is the absorbance at 9 half-lives and D_t is the absorbance at any time. These plots were always linear over 3 half-lives. It can be shown that if $(\text{porphyrin})_{\text{total}} = (\text{PH}_2) + (\text{PH}_3) + (\text{CuP})$, $\ln (D_t - D_\infty) = \ln (\text{PH}_2) + \text{constant}$. The copper porphyrin absorbed at 538 and 572 mμ. Copper perchlorate was analyzed by EDTA titrations.

Results and Discussion

The reaction was found to be first order in porphyrin (eq 2). Table I shows that at pH 3.80 and 4.65, the rate law is also first order in Cu(II). Table II gives the results of the rate dependence on hydrogen ion concentration. A linear relation between $(\text{Cu(II)})/k_{\text{obsd}}$ and (H^+) of the form given in eq 3 was observed.

$$\text{d}(\text{PH}_2)/\text{d}t = k_{\text{obsd}}(\text{PH}_2) \qquad (2)$$

$$(\text{Cu(II)})/k_{\text{obsd}} = a + b(\text{H}^+) \qquad (3)$$

TABLE I

RATE AS A FUNCTION OF Cu(II) (25°, $\mu = 0.5$)

Expt[a]	$10^3(\text{Cu(II)})_{\text{total}}$, M	10^3k_{obsd}, sec^{-1}	$k_{\text{obsd}}/\text{Cu(II)}_{\text{total}}$, $M^{-1}\,\text{sec}^{-1}$
1	1.76	5.64	3.21
2	2.65	8.72	3.29
3	3.64	10.86	2.99
4	4.42	11.85	2.69
5	5.30	15.20	2.87
6	6.24	16.95	2.72
7	7.06	19.09	3.06
8	8.82	22.78	3.23
9	9.73	26.40	2.99
		Av	3.00 ± 0.17
10	0.44	0.47	1.07
11	1.04	1.22	1.17
12	2.07	2.48	1.19
13	4.44	4.96	1.12
		Av	1.14 ± 0.04

[a] Experiments 1–9: pH 4.65, $(\text{porphyrin})_{\text{total}} = 7.34 \times 10^{-5}$ M. Experiments 10–13: pH 3.80, $(\text{porphyrin})_{\text{total}} = 5.35 \times 10^{-5}$ M.

TABLE II

RATE AS A FUNCTION OF pH (25°, $\mu = 0.5$)

Expt[a]	pH	10^3k_{obsd}, sec^{-1}	$(\text{Cu(II)})_{\text{total}}/k_{\text{obsd}}$, M sec Obsd	Calcd
1	3.78	1.163	0.891	0.886
2	3.83	1.255	0.825	0.815
3	3.90	1.414	0.733	0.718
4	4.00	1.700	0.609	0.607
5	4.25	2.257	0.459	0.456
6	4.75	3.550	0.292	0.305
7	5.20	3.710	0.279	0.260
8	5.60	4.810	0.215	0.240
9	3.80	...	0.878	0.855
10	4.65	...	0.333	0.323

[a] Experiments 1–8, $(\text{porphyrin})_{\text{total}} = 6.42 \times 10^{-5}$ M. Experiments 9–10, from Table I.

A least-squares analysis of the data in Table II gave $a = 0.235 \pm 0.006$ and $b = (3.93 \pm 0.061) \times 10^3$. This porphyrin has been shown to exist as three proton-related species in acid solutions[9]

$$\text{PH}_4{}^{2+} = \text{PH}_3{}^+ + \text{H}^+ \quad (K_4) \qquad (4)$$

$$\text{PH}_3{}^+ = \text{PH}_2 + \text{H}^+ \quad (K_3) \qquad (5)$$

$\text{p}K_4 \approx 0.3$ and $\text{p}K_3 \approx 4.7$ at 20°. Under the reaction conditions, PH_2 and $\text{PH}_3{}^+$ are the major species. We postulate the simple mechanism

$$\text{PH}_3{}^+ = \text{PH}_2 + \text{H}^+ \quad (K_3) \qquad (6)$$

$$\text{PH}_2 + \text{Cu(II)} \longrightarrow \text{Cu}^{\text{II}}\text{P} + 2\text{H}^+ \quad (k) \qquad (7)$$

With eq 7 being rate determining, it is readily shown that

$$k_{\text{obsd}} = kK_3(\text{Cu(II)})/[K_3 + (\text{H}^+)] \qquad (8)$$

In relation to eq 3, $a = 1/k$ and $b = 1/kK_3$. Thus, $k = 4.26 \pm 0.11$ M^{-1} sec^{-1} and $K_3 = (5.99 \pm 0.29) \times 10^{-5}$ M. This $\text{p}K_3$ value at 25° (4.2 ± 0.2) is in fair agreement with the independent spectroscopic value[9] of 4.7 at 20°. Using the derived k and K_3 values, Table II shows the good agreement between $(\text{Cu(II)}/k_{\text{obsd}})$ observed and calculated.

