken to be 1.7, 2.7, and 3.7 mdyn/Å for Ni(0), Pd(0), and Pt(0), respectively. The R–M–R bending bands must be below 100 cm^{-1} since they are calculated to be 90–80 cm^{-1}. Evidently, the value of K depends upon that of F. Therefore, we have calculated K values by changing F. The latter value is expected to be relatively constant among the metals studied. For a fixed F value we have always found that the order of the K values is $Ni(0) < Pd(0) < Pt(0)$ and that these values are separated by about 1.0 mdyn/Å from each other.

The order of the M–P stretching force constants obtained can be interpreted in terms of increasing π- or σ- (or both) bond order of the M–P bonds in the order $Ni(0) < Pd(0) < Pt(0)$. It is interesting to note that the Ni(0)–P stretching frequencies of $Ni[P(OC_2H_5)_3]_4$ assigned in this work (335–305 and 210 cm^{-1}) are much higher than that reported for $Ni[P(OCH_2)_3CCH_3]_4$ (157 cm^{-1}).[7] The nature of Ni–P bonds in these two compounds is expected to be similar. Also, the total masses of these two phosphine ligands are similar. Thus, the Ni–P stretching frequencies are expected to be similar as long as we approximate their normal vibrations by using a simple MR_4-type model. It is probable that the 157-cm^{-1} band of $Ni[P(OCH_2)_3CCH_3]_4$ corresponds to the 210 cm^{-1} of $Ni[P(OC_2H_5)_3]_4$ and that a band corresponding to the 335–305 cm^{-1} of the latter is obscured by the presence of other bands in the former compound. Even so, the Ni–P stretching frequencies are different between these two compounds. This result may suggest that a more complete calculation including all of the atoms of the ligands is necessary to account for the Ni–P stretching frequencies of metal phosphine complexes containing different ligands.

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Synthesis of Hexadecacarbonylhexacobalt

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Considerable confusion has existed regarding the neutral carbonyls in the cobalt subgroup. Cobalt is known to give $Co_2(CO)_8$ and $Co_4(CO)_{12}$, and rhodium is stated to give $Rh_2(CO)_8$, $Rh_4(CO)_{12}$, and $Rh_6(CO)_{16}$, while for iridium both $Ir_2(CO)_8$ and $Ir_4(CO)_{12}$ have been reported.[1] We now report the preparation of $Co_6(CO)_{16}$[2] which completes the series of the cobalt compounds. Later some information will be given about the isolation of $Ir_6(CO)_{16}$,[3] and some evidence will be adduced against the existence of the hypothetical $Rh_2(CO)_8$ and $Ir_2(CO)_8$.[3,4]

Experimental Section

Analyses have been carried out as reported in a previous paper.[5] $K_2[Co_6(CO)_{15}]$ and $K_4[Co_6(CO)_{14}]$ have been prepared according to the literature.[5,6] Infrared spectra have been recorded on a Perkin-Elmer 621 spectrophotometer.

Synthesis of $Co_6(CO)_{16}$.—A solution of $HgCl_2$ (6 g) and NaCl (6 g) in water (25 ml) was rapidly added to an aqueous solution (25 ml) of $K_2[Co_6(CO)_{15}]$ (4 g). A fine red-brown precipitate was formed, filtered off, washed with water, and vacuum dried over P_2O_5 for 24 hr. The infrared spectrum of this solid was consistent with that of a mixture (about 1:2) of $Co_4(CO)_{12}$ and $Co_6(CO)_{16}$.

The dry solid was washed five times with toluene (20 ml) until the toluene was only slightly brown and then was extracted with isopentane. During this extraction the temperature was controlled using a heating bath at 55°, and an atmosphere of carbon monoxide was maintained over the boiling isopentane, but on cooling the carbon monoxide was replaced by nitrogen. This prevented decomposition to cobalt metal during the boiling and formation of $Co_4(CO)_{12}$ during the cooling.

The first isopentane extract (12 hr) containing $Co_4(CO)_{12}$ mixed with $Co_6(CO)_{16}$ was discarded; then, after 48 hr of extraction, black crystals of $Co_6(CO)_{16}$ were obtained (0.305 g). *Anal.* Calcd for $Co_6(CO)_{16}$: C, 23.97; Co, 44.10. Found: C, 23.84; Co, 44.08. In the C=O stretching region of the infrared spectrum there are bands at 2113 w, 2061 vs, 2057 sh, 2026 w, 2020 w, 2018 w, 1806 w, 1772 vs cm^{-1} (Nujol mull). The same product was obtained starting from $Na_4[Co_6(CO)_{14}]$ or using iron trichloride as the oxidizing agent.

Reaction between $Co_6(CO)_{16}$ and Pyridine.—Pyridine (4 ml) and $Co_6(CO)_{16}$ (0.1096 g) were allowed to react together under high vacuum at room temperature for 15 min. Pumping out with a Toepler pump gave 0.705 cm^3 of gas (1.4%). The infrared spectrum of the solution showed only the band of the $Co(CO)_4^-$ anion at 1890 cm^{-1}; some metallic cobalt was also present.

Results

Oxidation of a water solution containing the pentadecacarbonylhexacobaltate(2−) or the tetradecacarbonylhexacobaltate(4−) anion with excess of a mild reagent such as iron trichloride or sodium tetrachloromercurate precipitates a mixture of $Co_4(CO)_{12}$ and $Co_6(CO)_{16}$.

