parameters and ν_{CN}. Data tabulated elsewhere[2] reveal no widespread correlation between C–N distances and ν_{CN}.

Finally, it is pointed out that the isotropic interactions responsible for the resolution in the nmr spectra of $Fe(R_1R_2dtc)_2(tfd)$ complexes are believed to be mainly dipolar in origin. Approximate calculations of the relevant geometric factors based on the known structure **1**[29] reveal that these factors should produce significant chemical shift differences among methylene protons of a given dtc ligand. Related conclusions have been reached by LaMar[59] for $Co(acac)_2(phen)$ species. An analysis of the isotropic shifts will be attempted upon completion of single-crystal paramagnetic resonance and magnetic susceptibility measurements of **1**.

Acknowledgment. This research was supported by the National Science Foundation under Grant No. GP-7576X. We thank Dr. D. Coucouvanis for a copy of ref 2 prior to publication, Drs. W. D. Horrocks, R. C. Fay, and I. Bernal for disclosure of unpublished results, and J. G. Gordon, II, and Dr. J. R. Hutchison for useful discussions.

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Synthesis and Properties of Hydridodinitrogentris(triphenylphosphine)cobalt(I) and the Related Phosphine–Cobalt Complexes

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Received May 29, 1970

Abstract: Hydridodinitrogentris(triphenylphosphine)cobalt(I) (**1**) was prepared from cobalt(II) and cobalt(III) acetylacetonates, organoaluminum compounds, triphenylphosphine, and molecular nitrogen. The effect of substitution of the triphenylphosphine ligands by other phosphine ligands on the infrared N_2 stretching band was studied. The nitrogen ligand coordinated to cobalt can be easily displaced reversibly by hydrogen and ammonia as shown in Figure 2. Complex **1** exhibits various chemical properties as shown in Figure 3 in agreement with its formulation as a hydride complex. Methylcobalt and ethylenecobalt complexes were also prepared in a similar manner using dimethylaluminum monoethoxide and diethylaluminum monoethoxide, respectively, and by employing an argon atmosphere. Reactions of the ethylene complex as shown in Figure 4 are consistent with its formulation as a zerovalent complex. Complex **1** catalyzes a variety of reactions such as the oxidation of triphenylphosphine, the reduction of nitrous oxide, the hydrogenation of ethylene, the dimerization and isomerization of olefins, and polymerization of vinyl compounds. The role of the cobalt–hydride bond in catalytic reactions involving olefins is discussed.

Since the discovery of nitrogen fixation under mild conditions by systems composed of transition metal compounds and reducing agents,[1] and the succeeding isolation of N_2-coordinated transition metal complexes by reaction of transition metal complexes with nitrogen compounds,[2,3] the problem of nitrogen fixation by transition metal complexes has attracted great interest.[4]

Previously we reported briefly the preparation of the N_2–cobalt complex which was the first example of the isolation of an N_2-coordinated complex prepared by a direct reaction of a transition metal complex with molecular nitrogen.[5] The complex was prepared by the reaction of cobalt(III) acetylacetonate, diethylaluminum monoethoxide, and triphenylphosphine in an atmosphere of nitrogen.

$$Co(acac)_3 + AlEt_2OEt + PPh_3 + N_2 \longrightarrow \underset{\mathbf{1}}{CoH(N_2)(PPh_3)_3}$$

We assigned the formula $Co(N_2)(PPh_3)_3$ to the complex at that time on the basis of elementary analysis, its infrared spectrum which did not exhibit a Co–H band, and a pyrolysis experiment which released 1.0 mol of N_2 and only 0.1 mol of H_2 per cobalt. Following our paper, apparently the same compound was prepared by Misono, Uchida, and Saito[6] using a similar method with triisobutylaluminum instead of diethylaluminum monoethoxide. They suggested that the N_2 complex may be a mixture of $Co(N_2)(PPh_3)_3$ and $CoH(H_2)(PPh_3)_3$. By a different method, Sacco and Rossi prepared $CoH(N_2)$-

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(1) M. E. Vol'pin and V. B. Shur, *Nature (London)*, **209**, 1236 (1966), and references cited therein.

(2) (a) A. D. Allen and C. V. Senoff, *Chem. Commun.*, 621 (1966); (b) A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu, and C. V. Senoff, *J. Amer. Chem. Soc.*, **89**, 5595 (1967); (c) A. D. Allen and F. Bottomley, *Accounts Chem. Res.*, **1**, 360 (1969).

(3) J. P. Collman and J. W. Kang, *J. Amer. Chem. Soc.*, **88**, 3459 (1966); J. P. Collman, M. Kubota, F. S. Vastine, J. Y. Sun, and J. W. Kang, *ibid.*, **80**, 5430 (1968).

(4) For recent reviews, see (a) R. Murray and D. C. Smith, *Coord. Chem. Rev.*, **3**, 429 (1968); (b) K. Kuchynka, *Catal. Rev.*, **3**, 111 (1969); (c) G. H. Olive and S. Olive, *Angew. Chem.*, **81**, 679 (1969); (d) references cited in a paper by T. Ito, S. Kitazume, A. Yamamoto, and S. Ikeda, *J. Amer. Chem. Soc.*, **92**, 3011 (1970); (e) T. Ito and A. Yamamoto, *Yuki Gosei Kagaku Kyokai Shi*, **28**, 598 (1970); (f) Yu. G. Borod'ko and A. E. Shilov, *Usp. Khim.*, **38**, 761 (1969).

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(6) A. Misono, Y. Uchida, and T. Saito, *Bull. Chem. Soc. Jap.* **40**, 700 (1967); A. Misono, Y. Uchida, T. Saito, and K. M. Song, *Chem. Commun.*, 419 (1967).

$(PPh_3)_3$ from $CoH_3(PPh_3)_3$ (**2**) with molecular nitrogen.[7,8] Later, the structure of complex **1** with the N_2 ligand bonded linearly with cobalt and in the trans position to the Co–H bond was established by an X-ray analysis of the N_2 complex,[9a,b] and the presence of the hydridic hydrogen was also observed in an nmr spectrum of **1**.[9c] We have also confirmed by chemical reactions of the N_2 complex that formulation of the complex as the hydride is more reasonable than formulation as a zerovalent cobalt complex, and additionally confirmed that other cobalt complexes without hydride can be formed under certain conditions. This paper is concerned with the synthesis and properties of the N_2-coordinated cobalt complex $CoH(N_2)(PPh_3)_3$ and of some related cobalt–phosphine complexes.

Results and Discussion

Preparations of Phosphine–Cobalt Complexes. Hydridodinitrogentris(triphenylphosphine)cobalt(I) (**1**) can be prepared by the reaction of cobalt(III) and cobalt(II) acetylacetonates with organoaluminum compounds and triphenylphosphine in ether in an atmosphere of nitrogen. As the organoaluminum compound, diethylaluminum monoethoxide, triethylaluminum, or triisobutylaluminum can be used. Initially, diethylaluminum monoethoxide was used, but in later experiments triisobutylaluminum was employed since it gives better yields (60–70%). Cobalt tris- and bisacetylacetonates give the same results as cobalt acetylacetonate, but because of the ease of synthesis, cobalt trisacetylacetonate was used throughout the experiment. The reaction of anhydrous cobalt dichloride with triphenylphosphine and diethylaluminum monoethoxide under nitrogen gave $CoCl_2(PPh_3)_2$ and $CoCl(PPh_3)_3$, but no nitrogen complex was obtained.

When dimethylaluminum monoethoxide was used in an argon atmosphere, methyltris(triphenylphosphine)cobalt, $CoCH_3(PPh_3)_3$ (**3**), was obtained. The formation of the methyl–cobalt complex suggests that the reactions of cobalt acetylacetonates with ethyl- and isobutylaluminum compounds to give $CoH(N_2)(PPh_3)_3$ also proceed through the formation of intermediate alkyl–cobalt complexes as in the reactions of iron, cobalt, and nickel acetylacetonates with dipyridyl and diethylaluminum monoethoxide, affording ethyl–transition metal complexes.[10] In our efforts to isolate the unstable ethylcobalt complex by the reaction of cobalt acetylacetonate, diethylaluminum monoethoxide, and triphenylphosphine in an argon atmosphere and in ether solution, we found that dark brown crystals[11] were obtained and the composition of the unstable crystals corresponded to formulation as a zerovalent cobalt complex, $[Co(C_2H_4)(PPh_3)_3]$ (**4**). The complex may be dimeric, but owing to the instability of the complex its molecular weight could not be determined. The chemical properties of the complex which will be described later indicated the absence of any hydridic hydrogen. The variation of the products from $Co(acac)_3$, $AlEt_2OEt$, and PPh_3 under similar reaction conditions, except for the difference of atmosphere, suggests that N_2 is playing the role of a ligand in the splitting of the ethyl–cobalt bond. We assume that when N_2 is coordinated to the cobalt complex, abstraction of a hydrogen from the ethyl group, forming a cobalt hydride bond, may be favored, whereas in the absence of N_2, a homolytic fission of the ethyl–cobalt bond may be favored, followed by a disproportionation of the ethyl groups to form ethane and ethylene, the latter of which combines with the zerovalent cobalt complex, affording $[Co(C_2H_4)(PPh_3)_3]$.

On the other hand, the reaction of cobalt(III) acetylacetonate, 1,2-bis(diphenylphosphino)ethane (DPPE), and diethylaluminum monoethoxide yielded the known complexes $Co(DPPE)_2$[12] and $CoH(DPPE)_2$[13] both in argon and nitrogen atmospheres, whereas the reaction of DPPE with $CoH(N_2)(PPh_3)_3$ gave only $CoH(DPPE)_2$.[7,14]

Infrared Spectra of the Nitrogen Complex. The infrared spectrum of $CoH(N_2)(PPh_3)_3$ recrystallized from toluene exhibits a sharp band in benzene solution at 2088 cm⁻¹ which is assigned to the N_2 stretch, but no band assignable to ν_{Co-H} was observed. When we first obtained the dinitrogen complex, it was not known whether the N_2 ligand was coordinated to cobalt in an "end-on" or in a "side-on" manner. We expected that the two modes of coordination might be differentiated by examining the infrared spectrum of the dinitrogen complex partially labeled with ^{15}N. In addition to the $\nu_{^{14}N\equiv^{14}N}$ and $\nu_{^{15}N\equiv^{15}N}$ bands, the appearance of two $\nu_{^{15}N\equiv^{14}N}$ absorptions corresponding to $Co—^{14}N\equiv^{15}N$ and $Co—^{15}N\equiv^{14}N$ species were anticipated for the linear structure and no splitting for the side-on structure. Shilov and coworkers[15] observed the splitting of the $\nu_{^{15}N\equiv^{14}N}$ band in $[Ru(N_2)(NH_3)_5]^{2+}$ by 4 cm⁻¹, whereas Eischens did not observe the splitting in the case of nitrogen chemisorbed on nickel.[16]

In Figure 1 is shown the infrared spectrum of $CoH(N_2)(PPh_3)_3$ prepared by the reaction of $CoH_3(PPh_3)_3$ with nitrogen gas containing 70.4% ^{15}N. In support of the assignment of the original band at 2088 cm⁻¹ to an N_2 stretch, three bands corresponding, respectively, to $\nu_{^{14}N\equiv^{14}N}$, $\nu_{^{14}N\equiv^{15}N}$, and $\nu_{^{15}N\equiv^{15}N}$ are observed. However, no splitting of the $\nu_{^{14}N\equiv^{15}N}$ band was observed even with a high-resolution grating spectrometer with a spectral slit width of 0.5 cm⁻¹. The failure to observe the $\nu_{^{15}N\equiv^{14}N}$ band split does not necessarily ex-

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[7] (a) A. Sacco and M. Rossi, *Chem. Commun.*, 316 (1967); (b) *Inorg. Chim. Acta*, 2, 127 (1968).

[8] Recently another route for preparing complex 1 was reported: (a) M. Rossi and A. Sacco, *Chem. Commun.*, 471 (1969); (b) S. Otsuka and T. Taketomi, presented at the 19th Symposium on Coordination Chemistry, Sendai, Japan, Oct 1969.

[9] (a) J. H. Enemark, B. R. Davis, J. A. McGinnety, and J. A. Ibers, *Chem. Commun.*, 96, (1968); (b) B. R. Davis, N. C. Payne, and J. A. Ibers, *J. Amer. Chem. Soc.*, 91, 1240 (1969); (c) A. Misono, Y. Uchida, M. Hidai, and M. Araki, *Chem. Commun.*, 1044 (1968).

[10] A. Yamamoto, K. Morifuji, S. Ikeda, T. Saito, Y. Uchida, and A. Misono, *J. Amer. Chem. Soc.*, 87, 4652 (1965); 90, 1878 (1968); T. Saito, Y. Uchida, A. Misono, A. Yamamoto, K. Morifuji, and S. Ikeda, *J. Organometal. Chem.*, 6, 572 (1966); *J. Amer. Chem. Soc.*, 88, 5198 (1966).

[11] Wilke, *et al.*, claimed in a patent (German Patent 1191375) that a dark green complex, $Co(PPh_3)_4$, was obtained by a reaction of $Co(acac)_2$, $AlEt_2OEt$, and PPh_3 in benzene in an argon atmosphere. However, we have been unable to obtain the dark green complex either by starting from $Co(acac)_3$ or from $Co(acac)_2$.

[12] A. Sacco and M. Rossi, *Chem. Commun.*, 602 (1965).

[13] (a) A. Sacco and R. Ugo, *J. Chem. Soc.*, 9012 (1964); (b) F. Zingales, F. Canziani, and A. Chiesa, *Inorg. Chem.*, 2, 1303 (1963).

[14] Recently a quantitative preparation of $CoH(DPPE)_2$ from $Co(acac)_3$, DPPE, and Bu_2AlH in a nitrogen atmosphere has been reported: J. Loberth, H. Nöth, and P. V. Rinze, *J. Organometal. Chem.*, 16, P1 (1969).

[15] Yu. G. Borod'ko, A. K. Shilova, and A. E. Shilov, *Dokl. Akad. Nauk SSSR*, 176, 1297 (1967).

[16] R. P. Eischens and J. Jacknow, *Proc. Int. Congr. Catal., 3rd, 1964*, 628 (1965); R. P. Eischens, Preprint, The Japan–U. S. A. Seminar on Catalytic Science, A-4-1, Tokyo, Japan, 1968.

clude the linear structure. We assume that the lack of splitting of the $\nu_{^{14}N\equiv^{15}N}$ band may be caused because the force constant of the Co–N stretch is too small compared with that of N≡N. We could not detect a band assignable to $\nu_{Co-N^{17}}$ in a higher frequency region over 400 cm^{-1}. Srivastava and Bigorgne assigned a band at 533 cm^{-1} to Co–N stretch,[18] but we could not detect any shifted band on partial substitution of ^{14}N with ^{15}N. The other purpose of labeling with ^{15}N was to reduce the intensity of the $\nu_{^{14}N\equiv^{14}N}$ band to see if a band due to ν_{Co-H} is hidden behind this strong band. However, we could not still detect the ν_{Co-H} band. Ibers and his coworkers[9a] observed two bands at 2085 and 2105 cm^{-1} for a sample prepared in ether, and suspected that these might be due to the Co-H and N-N stretching frequencies. We observed the similar two bands at 2083 and 2100 cm^{-1} for a sample which was prepared in diethyl ether and solvated with the ether. However, for a sample recrystallized from toluene, bands barely resolvable by a high-resolution spectrometer were observed at 2084 and 2087 cm^{-1} for a solid sample, and in solution only a single band was observed at 2088 cm^{-1}. Therefore, we conclude that the splitting was caused by a crystal effect[7,14,18,19] and is not to be ascribed to ν_{Co-H} and ν_{N_2} bands. The reason for the failure to observe the ν_{Co-H} band is not clear, but some examples of hydrido complexes which do not show any detectable ν_{M-H} band are known.[7b,20]

In order to study the effect of ligands on the bonding of nitrogen, we added various phosphine ligands to a benzene solution containing $CoH(N_2)(PPh_3)_3$ and observed the shift of the ν_{N_2} band.[21] When increasing amounts of tri-*n*-butylphosphine were added, stepwise shifts of the ν_{N_2} band were observed; the original band at 2088 cm^{-1} shifted to 2075, then to 2061, and further down to 2048 cm^{-1} with little intensity change. The last band disappeared when argon was swept through the solution and reappeared on sweeping the solution with nitrogen. Further addition of tributylphosphine caused the irreversible disappearance of the ν_{N_2} band. These results may be explained by assuming the following equilibria

$$\underset{\nu_{N_2}\ 2088\ \text{cm}^{-1}}{CoH(N_2)(PPh_3)_3} + PBu_3 \rightleftharpoons \underset{\nu_{N_2}\ 2075\ \text{cm}^{-1}}{CoH(N_2)(PPh_3)_2(PBu_3)} + PPh_3$$

$$CoH(N_2)(PPh_3)_2(PBu_3) + PBu_3 \rightleftharpoons \underset{\nu_{N_2}\ 2061\ \text{cm}^{-1}}{CoH(N_2)(PPh_3)(PBu_3)_2} + PPh_3$$

$$CoH(N_2)(PPh_3)(PBu_3)_2 + PBu_3 \rightleftharpoons \underset{\nu_{N_2}\ 2048\ \text{cm}^{-1}}{CoH(N_2)(PBu_3)_3} + PPh_3$$

$$CoH(N_2)(PBu_3)_3 + PBu_3 \rightleftharpoons CoH(PBu_3)_4 + N_2$$

Tributylphosphine is a more electron-releasing ligand than triphenylphosphine, and this may be the reason for the lowering of ν_{N_2} band on substitution of triphenylphosphine by tributylphosphine. The flowing of electrons from the ligand to cobalt may enhance the back-donation of electrons from cobalt to nitrogen, thus loosening the N≡N bond. The observation of the four ν_{N_2} bands in the solution with addition of tributylphosphine suggests the presence of four N_2 complexes with different combinations of the phosphine ligands in the solution, and the assignments are shown in the above equations. If these assignments are correct, the band at 2048 cm^{-1} corresponds to $CoH(N_2)(PBu_3)_3$[22] and the reversible appearance of this band may be explained by means of the last equation. The addition of excess tributylphosphine is considered to cause the shift of the equilibrium to the right, interfering with the combination of nitrogen with the cobalt complex. No new band ascribable to the Co–H stretch was observed in benzene solutions.