The isolation of the hexadecacarbonylhexacobalt offers special difficulties due to its low solubility, low thermal stability, and high reactivity. The best results have been obtained by fractional extraction with isopentane. The hexadecacarbonylhexacobalt has been isolated as black, well-formed crystals (brown in mull). In nitrogen it decomposes at 110–120°; under vacuum (0.001 Torr), at 70–80° without sublimation. In air

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the crystals are moderately stable, being incompletely decomposed in 24 hr.

Hexadecacarbonylhexacobalt reacts rapidly with many Lewis bases: with pyridine, methanol, acetone, and wet diethyl ether derivatives of the $Co(CO)_4^-$ anion are formed. With 2-propanol and anhydrous diethyl ether the reaction product is $Co_4(CO)_{12}$. With tetrahydrofuran both products are obtained. In every case a minor amount of cobalt metal is also formed. With pyridine some carbon monoxide is evolved (1.4%).

Crystalline $Co_6(CO)_{16}$ is stable both to water and to 0.1 *N* hydrochloric acid. Sodium methylate in methanol gives a dark solution containing the $Co_6(CO)_{15}^{2-}$ and $Co(CO)_4^-$ anions. In toluene $Co_6(CO)_{16}$ reacts slowly with carbon monoxide at atmospheric pressure and room temperature to give $Co_4(CO)_{12}$.

Discussion

The insolubility of the neutral carbonyls in water is probably responsible for the formation of a mixture of $Co_4(CO)_{12}$ and $Co_6(CO)_{16}$ by oxidation. Under such heterogeneous conditions neither the excess oxidant nor the water itself is able to attack rapidly the neutral carbonyls. It is known that under homogeneous conditions there is a complete oxidation of cobalt carbonyls to metal halides.[7]

It was not possible to ascertain whether the $Co_6(CO)_{16}$ is formed *via* the $Co_6(CO)_{15}^{2-}$ anion when using a derivative of the $Co_6(CO)_{14}^{4-}$ anion as starting material. The oxidation of a tetrahydrofuran solution of $Na_4[Co_6(CO)_{14}]$ with deficiency of iodine gave a mixture of $Na_2[Co_6(CO)_{15}]$ and $Na[Co(CO)_4]$, but this oxidation may have been complicated by the reaction with the carbon monoxide liberated.[6]

The reactivity of $Co_6(CO)_{16}$ with Lewis bases (B) agrees with the reactivity of octacarbonyldicobalt[1] and of dodecacarbonyltetracobalt.[1,5] In order to explain the different products formed in this process, we have considered three possible different reactions. Reaction 1 would be expected to give the tetracarbonylcobaltate anion without any evolution of carbon monoxide. Reaction 2 should yield $Co_4(CO)_{12}$ with some metallic cobalt. Reaction 2 is eventually followed by reaction 3, the usual reaction between $Co_4(CO)_{12}$ and Lewis bases.[1,5] In this case the formation of cobalt metal, of tetracarbonylcobaltate anion, and of free carbon monoxide (11.1%) should occur.

$$Co_6(CO)_{16} + 12B \rightleftharpoons 2[CoB_6][Co(CO)_4]_2 \qquad (1)$$

$$3Co_6(CO)_{16} \xrightarrow{B} 4Co_4(CO)_{12} + 2Co \qquad (2)$$

$$3Co_4(CO)_{12} + 24B \longrightarrow 4[CoB_6][Co(CO)_4]_2 + 4CO \qquad (3)$$

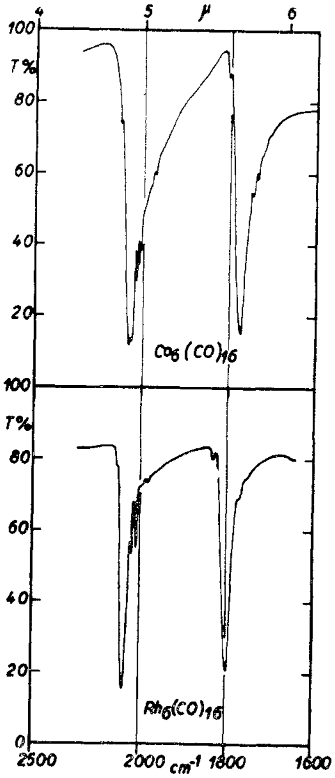

Figure 1.—Infrared spectra of $Co_6(CO)_{16}$ and $Rh_6(CO)_{16}$ (Nujol mull).

The available data show that these processes are concurrent. Pyridine, methanol, acetone, and wet diethyl ether give the product expected for reaction 1, but, at least in the case of pyridine, reactions 2 and 3 also contribute to a minor extent as it is shown by the evolution of some carbon monoxide (1.4%). 2-Propanol and anhydrous diethyl ether give the product expected from reaction 2.

The reactivity of $Co_6(CO)_{16}$ toward carbon monoxide agrees with the similar reactivity of other octahedral cobalt clusters such as the derivatives of the pentadecacarbonylhexacobaltate(2−)[5] and of the tetradecacarbonylhexacobaltate(4−).[6]

The infrared spectra of $Co_6(CO)_{16}$ and of $Rh_6(CO)_{16}$ are compared in Figure 1. Similarity of the infrared spectra and isomorphism[8] demonstrate the presence of a structure common to both compounds. It is known that in the case of rhodium the metal atoms are bonded to twelve terminal and four "face" bridging carbon monoxide groups.[9]

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