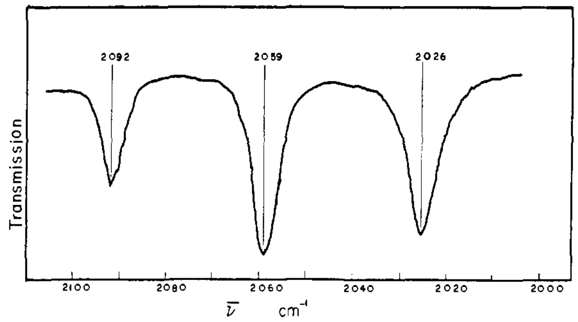

Figure 1. ν_{N_2} bands of $CoH(N_2)(PPh_3)_3$ labeled with ^{15}N. Absorptions at 2092, 2059, and 2026 cm^{-1} correspond to ν_{N_2} bands of Co—^{14}N≡^{14}N, {Co—^{14}N≡^{15}N + Co—^{15}N≡^{14}N} unresolved, and Co—^{15}N≡^{15}N, respectively.

Quite similar shifts of the ν_{N_2} band were observed with tri-*n*-octylphosphine, and the ν_{N_2} band of the complex containing trioctylphosphine was shifted to 2042 cm^{-1} when excess trioctylphosphine was added.

The addition of 1 mol of 1,2-bis(diphenylphosphino)-ethane/mol of **1** caused intensity decrease of the ν_{N_2} band without shift. The band disappeared on sweeping the solution with argon and reappeared on admittance of the nitrogen gas. When more than 2 mol of the di(tertiary phosphine) was added, the ν_{N_2} band was not observable. This may be caused by higher stability of the bis(diphosphine)-cobalt complex. With the combination of two di(tertiary phosphine) ligands with cobalt, the nitrogen molecule is considered to be blocked from coordination with cobalt. We obtained $CoH(DPPE)_2$ as crystals by addition of the di(tertiary phosphine) to $CoH(N_2)(PPh_3)_3$.[7]

The addition of triethyl phosphate caused changes in the spectrum similar to those caused by the addition of the di(tertiary phosphine). The addition of phosphorus trichloride caused the decomposition of the cobalt complex to a cobalt dichloride.

Reactions of $CoH(N_2)(PPh_3)_2$. (a) Reversible Reactions. In order to characterize the properties of this unusual complex, we carried out various reactions, as shown in Figures 2 and 3. One remarkable property

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[17] In the case of $[Ru(NH_3)_5N_2]^{2+}$ two ν_{Ru-N_2} bands assignable to $\nu_{Ru-^{15}N^{14}N}$ and $\nu_{Ru-^{14}N^{15}N}$ bands have been observed: J. N. Armor and H. Taube, *J. Amer. Chem. Soc.*, **92**, 2560 (1970).

[18] S. C. Srivastava and M. Bigorgne, *J. Organometal. Chem.*, **19**, 241 (1969).

[19] Such splitting phenomena were also observed in Os–N_2 complexes when the spectra were taken in the solid state: (a) J. Chatt, G. J. Leigh, and R. L. Richards, *Chem. Commun.*, 515 (1969); (b) Yu. G. Borod'ko, S. M. Vynogradova, Yu. P. Myakov, and D. D. Mozjukhin, in press; *Zh. Strukt. Khim.*, in press.

[20] J. M. Smith, W. Fellman, and L. H. Jones, *Inorg. Chem.*, **4**, 1361 (1965).

[21] A. Yamamoto, S. Kitazume, L. S. Pu, and S. Ikeda, *Proc. Int. Conf. Coord. Chem., 10th, 1967*, 119 (1968).

[22] Recent isolation of $CoH(N_2)(PBu_3)_3$ showing the N_2 band at 2050 cm^{-1} supports the above assignment,[8] whereas Misono, *et al.*,[23] observed the ν_{N_2} band for the same complex at 2032 cm^{-1}. The reason for the discrepancy between the reports is not clear.

[23] A. Misono, Y. Uchida, T. Saito, M. Hidai, and M. Araki, *Inorg. Chem.*, **8**, 168 (1969).

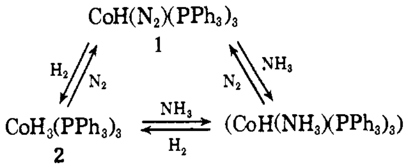

Figure 2. Reversible displacement reaction of ligands attached with hydridodinitrogentris(triphenylphosphine)cobalt(I) by N_2, H_2, and NH_3.

of the complex is its ability to reversibly exchange its coordinated N_2 with simple molecules.[7,24] Figure 2 summarizes the reversible exchange reactions. $CoH(N_2)(PPh_3)_3$ (**1**) can be converted to $CoH_3(PPh_3)_3$ (**2**) by the reaction of a benzene solution containing **1** with hydrogen and *vice versa.* $CoH_3(PPh_3)_3$ shows three ir bands, assignable to the Co–H stretch, at 1940, 1890, and 1760 cm^{-1}. The reaction of **1** with deuterium gave a deuteride complex having an ir band at 1260 cm^{-1}, which is considered to be shifted from the ν_{Co-H} band at 1760 cm^{-1} ($\nu_{Co-H}/\nu_{Co-D} = 1.4$). No distinct bands were observed around 1380 and 1350 cm^{-1}, where ν_{Co-D} bands corresponding with the ν_{Co-H} bands at 1940 and 1890 cm^{-1} are expected.[7] The reaction product of **1** with deuterium showed other new bands in the region ranging from 700 to 900 cm^{-1} which may be attributed to C–H out-of-plane vibrations of the trisubstituted benzene. These bands are also observed in the reaction product of $RuH_2(PPh_3)_4$ with deuterium[4d] and are considered to be caused by an exchange reaction of orthohydrogens of the phenyl groups of the triphenylphosphine ligands. In the gas phase are observed H_2, HD, and D_2 evolved as the result of the exchange reaction which was independently reported by Parshall who explained the composition of the gas as the statistical exchange product of 18 orthohydrogens and one hydridic hydrogen with deuterium gas.[25] The exchange reaction was observed, although not complete, even between the solid complex and deuterium. Similar reversible reactions are observed between complex **2** and ammonia and between the ammonia complex and **1**. Although the ammonia complex could not be isolated in a crystalline form, the amount of ammonia combined with cobalt was determined to be 1 mol/cobalt by titration of the ammonia released from the ammonia complex by the reaction with nitrogen.[26] In the cases of the reactions of ethylene with **1**, **2**, and the ammonia complex, similar ostensibly reversible exchange reactions were observed.[24] However, we later found out that catalytic processes are involved and the reactions are in fact not reversible.

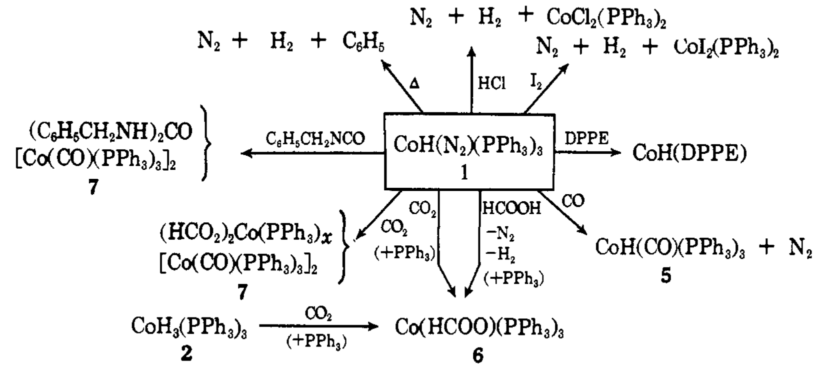

Figure 3. Irreversible reactions of $CoH(N_2)(PPh_3)_3$ with various reagents.

(b) Irreversible Reactions. Irreversible reactions of **1** are summarized in Figure 3. These reactions were carried out with the dinitrogen complex obtained with triisobutylaluminum as the reducing agent and most of the reactions of **1** support its formulation as the hydride. The chemical reactions of **1** have been also studied independently by Sacco and Rossi,[7] and duplicated descriptions will be avoided.

Thermal decomposition, iodolysis, and the reaction of **1** with HCl released 1 mol of N_2 and some hydrogen, the amount of which varied (see Experimental Section). The reaction of **1** with CO afforded N_2 and $CoH(CO)(PPh_3)_3$ (**5**), the composition of which was confirmed by ir and nmr spectroscopy and by chemical reactions.[27]

The reaction of CO_2 with **1** in benzene or tetrahydrofuran solution containing triphenylphosphine at room temperature led to an insertion product of CO_2 in the Co–H bond.[28] The formate complex, obtained as green crystals, showed strong ir bands at 1620 and 1300 cm^{-1} which were assigned to antisymmetric and symmetric vibrations of the carboxylate group bonded to cobalt. The reaction of the green formate complex with excess methyl bromide in the presence of triphenylphosphine in toluene at -30 to $\sim 0°$ yielded methyl formate. Dry hydrogen chloride also released the formic acid, which was also confirmed by infrared spectroscopy. Pyrolysis of the complex $(HCO_2)Co(PPh_3)_3$ (**6**) at 250° gave CO_2, CO, and H_2 in an approximate ratio of 6:1:1. The ratio of (CO_2 + CO) evolved per mole of the cobalt complex was 0.85. Acidolysis of **6** with concentrated deaerated sulfuric acid released 0.88 mol of CO and 0.49 mol of H_2 per mole of the complex. The reaction is considered to proceed according to the following equation

$$HCO_2Co(PPh_3)_3 + H_2SO_4 \longrightarrow CO + {}^1/_2H_2 + H_2O + CoSO_4$$

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(24) For a preliminary communication, see A. Yamamoto, L. S. Pu, S. Kitazume, and S. Ikeda, *J. Amer. Chem. Soc.*, **89**, 3071 (1967).

(25) G. W. Parshall, *ibid.*, **90**, 1669 (1968).

(26) In a similar experiment of $RuH_2(N_2)(PPh_3)_3$ with ammonia an ammonia adduct of a composition $RuH_2(NH_3)(PPh_3)_3$ was isolated: W. H. Knoth, *ibid.*, **90**, 7172 (1968).

(27) **5** and other carbonyl complexes have been also obtained by Misono, *et al.*: (a) A. Misono, Y. Uchida, M. Hidai, and T. Kuse, *Chem. Commun.*, 981 (1968); (b) A. Misono, Y. Uchida, M. Hidai, M. Araki, K. Kudo, and T. Hikita, reported at the Symposium on Organometallic Compounds, Osaka, Japan, Oct 1969.

(28) Preliminary communication was previously made: L. S. Pu, A. Yamamoto, and S. Ikeda, *J. Amer. Chem. Soc.*, **90**, 3896 (1968).

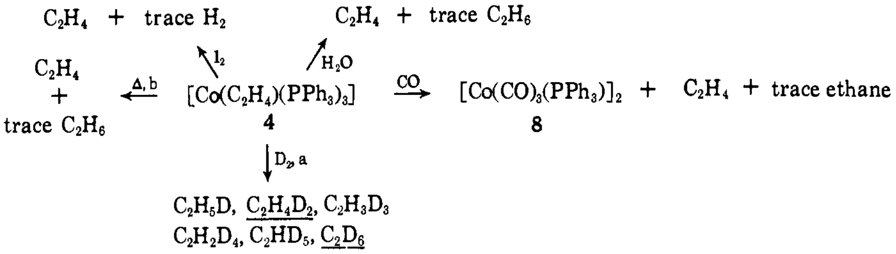

Figure 4. Reactions of $[Co(C_2H_4)(PPh_3)_3]$. Underlined ethanes in step a are main products. In b, the amount of C_2H_6 evolved varied depending on the heating rate and maximum heating temperature.

The chemical properties of **6** support the formulation of the complex as a formate of Co(I). The same complex was also obtained from $H_3Co(PPh_3)_3$ by a similar reaction in the presence of triphenylphosphine. The formate complex **6** was also obtained by the reaction of **1** with an equimolar amount of formic acid in the presence of triphenylphosphine. The reaction produced 1 mol of N_2 and H_2, respectively, per mole of **1**, and the green complex thus obtained was proved identical with **6** derived from $HCo(N_2)(PPh_3)_3$ or $H_3Co(PPh_3)$ by reactions with CO_2. The green complex **6** is unstable in benzene solution, and attempts to recrystallize the complex resulted in the decomposition of the complex and the formation of a light-brown colored diformate–Co(II) complex containing triphenylphosphine.

When the reaction of **1** with CO_2 was carried out in the absence of triphenylphosphine in toluene or tetrahydrofuran solution, the green monoformate complex **6** was not isolable and brown crystals of a composition $[Co(CO)(PPh_3)_3]_2$ (**7**) and a light yellow powder of Co(II) diformate were obtained. The light yellow powder was readily converted in moist air to a pink-colored diformate $(HCO_2)_2Co \cdot 2H_2O$ which gave formic acid on reaction with hydrogen chloride. Thermal decomposition of the light yellow powder at 260° released CO_2 and small amounts of CO and H_2.

As an extension of the reactions of $CoH(N_2)(PPh_3)_3$ with CO and CO_2, the reaction of **1** with benzyl isocyanate was also studied. The reaction gave, although in low yields, $[Co(CO)(PPh_3)_3]_2$ (**7**) and dibenzylurea, $PhCH_2NHCONHCH_2Ph$. The carbonyl complex is considered to be dimeric with CO bridges, in view of the low CO stretching frequency at 1877 cm^{-1} and its diamagnetism.[29] The chemical reactions of **7** supported its formulation as $[Co(CO)(PPh_3)_3]_2$ (see Experimental Section).

The bulk of the physical and chemical evidence supports the presence of the hydridic hydrogen in the dinitrogen complex **1**. Partially correcting our previous report,[5] we consider now the formulation as hydride, $CoH(N_2)(PPh_3)_3$, is more reasonable for the dinitrogen complex, at least for the one obtained with triisobutylaluminum. For the dinitrogen complex obtained with $AlEt_2OEt$, however, the possibility of formation of a zerovalent complex[30] cannot be ruled out completely, as will be seen from the description of a zerovalent complex in the following section.

Reactions of $[Co(C_2H_4)(PPh_3)_3]$. In contrast with $CoH(N_2)(PPh_3)_3$, the chemical properties of the dark brown complex with a composition of $[Co(C_2H_4)(PPh_3)_3]$ (**4**) obtained by the reaction of $Co(acac)_3$, $AlEt_2OEt$, and PPh_3 in an argon atmosphere support its formulation as a zerovalent cobalt complex, presumably dimeric. The ethylene complex **4** is stable below 0° and can be recrystallized from toluene or tetrahydrofuran at low temperature. The reactions of **4** are summarized in Figure 4. Thermal decomposition of **4** released 0.7 to ~0.8 mol of ethylene/cobalt accompanied by a trace of ethane, and no hydrogen evolution was observed. Hydrolysis of **4** yielded 1.0 mol of ethylene/Co and a small amount of ethane; no hydrogen was evolved. Iodolysis afforded C_2H_4 and a small amount of H_2; no hydrogen iodide was detected. The amount of ethylene evolved was about 60% of the calculated value. The reaction of **1** with CO in *m*-xylene led to the formation of a known complex, $[Co(CO)_3(PPh_3)]_2$,[31] in 84% yield and 0.94 mol/Co of a gas composed of 99.4% ethylene and 0.6% ethane. Complex **4** released the coordinated ethylene but did not give the dinitrogen complex **1** on passing nitrogen for 2 hr through a benzene solution kept at 5°. However, when nitrogen was introduced to a benzene solution containing **4** which was partially decomposed by heating it below 40°, the ν_{N_2} peak at 2088 cm^{-1} indicating the formation of an N_2 complex was observed. The reason of the formation of the N_2 complex by this procedure is not clear at the moment. In contrast to the dinitrogen complex **1**, the reaction of CO_2 with **4** did not yield the formate complex **6**, and the complex **4** without the hydride ligand did not show a catalytic activity of dimerizing ethylene (*vide infra*). The reaction of the ethylene complex **4** with deuterium was expected to yield $C_2H_4D_2$. One mole of ethane was produced per cobalt, but it contained in addition to the main product, $C_2H_4D_2$, other deuterated ethanes, C_2D_6, C_2HD_5, $C_2H_2D_4$, $C_2H_3D_3$, and C_2H_5D, as revealed by mass spectroscopic analysis of the ethane produced. This result indicated that a rapid exchange reaction is taking place between the hydrogen on ethylene and the hydridic deuterium formed by the reaction of **4** with D_2, and also between the hydridic deuterium and hydrogens in ortho positions of the phenyl groups of the triphenylphosphine ligands.

Reactions of $CH_3Co(PPh_3)_3$. The methyl–cobalt complex **3** prepared by the reaction of cobalt tris(acetylacetonate), dimethylaluminum monoethoxide, and triphenylphosphine in an argon atmosphere is moderately stable and slowly decomposes at room temperature. It can be recrystallized from tetra-

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(29) A similar complex having the same composition and a different ir band at 1904 cm^{-1} was recently reported: J. Palagyi, G. Palyi, and L. Marko, *J. Organometal. Chem.*, 11, 654 (1968).

(30) Chatt assumed the presence of $CoN_2(PPh_3)_3$ in the reaction product of $Co(acac)_3$, $AlEt_3$, and PPh_3 in ether under nitrogen: J. Chatt, R. L. Richards, J. R. Sanders, and J. E. Fergusson, *Nature (London)*, 221, 551 (1969).

(31) W. Hieber and E. Lindner, *Chem. Ber.*, 94, 1417 (1961).

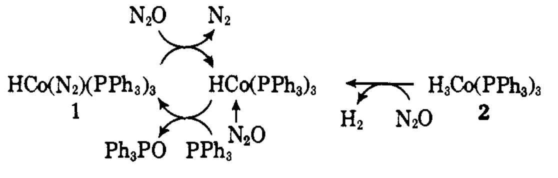

Figure 5. A possible reaction scheme for a catalytic reduction of nitrous oxide to nitrogen and a catalytic oxidation of triphenylphosphine to triphenylphosphine oxide.

hydrofuran or toluene solution. On thermal decomposition at 135° methane was released, and alcoholysis with decanol gave 1.0 mol of methane/Co. On bubbling nitrogen through a benzene solution containing **3**, a week band at 2088 cm^{-1} was sometimes observed. When nitrogen was swept after the pretreatment of the solution with hydrogen, the band appeared at 2088 cm^{-1} at full intensity.

Catalytic Reactions with $CoH(N_2)(PPh_3)_3$. As described in the treatment of reversible reactions of $CoH(N_2)(PPh_3)_3$, nitrogen coordinated with cobalt can be easily displaced by hydrogen, but no ammonia is formed in the reaction, and attempts to find a condition to convert molecular nitrogen to ammonia have been unsuccessful. In order that the catalytic nitrogen fixation from molecular nitrogen and hydrogen by the complex proceed, at least the following five conditions should be satisfied: (1) enough activation of molecular nitrogen (loosening of the $N{\equiv}N$ bond), (2) enough activation of molecular hydrogen, (3) hydrogen transfer from the activated hydrogen to nitrogen, (4) splitting of the N—N bond, (5) displacement of the product from the complex by nitrogen or hydrogen. The lack of any of the above conditions may lead to failure to find catalytic nitrogen fixation by the complex. The present complex fulfills the second and fifth conditions; *i.e.*, the molecular hydrogen can be activated enough to form hydride **2** and the ammonia ligand coordinated with cobalt can easily be displaced by either nitrogen or hydrogen. The coordinated N_2 ligand is activated to some extent, as we can see from the shift of the N_2 absorption from 2330 cm^{-1} for free nitrogen to 2088 cm^{-1} for the coordinated N_2 ligand. However, the activation may not be great enough to cause reaction with hydrogen, or the condition to cause hydrogen transfer from a hydride ligand to the coordinated nitrogen may not have been fulfilled.

Biological nitrogen-fixing systems, on the other hand, show several unusual activities such as the reduction of olefinic substances and nitrous oxide, the competitive inhibition of N_2-fixing activity by hydrogen and carbon monoxide, and catalytic formation of HD from D_2.[32] The present nitrogen complex **1** bears many of the characteristics of the biological N_2-fixing systems and the complex serves as a model to study the mechanism of nitrogen fixation. In fact, the dinitrogen complex is as versatile as the well-known Vaska complex and demonstrates a variety of catalytic activities such as oxidation, reduction, oligomerization, and polymerization.

(a) Oxidation and Reduction. The dinitrogen complex **1** is readily oxidized by air, but when the oxidation is carried out under mild conditions in the presence of triphenylphosphine, **1** behaves as an oxidation catalyst of triphenylphosphine to its oxide. Presumably the oxidation proceeds through the formation of an intermediate O_2 adduct of the triphenylphosphine–cobalt complex as in iridium–, platinum–, palladium–, and nickel–phosphine analogs.[33]

Nitrous oxide is reduced to nitrogen by **1** with concomitant oxidation of the triphenylphosphine ligands to triphenylphosphine oxide.[34] When the reaction was carried out in the presence of triphenylphosphine, catalytic oxidation of triphenylphosphine occurred. In a similar experiment with nitrous oxide and $CoH_3(PPh_3)_3$ (**2**), evolution of N_2 and H_2 was observed and the intermediary formation of the N_2 complex **1** was indicated by the appearance of the ν_{N_2} peak when a benzene solution containing **2** and triphenylphosphine was brought in contact with nitrous oxide gas for a short period. The catalytic reduction of N_2O to N_2 accompanied by the oxidation of triphenylphosphine to triphenylphosphine oxide is considered to proceed through a reaction scheme as shown in Figure 5. Nitrogen or hydrogen may be displaced by N_2O from complex **1** or **2** and an intermediate complex coordinated with N_2O may be formed. The N_2O ligand on the complex may be split to N_2 and oxygen, which attacks a triphenylphosphine ligand and converts it to triphenylphosphine oxide. If the triphenylphosphine oxide ligand is displaced by triphenylphosphine present in the solution, complex **1** may be regenerated with concomitant formation of triphenylphosphine oxide in the solution, as indicated by the infrared spectrum of the solution. The regenerated complex **1** may be again converted to the N_2O-coordinated complex, and thus the cyclic process will catalytically reduce N_2O to N_2 and oxidize triphenylphosphine to triphenylphosphine oxide. Nitrous oxide has been known as an extremely inert gas at room temperature and atmospheric pressure, and its catalytic reduction by transition metal complexes has been reported only recently.[35] The analogy between the activity of the nitrogenase and the catalytic activity of the present N_2–cobalt complex is noteworthy.

(b) Hydrogenation of Ethylene. Complex **1** catalyzes the hydrogenation of ethylene to ethane at room temperature and reduced pressure. Probably the coordinated N_2 may be displaced by ethylene and an intermediate ethylene-coordinated complex $[CoH(C_2H_4)(PPh_3)_3]$ may be formed, which, through insertion of the coordinated ethylene into the Co–H bond, may turn to an ethyl–cobalt complex. The reaction of hydrogen with the ethyl complex with the formation of ethane will regenerate the cobalt hydride complex which is to be coordinated again by ethylene to repeat the catalytic cycle.

(c) Polymerization and Isomerization of Olefins. The catalytic dimerizations of ethylene and propylene by **1** take place at ambient temperature and pressure.[36] **1** also catalyzes the isomerization of 1-butene to 2-butenes. The oligomerization and isomerization are

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(32) R. W. F. Hardy and R. C. Burns, *Annu. Rev. Biochem.*, 37, 331 (1968).

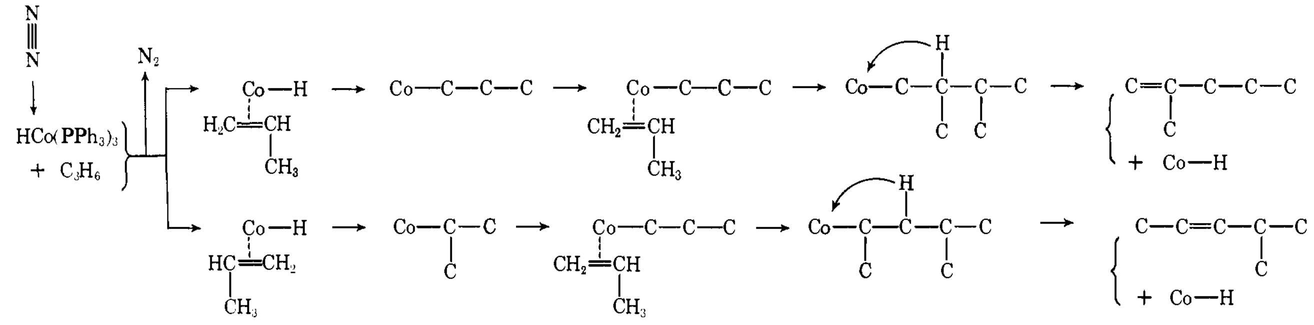
(33) (a) L. Vaska, *Accounts Chem. Res.*, 1, 335 (1968); (b) S. Takahashi, K. Sonogashira, and N. Hagihara, *Nippon Kagaku Zasshi*, 87, 610 (1966); (c) G. Wilke, H. Schott, and P. Heimbach, *Angew. Chem.*, 79, 62 (1967).

(34) Preliminary communication, L. S. Pu, A. Yamamoto, and S. Ikeda, *Chem. Commun.*, 186 (1969).

(35) R. G. S. Banks, R. J. Henderson, and J. M. Pratt, *ibid.*, 387 (1967); *J. Chem. Soc. A.*, 2886 (1968).

(36) Preliminary communication, L. S. Pu, A. Yamamoto, and S. Ikeda, *J. Amer. Chem. Soc.*, 90, 7170 (1968).

Scheme I. Dimerization Mechanism of Propylene by $CoH(N_2)(PPh_3)_3$[a]



[a] Triphenylphosphine ligands are omitted in the dimerization mechanism.

considered to proceed through a common intermediate, $HCo(PPh_3)_3$, coordinated with the substrate, in analogy with the hydrogenation of ethylene. The catalytic activity of the complex to dimerize ethylene and propylene was not particularly high. The butenes produced consisted of 72% *trans*-2-butene, 26% *cis*-2-butene, and 2% 1-butene, and small amounts of ethylene trimers and ethane were also formed. The addition of 3 mol of tri-*n*-butylphosphine/mol of **1** reduced the dimerization rate considerably, but the addition of triphenylphosphine had little effect on the rate. The composition of the butene fraction was similar to that of the system without tributylphosphine. The propylene dimerization with **1** proceeded similarly, and with 0.32 mmol of complex **1** in *m*-xylene 17 mmol of propylene dimers containing 2-methyl-1-pentene and 4-methyl-*trans*-2-pentene as the main products was produced.

The formation of 2-methyl-1-pentene and 4-methyl-2-pentene as the main dimerization products suggests that insertion and elimination reactions as shown in Scheme I are predominant. In this scheme the initially coordinated N_2 ligand is displaced by the substrate and not involved in the catalysis. The true active species may be a cobalt hydride coordinated with the substrate.

Some isomerization reactions are also involved in the dimerization of ethylene and propylene by **1**. We studied the isomerization of 1-butene, a dimerization product of ethylene by **1**, and found that a rapid isomerization is taking place, as shown in Figure 6. 1-Butene (15 mmol) was isomerized by about 1 mmol of **1** in *m*-xylene solution at room temperature and the compositions of butenes in the gas phase and liquid phase were analyzed, respectively, by gas chromatography. It is seen from Figure 6 that 1-butene is rapidly isomerized to *trans*-2-butene and *cis*-2-butene, the latter of which further isomerizes to *trans*-2-butene to reach an equilibrium composition.

In addition to catalyzing the oligomerization of olefins, the dinitrogen–cobalt hydride complex **1** and the methyl–cobalt complex **3** catalyze the polymerization of vinyl monomers such as acrylonitrile, methacrylonitrile, and methyl methacrylate to high molecular weight polymers. The polymerization activities parallel those of alkyliron- and -cobalt–dipyridyl complexes[10,37] and suggest that the cobalt–alkyl and cobalt–hydride bonds initiate the polymerization of the vinyl monomers. The detail of the polymerization by these phosphine complexes will be reported separately.

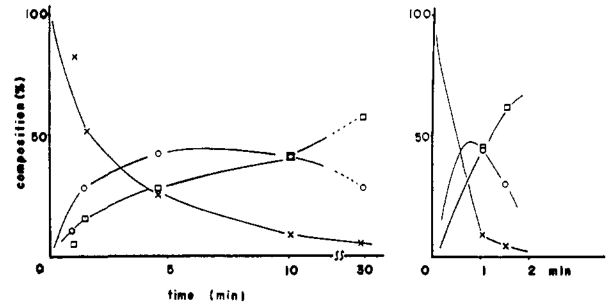


Figure 6. Isomerization of 1-butene by $CoH(N_2)(PPh_3)_3$: left-hand curves, gas phase; right-hand curves, liquid phase; ×, 1-butene; □, *trans*-2-butene; ○, *cis*-2-butene.

Experimental Section

General. All preparations and recrystallizations were carried out in a nitrogen or argon atmosphere, or *in vacuo*. Solvents were dried by usual procedures, distilled, and stored under argon or nitrogen.

Routine infrared spectra were recorded on Shimadzu IR 27C and IR 27K spectrometers. A Perkin-Elmer 125 grating spectrophotometer was used when accurate measurements were required. KBr pellets, Nujol mulls, or benzene solutions were prepared under an inert atmosphere. In the $^{15}N_2$-labeling experiments, N_2 gas containing ^{15}N was prepared from $(NH_4)_2SO_4$ labeled with ^{15}N. The $^{15}N_2$ gas was introduced into a benzene solution containing trihydridotris(triphenylphosphine)cobalt (**2**) in a vacuum line. The solution was then degassed by a freeze-and-thaw method and again the $^{15}N_2$ gas was introduced. The procedure was repeated three times and the solution was evaporated to dryness to give hydridodinitrogentris(triphenylphosphine)cobalt labeled with $^{15}N_2$.

Experiments to study the effect of addition of other phosphines were carried out in benzene. The dinitrogen complex **1** was dissolved in benzene and aliquots of benzene solutions containing the phosphine were added, keeping the concentration of **1** in the prepared solution constant. The ir spectra of the solutions were observed with a Perkin-Elmer 125.

Proton nmr spectra were determined on a Jeolco 4H 100 spectrometer. Mass spectra were taken with a Hitachi RMU 5B spectrometer. Microanalyses were performed by Mr. T. Saito of our laboratory. Cobalt analysis was carried out with a complex titration method by using EDTA. Analytical data of the cobalt–phosphine complexes are summarized in Table I.

Analysis of noncondensable gases at liquid nitrogen temperature was carried out by mass spectrometry after collecting the noncondensable gas by the use of a Toepler pump, by which the volume of the gas was also measured.

Materials. Cobalt tris(acetylacetonate) and bis(acetylacetonate) were prepared as described in the literature.[38,39] Diethylaluminum

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(37) A. Yamamoto, T. Shimizu, and S. Ikeda, *Polym. J.* (*Japan*), 1, 171 (1970); *Makromol. Chem.*, 136, 297 (1970).

(38) B. E. Bryant and W. C. Fernelius, *Inorg. Syn.*, 5, 188 (1957).

(39) "Gmelin's Handbuch der Anorganische Chemie," Vol. 58, Verlag Chemie, Weinheim, 1963, p 140.

Table I. Analytical Data of Cobalt–Phosphine Complexes

				Calcd, %				Found, %				
No.	Formula	Color	Mp, °C	C	H	N	Co(Cl)	C	H	N	Co(Cl)	Remarks
1	$CoH(N_2)(PPh_3)_3$	Orange		74.2	5.3	3.2	6.7	74.2	5.4	3.2	6.9	
2	$CoH_3(PPh_3)_3$	Yellow		76.4	5.7	0	7.0	77.0	6.1	0	7.1	
3	$CoCH_3(PPh_3)_3$	Brown		76.7	5.6	0	6.9	76.1	5.7	0	7.0	
4	$[Co(C_2H_4)(PPh_3)_3]$	Dark brown		77.0	5.7	0	6.7	76.6	5.8	0	6.7	
5	$CoH(CO)(PPh_3)_3$	Light orange	176–178 dec	75.5	5.3	0		75.6	5.6	0		
6	$Co(HCO_2)(PPh_3)_3$	Green	217–220 dec	74.2	5.2	0		73.6	5.2	0		*a*
								74.7	5.3	0		*b*
7	$[Co(CO)(PPh_3)_3]_2$	Brown	158–160 dec	75.6	5.2	0		75.5	5.4	0		*c*
			158–160 dec					75.3	5.8	0		*d*
8	$[Co(CO)_3(PPh_3)]_2$	Reddish brown		62.2	3.7	0		62.1	3.7	0		*e*
	$CoCl_2(PPh_3)_2$	Blue	235–240 dec	66.1	4.6	0	(10.9)	66.4	4.9	0	(10.3)	
	$CoH(DPPE)_2$	Red	267–269 dec	72.9	5.8	0		73.1	5.6	0		

[a] Prepared from **1** and CO_2 in the presence of triphenylphosphine. [b] Prepared from **1** and formic acid in the presence of triphenylphosphine. [c] Prepared from **1** and CO_2 in the absence of triphenylphosphine. [d] Prepared from **1** and benzyl isocyanate. [e] Prepared from **4** and CO.

monoethoxide was prepared as previously reported.[10] Dimethylaluminum monoethoxide was prepared in an analogous manner from trimethylaluminum and ethanol. Triisobutylaluminum was used as purchased from Ethyl Corp. Ltd. Triphenylphosphine was used as purchased, mp 79–80.5°. 1,2-Bis(diphenylphosphino)ethane (DPPE) was prepared from triphenylphosphine and 1,2-dichloroethane,[40] mp 143–144° (lit. 143–144°).

Preparation of Hydridodinitrogentris(triphenylphosphine)cobalt(I) (1). In a typical experiment, 26.5 g (105 mmol) of triphenylphosphine and 10.0 g (30 mmol) of cobalt(III) tris(acetylacetonate) were suspended in 300 ml of diethyl ether, and 30 ml (120 mmol) of triisobutylaluminum was added to the suspension cooled at −50° under a nitrogen atmosphere. The reaction mixture was stirred and the temperature was raised gradually to room temperature, with nitrogen passing through the reaction mixture. After the reaction proceeded for 3 hr at room temperature, orange crystals deposited from the dark red solution. The crystals were filtered, washed several times with ether or hexane, and dried *in vacuo*. The crystals were recrystallized from toluene; yield 16.9 g (69%). The preparation with diethylaluminum monoethoxide was done similarly and the yield was 40–60%. Preparation using cobalt(II) bis(acetylacetonate) was carried out similarly and the same product was obtained.

Reactions of Hydridodinitrogentris(triphenylphosphine)cobalt (1). (i) **Reversible Displacement Reactions of Coordinated Nitrogen with Hydrogen, Ethylene, and Ammonia.** Reversible displacement reactions were carried out in benzene or toluene solutions of **1** and each gas was bubbled through a benzene solution for a stable complex or through a toluene solution kept below −5° for an unstable complex. The displacement reaction of the coordinated N_2 ligand of **1** by H_2 was observed by disappearance of the ν_{N_2} band at 2088 cm^{-1} in a benzene solution with a color change from red to yellow and appearance of ν_{Co-H} bands at 1940 and 1760 cm^{-1}. This process was reversed by introduction of nitrogen gas to the solution. On sweeping ammonia through a benzene solution containing **1**, the ν_{N_2} peak disappeared, accompanied by a color change from red to dark red, and the solution turned red again on bubbling with nitrogen gas, accompanied by the appearance of the ν_{N_2} band. The amount of ammonia combined with the cobalt complex was determined by titration of an sulfuric acid solution in which the liberated ammonia was collected by sweeping the benzene solution containing the ammonia-coordinated complex. In order to avoid the error by dissolved ammonia in the solution, argon gas was bubbled through the solution for 30 min before the reaction with nitrogen. The amount of ammonia coordinated with cobalt was about 1.0 mol/Co.

(ii) **Irreversible Reactions.** a. **Thermal Decomposition.** Complex **1** (0.625 g, 0.733 mmol), prepared with $AlEt_2OEt$ and recrystallized from toluene, was heated under vacuum at temperature starting at room temperature and ending at 170°. The pyrolysis product consisted of N_2 (0.71 mmol), H_2 (0.063 mmol), benzene (0.05 g), and a trace of ethylene (6×10^{-3} mmol).

Pyrolysis of the dinitrogen complex prepared with triisobutylaluminum gave a similar result, forming N_2 and H_2 in a molar ratio of 10:1, but no ethylene in the pyrolysis product.

When a crude product of **1** prepared in diethyl ether was decomposed, the pyrolysis product contained the ether.

b. **Iodolysis.** In a vacuum system 0.430 g (0.493 mmol) of **1** in 15 ml of benzene was decomposed with a benzene solution containing excess iodine (1.5 mol). The amounts of nitrogen and hydrogen evolved were 0.518 mmol (1.05 mol/Co) and 0.149 mmol (0.61 g-atom of H/Co), respectively.

c. **Reaction with Hydrogen Chloride.** $CoH(N_2)(PPh_3)_3$ (0.8 g, 0.9 mmol) was dissolved in 35 ml of tetrahydrofuran and dry hydrogen chloride was passed through the solution for 30 min at room temperature. The original red color turned to green in 10 min and blue crystals precipitated in 15 min, with the formation of a dark green supernatant from which triphenylphosphine was recovered. The gas evolved at the outset of the reaction consisted of nitrogen and hydrogen in a ratio of 1:0.6, as shown by mass spectrometry. The crystals are insoluble in benzene, hexane, toluene, and diethyl ether and soluble in chloroform and acetone, and were recrystallized from acetone; yield 63% as $CoCl_2(PPh_3)_2$; mp 235–240°.

d. **Reaction with Carbon Monoxide and the Synthesis of Hydridocarbonyltris(triphenylphosphine)cobalt (5).** Carbon monoxide gas was bubbled through a benzene solution containing **1** for 30 min at room temperature. Upon concentration or addition of hexane to the solution, light orange crystals deposited which were collected and dried, mp 176–178°.

The ir spectrum of the complex showed a strong absorption at 1920 and medium bands at 1947 and 1971 cm^{-1}. The proton nmr spectrum of the carbonyl complex in tetrahydrofuran showed a quartet at τ 23 with relative intensities of 1:3:3:1 and $J_{P-H} = 50$ Hz.

Thermal decomposition of the carbonyl complex (0.265 g, 0.304 mmol) at 240° released 4.57 ml (STP) of CO (0.67 mol/Co) and 0.38 ml (STP) of H_2 (0.056 mol/Co).

Iodolysis of the carbonyl complex (0.059 mmol) with 4 ml of toluene solution containing 80 mg of iodine afforded 1.27 ml (STP) of CO (0.97 mol/Co) and 0.29 ml (STP) of H_2 (0.22 mol/Co).

e. **Reaction of 1 with Carbon Dioxide and Synthesis of Tris(triphenylphosphine)cobalt Monoformate (6).** Carbon dioxide gas freed from oxygen was passed through a benzene solution (250 ml) containing 6.2 g (7.3 mmol) of **1** and 5.2 g (20.0 mmol) of triphenylphosphine at room temperature for 30 min. The original red color changed gradually to green. The brown precipitate which deposited was removed by filtration, and upon concentration of the filtrate green crystals were obtained which were washed with 20 ml of ether, dried, and analyzed, mp 217– 220° dec, yield 30–45%.

When the reaction of $CoH(N_2)(PPh_3)_3$ with carbon dioxide was carried out in the absence of excess triphenylphosphine in toluene or tetrahydrofuran at room temperature for 1-*ca.* 2 hr, a yellow precipitate formed. The yellow precipitate was separated by filtration and from the filtrate brown crystals having the composition $[Co(CO)(PPh_3)_3]$ (**7**) were obtained on concentration of the solution: mp 158–160° dec, ir ν_{CO} 1877 cm^{-1}, yield 4%.

The composition of the yellow precipitate varied and attempts to purify it failed. The complex changed to a pink-colored substance in contact with moist air. The pink precipitate was washed with benzene repeatedly in air and identified as $(HCO_2)_2Co \cdot 2H_2O$ by elemental analysis and comparison of the ir spectrum with an authentic sample.

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[40] W. Hewertson and H. R. Watson, *J. Chem. Soc.*, 1490 (1962).

Anal. Calcd for $C_2H_6O_6Co$: C, 13.0; H, 3.3. Found: C, 13.4; H, 3.6.

f. **Reaction with Benzyl Isocyanate.** To an ether solution containing $CoH(N_2)(PPh_3)_3$ was added 1.5 mol/Co of benzyl isocyanate at room temperature. The reaction proceeded gradually with gas evolution, the solution turned from red to dark brown, and a precipitate formed. The precipitate was filtered and the filtrate was concentrated. Brown crystals of composition $[Co(CO)(PPh_3)_3]$ were obtained in 3-6% yield, mp 158-160°.

The precipitate was extracted with benzene and on concentration of the benzene extract white crystals were obtained (2% as dibenzylurea), mp ~169-170°. The melting point and ir spectrum were in agreement with those of an independently prepared sample of dibenzylurea. Thermal decomposition of 0.064 g (0.073 mmol) of $[Co(CO)(PPh_3)_3]_2$ at 210° for 1 hr yielded 1.09 ml (STP) of carbon monoxide (CO/Co, 0.67). Iodolysis of 0.057 g (0.066 mmol) of the same sample in 4 ml of benzene with 113 mg of iodine in a vacuum system liberated 1.51 ml (STP) of carbon monoxide (CO/Co, 1.02). In neither experiment was evolution of hydrogen detected.

Preparation of $CoH(DPPE)_2$ and $Co(DPPE)_2$ from Cobalt Acetylacetonate, $AlEt_2OEt$, and DPPE (1,2-Bis(diphenylphosphino)-ethane). Cobalt acetylacetonate (3.0 g, 8.4 mmol) and DPPE (7.0 g, 17.6 mmol) were suspended in 100 ml of ether, and 5.1 ml of diethylaluminum monoethoxide was added to the suspension in an argon atmosphere. After the suspension was stirred for 5 hr at room temperature red crystals deposited. The crystals were washed three times with a mixture of 20 ml of hexane and 40 ml of ether. The crystals were further washed with 350 ml of toluene, and 2.5 g of red crystals was collected: mp 267-269° dec (lit. 280[13a] and 265°[13b]), ir ν_{Co-H} 1882 cm^{-1} (lit. 1884 cm^{-1} [13b]), yield as $CoH(DPPE)_2$ 35%. The washings were concentrated to get 1.3 g of violet crystals: mp 228-232° dec (lit.[13a] 227-230°), yield as $Co(DPPE)_2$ 18%.

Preparation of Trihydridotris(triphenylphosphine)cobalt (2). Deoxygenated hydrogen gas was bubbled through a benzene solution (50 ml) containing 2.8 g of $CoH(N_2)(PPh_3)_3$ for 1 hr at room temperature. The original red color of the solution turned to yellow and yellow crystals deposited. The solution was concentrated to 10 ml and the crystals were filtered, washed with 30 ml of hexane under argon, and dried *in vacuo*.

Addition of 100 mmol of D_2O to 0.83 mmol of $CoH_3(PPh_3)_3$ caused the evolution of 1.10 mmol (1.33 mol/Co) of hydrogen, the composition of which was shown to be a mixture of D_2, HD, and H_2 in a ratio of 1:2.8:2.5. Pyrolysis of **2** (0.55 mmol) at 170° released 0.39 mmol (0.71 mol/Co) of hydrogen and 0.6 mmol of benzene.

Preparation of Methyltris(triphenylphosphine)cobalt (3). The preparation was carried out under argon. Cobalt tris(acetylacetonate) (10.8 g, 30 mmol) and triphenylphosphine (23.6 g, 90 mmol) were dissolved in 190 ml of toluene, and dimethylaluminum monoethoxide (39.5 g, 120 mmol) was added to the solution keeping the temperature between −5 and ~0°. The reaction mixture turned dark red in 30 min and a brown precipitate was formed. After 4 hr the precipitate was separated by filtration, washed with ether, and dried *in vacuo*. The complex was recrystallized by dissolving it in 400 ml of tetrahydrofuran cooled at −5° and concentrating the solution at this temperature to 200 ml. Brown needles deposited and were washed with ether and hexane; yield 4.0 g (15%).

The infrared spectrum of the methyl complex in a benzene solution showed two ν_{C-H} (aliphatic) bands at 2860 and 2970 cm^{-1}. The esr spectrum of the complex showed no signal.

Pyrolysis of **3** (0.538 g, 0.604 mmol) to 135° released 0.544 mmol of a gas composed of methane (0.328 mmol), ethylene, ethane (0.084 mmol in a ratio of 1.7:1), and a trace of H_2. The amount of gas evolved corresponds to 82% of the calculated value for $CH_3Co(PPh_3)_3$. Benzene (0.132 mmol) was also formed.

Addition of decanol (5 ml) to 0.655 g (0.75 mmol) of $CH_3Co(PPh_3)_3$ in a vacuum system at room temperature released 0.95 mmol of a gas composed of methane (0.78 mmol), ethylene, ethane (0.034 mmol in a ratio of 3:1), and hydrogen (0.105 mmol).

Passing nitrogen gas through a 2% benzene solution of $CH_3Co(PPh_3)_3$ caused the decrease of bands between 2800 and 3000 cm^{-1} and the appearance of a weak ν_{N_2} peak was sometimes observed, but the intensity did not increase on further reaction of the complex with nitrogen. When nitrogen was introduced after the reaction of the solution containing $CH_3Co(PPh_3)_3$ with hydrogen at 0°, a much stronger ν_{N_2} peak was observed.

Preparation of Ethylenetris(triphenylphosphine)cobalt (4). In an argon atmosphere, 10.1 ml (67.2 mmol) of diethylaluminum monoethoxide was added to a suspension of cobalt tris(acetylacetonate) (6.0 g, 16.8 mmol) and triphenylphosphine (22.0 g, 84.0 mmol) in ether cooled at −10°. The reaction mixture was then stirred at 0–*ca.* 5° for 11 hr, during which ethane and ethylene were evolved and dark brown crystals deposited. Hereafter, the complex was kept below −15° and separated from the solution, washed with hexane, and dried *in vacuo* to give 10.6 g (72% yield) of $[Co(C_2H_4)(PPh_3)_3]$. The complex was recrystallized from cold toluene.

Reactions of Ethylenetris(triphenylphosphine)cobalt. a. Iodolysis. In the same manner as the iodolysis of the dinitrogen complex, 0.35 g of **4** in 20 ml of toluene was treated at room temperature for 2.5 hr with a toluene solution containing 1.0 g of iodine. The evolved gas amounted to 2.73 ml (STP) and consisted mostly of ethylene, with about 1% hydrogen.

b. Reaction of 4 with Carbon Monoxide and the Formation of $[Co(CO)_3(PPh_3)]_2$ (8). In a vacuum system, an excess of carbon monoxide was introduced into a *m*-xylene solution containing 0.88 g of **4** cooled at −25° and the temperature was gradually raised to room temperature with stirring of the solution. After reaction for 2 hr at room temperature, reddish brown crystals deposited, which were separated by filtration, washed several times with benzene, and dried *in vacuo*. The yield of the complex as $[Co(CO)_3(PPh_3)]_2$ was 84%, ir ν_{CO} 1950 cm^{-1}.

The amount of gas evolved in the reaction was 0.94 mmol, which corresponded to 0.94 mol/Co. The gas consisted of 99.4% ethylene and 0.6% ethane.

c. **Thermal Decomposition of 4.** The complex was heated in a vacuum system and evolved gas was analyzed by gas chromatography. The ratio of evolved ethylene to ethane varied between 70:1 and 6:1, depending on the heating rate and the maximum temperature, but no hydrogen evolution was observed. The total amount of gas evolved when the sample was heated up to 150° was 77 mol%/cobalt.

d. **Hydrolysis.** Excess water was added to $[Co(C_2H_4)(PPh_3)_3]$ (0.401 g, 0.459 mmol) in a vacuum system, and later benzene was added to dissolve the complex. The system was stirred for 5 hr at 5° and then the temperature was gradually raised to 50°. Ethylene and ethane were evolved in a ratio of 15:1, but no hydrogen was formed. The total amount of gas evolved was 0.46 mmol.

e. **Reaction of 4 with D_2.** Excess deuterium gas was introduced into 30 ml of a *m*-xylene solution containing 1.35 g of **4** in a vacuum system, and the solution was stirred for 2.5 hr at −15 to 20°. The condensable gas at liquid nitrogen temperature was collected and analyzed. The gas was identified as ethane and amounted to 1.48 mmol, *i.e.*, 0.96 mol/Co. Mass spectrometric analysis of the gas revealed the presence of C_2H_5D, $C_2H_3D_3$, $C_2H_2D_4$, C_2HD_5, and C_2D_6 in addition to $C_2H_4D_2$, which constituted the main product.

Catalytic Reactions of $CoH(N_2)(PPh_3)_3$. a. Oxidation of Triphenylphosphine by Oxygen. Triphenylphosphine (1.90 mmol) and $CoH(N_2)(PPh_3)_3$ (0.38 mmol) were dissolved in 20 ml of toluene and cooled at −70° in a vacuum system. The solution was brought into contact with oxygen with stirring and the temperature was gradually raised. At −40° the red solution turned to a deep red color. The temperature was further raised to room temperature and the formation of a gray substance was observed. After separation of the gray substance, 2.73 mmol of triphenylphosphine oxide (mp ~156-159°) was recovered from the solution. Recrystallization of the crude triphenylphosphine oxide from a mixture of benzene and hexane gave 1.87 mmol of white needles of triphenylphosphine oxide.

Anal. Calcd for $C_{18}H_{12}OP$: C, 77.6; H, 5.36. Found: C, 77.4; H, 5.34

b. **Reduction of Nitrous Oxide with Oxidation of Triphenylphosphine.** Hydridodinitrogentris(triphenylphosphine)cobalt (0.62 g, 0.71 mmol) and triphenylphosphine (1.86 g, 7.1 mmol) were dissolved in toluene and the solution was brought in contact with 1.5 l. of nitrous oxide at 700 mm and at −5 to 20°. The red solution turned through light green to blue with effervescence. After the completion of the reaction the solution was evaporated to dryness and the residue was extracted with a mixture of benzene and hexane. From the extract 2.53 g of a white substance was recovered, which on recrystallization from benzene–hexane gave 1.22 g (4.4 mmol) of triphenylphosphine oxide, mp 158-159°.

c. **Hydrogenation of Ethylene.** $CoH(N_2)(PPh_3)_3$ (1.10 g, 1.25 mmol) was dissolved in benzene in a vacuum system and a mixture of ethylene (91 mmol) and hydrogen (104 mmol) was introduced. After reaction for 23 hr at room temperature (17–*ca.* 21°), the gas was analyzed by gas chromatography which revealed the formation of 20 mmol of ethane and butane.

d. **Dimerization of Ethylene and Propylene.** To $CoH(N_2)(PPh_3)_3$ (0.55 g, 0.63 mmol) was added 10 ml of *m*-xylene saturated with ethylene in a sealed system and the complex was dissolved with stirring. The decrease of the initial ethylene pressure (710 mm) was followed by using a mercury manometer. After the reaction proceeded for 32 hr at 26.5–29.6° the gaseous products were separated from the solution and analyzed. The formation of 40.6 mmol of butenes (*trans*-2-butene, 72%; *cis*-2-butene, 26%; 1-butene, 2%) and 0.57 mmol of ethane was observed. A similar experiment with 0.79 g (0.92 mmol) of **1** in 30 ml of *m*-xylene at 0° with an initial ethylene pressure of 700 mm (179 mmol) for 24 hr produced 26 mmol of butenes and 0.84 mmol of ethylene trimers.

Addition of 2.7 mmol of tri-*n*-butylphosphine to 0.92 mmol of **1** caused a decrease in the yield of butenes from 13 mmol in the absence of tri-*n*-butylphosphine to 9.0 mmol in the presence of the ligand.

The dimerization of propylene was carried out analogously to the dimerization of ethylene. In a typical dimerization experiment, 190 mmol of propylene with an initial pressure of 753 mm was brought in contact with 0.32 mmol of **1** in 7 ml of *m*-xylene for 47 hr at 25°, and about 17 mmol of propylene dimers was produced. The product as identified by gas chromatography contained 72.5% 2-methyl-1-pentene, 17.6% 4-methyl-*trans*-2-pentene, 2.2% 2-methyl-2-pentene, 2.1% 4-methyl-*cis*-2-pentene, and 1.1% of unidentified propylene dimers, in addition to a small amount of propane. The formation of 2-methyl-1-pentene was also confirmed by nmr and ir spectroscopy after its separation by preparative gas chromatography.

e. **Isomerization of Butene.** In a similar manner to the dimerization of ethylene and propylene the isomerization of 14.8 mmol of 1-butene by 1 mmol of $CoH(N_2)(PPh_3)_3$ in 30 ml of *m*-xylene was carried out at 25°. The compositions of the gas phase and the liquid phase were analyzed by taking out the samples by a hypodermic syringe after appropriate intervals.

Acknowledgment. The authors are very grateful for the experimental assistance of Mr. T. Yamamoto, Mr. Y. Kubo, and Mr. M. Takahashi. The assistance of Mr. Y. Morikawa in the preparation of $^{15}N_2$ gas is also gratefully acknowledged.

Kinetics and Mechanisms of the Reduction of Cobalt(III) Complexes by Uranium(III) Ions[1a]

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Abstract: Kinetics studies have been carried out on the reduction of Co(III) complexes by U^{3+} in perchloric acid solutions. The $Co(NH_3)_5X^{2+}$-type complexes react at relative rates strongly suggesting an inner-sphere mechanism, on the basis of the extent of stabilization of the transition state by different X groups. For X = H_2O the $[H^+]$ dependence suggests that an OH-bridged precursor complex is formed, the stability of which has a marked effect on the reaction kinetics. $Co(NH_3)_6^{3+}$ reacts by an outer-sphere mechanism, and its reaction is strongly catalyzed by free anions, most markedly by F^- and NCS^-. The complexes $Co(NH_3)_5NO_3^{2+}$ and $Co(NH_3)_5NO_2^{2+}$ suffer ligand reduction as well as Co(III) reduction.

Transition metal ions such as Cr^{2+}, V^{2+}, Fe^{2+}, Eu^{2+}, $Cr(bipy)_3^{2+}$, $Ru(NH_3)_6^{2+}$, $Co(CN)_5^{3-}$, and Cu^+ readily reduce Co(III) complexes. Recent years have seen extensive kinetic studies on these reactions, leading not only to the fundamental distinction between the inner-sphere and outer-sphere mechanisms, but also to the resolution, at least in part, of the factors controlling the mechanism adopted and the reaction rate.[2-4] We have sought to extend the studies to include novel and previously unstudied metal ions such as Yb^{2+} and U^{3+}, reactions of the latter being the subject of this paper. A preliminary report of part of this work has been published.[5]

Typical of the reactions whose kinetics have been studied is the reduction of $Co(NH_3)_5Br^{2+}$ according to the equation

$$Co(NH_3)_5Br^{2+} + U^{3+} + 5H^+ = Co^{2+} + U^{4+} + 5NH_4^+ + Br^- \qquad (I)$$

The chemistry of U^{3+}_{aq} has not been widely studied, possibly because textbooks refer to it being quite unstable. Although U^{3+} is a strong reducing agent

$$U^{4+} + e^- = U^{3+} \qquad E^0 = -0.63\ V^{6}$$

clearly capable of reducing $H_2O(H_3O^+)$ to hydrogen and perchlorate ion to chloride ion, these reactions proved to be negligible, as reported by Sato.[7] For the reactions studied here, most of which were fairly rapid, no deterioration of the U(III) solutions was noted over several hours.

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(1) (a) Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission, Contribution No. 2792; (b) Fellow of the Alfred P. Sloan Foundation, 1968–1970.

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