The sulfonated deuteroporphyrin has an extremely wide pH solubility range. Most carboxylic acid porphyrins flocculate at pH 4 and *meso*-tetrapyridylporphine (TPyP) is soluble[13] only below pH 3.5. Thus the complications of phase equilibria present when adding detergents to solubilize porphyrins[2] or mixed-solvent systems with varied rate–solvent effects[5] are absent with this compound. No evidence appeared in this reaction for a "sitting atop" intermediate,[14] as found in the incorporation of Cu(II) into TPyP in aqueous solutions.[6]

The reactive species of this porphyrin appears to be the unprotonated free base (PH_2). In contrast to other porphyrin insertion reactions,[5–7] the rate dependence of pH can fairly unambiguously be ascribed to a porphyrin $(\text{PH}_3{}^+\text{–PH}_2)$ and not a metal ion $(\text{M(H}_2\text{O)–M(OH)})$ preequilibrium. Since the activated complex contains the free base and a copper ion, there is no information on the subsequent steps whereby the two protons are removed and Cu(II) is inserted.

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CONTRIBUTION FROM THE DEPARTMENT
OF INDUSTRIAL CHEMISTRY,
UNIVERSITY OF TOKYO, HONGO, TOKYO, JAPAN

The Ligand Effects on the N≡N Bond in the Nitrogen Complexes of Cobalt

BY A. MISONO, Y. UCHIDA, T. SAITO,
M. HIDAI, AND M. ARAKI

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We have previously reported that a nitrogen-coordinated complex is prepared by the reduction of cobalt(III) acetylacetonate with triisobutylaluminum in the presence of triphenylphosphine under a nitrogen atmosphere.[1] Yamamoto, *et al.*, also prepared the same complex by an analogous method.[2] Although we

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(2) A. Yamamoto, S. Kitazume, L. S. Pu, and S. Ikeda, *Chem. Commun.*, 79 (1967).

have previously supposed the above nitrogen-coordinated complex to be a mixture of $CoN_2[(C_6H_5)_3P]_3$ and $CoN_2H[(C_6H_5)_3P]_3$, recent X-ray structural analysis on the nitrogen complex[3] and the nmr spectrum of this complex[4] indicate that this is correctly formulated as $CoN_2H[(C_6H_5)_3P]_3$. On the other hand, Sacco, *et al.*, prepared the same nitrogen complex, $CoN_2H[(C_6H_5)_3P]_3$, by the reaction of $CoH_3[(C_6H_5)_3P]_3$ with nitrogen.[5] In this note we report the ligand effects on the N≡N bond in nitrogen complexes of cobalt.

Experimental Section

The infrared and nmr spectra were recorded on a Nihon-Bunko double-beam DS-301 spectrometer and Nihon-Denshi Model C-60, respectively.

Cobalt(III) acetylacetonate was prepared by the usual method.[6] Tri-*n*-butylphosphine, triphenyl phosphite, triphenylamine, triphenylarsine, and 2,2′-bipyridyl were commercially obtained. Tri-*p*-tolylphosphine and diphenylphosphine were prepared by the methods of Mann and Chaplin[7] and Hewertson and Watson,[8] respectively. Diphenylethylphosphine was prepared by the reaction of ethyldichlorophosphine[9] with phenylmagnesium bromide, and diphenylmethylphosphine was prepared by the reaction of sodium diphenylphosphide[8] with methyl iodide. Triethylphosphine was synthesized from triethylaluminum and phosphorus trichloride. Bis(*o*-diphenylphosphinophenyl)phenylphosphine and 1,1,1-tris(diphenylphosphinomethyl)ethane were prepared by the method of Hewertson and Watson.[8] Bis(3-diphenylphosphinopropyl)phenylphosphine was prepared by a method similar to that of bis(2-diphenylphosphinoethyl)phenylphosphine.[8] Triisobutylaluminum, obtained commercially, was used after distillation. All of the solvents were purified by the usual methods and distilled under nitrogen.

Every operation was carried out under nitrogen. Nitrogen complexes were prepared typically as follows. To the mixture of cobalt(III) acetylacetonate (3 mmol), tri-*p*-tolylphosphine (9 mmol), and toluene (10 ml) was added triisobutylaluminum (1.3 ml) with stirring at −40°. Then nitrogen gas was bubbled through the reaction solution at 0–10°. The color of the solution changed from green to red, and after several hours all of the reactants dissolved in toluene. By allowing the homogeneous solution to remain undisturbed, the orange crystalline complex precipitated. The complex was washed with ether and petroleum ether (bp 45–70°) and dried *in vacuo* (*ca.* 30% yield).

Results and Discussion

When triphenyl phosphite, triphenylamine, triphenylarsine, 2,2′-bipyridyl, bis(*o*-diphenylphosphinophenyl)phenylphosphine, 1,1,1-tris(diphenylphosphinomethyl)ethane, and bis(3-diphenylphosphinopropyl)phenylphosphine were used as ligands instead of triphenylphosphine, nitrogen complexes of cobalt could not be obtained. However, when tri-*p*-tolylphosphine, diphenylethylphosphine, tri-*n*-butylphosphine, and triethylphosphine were used as ligands (L), nitrogen complexes of cobalt, $CoHN_2L_3$, were obtained. On the other hand, in the case of diphenylmethylphosphine and diphenylphosphine, hydrido complexes, $CoHL_4$, were isolated.

Hydridonitrogentris(tri-*p*-tolylphosphine)cobalt, $CoHN_2[(CH_3C_6H_4)_3P]_3$, is an orange, crystalline solid, soluble in toluene and benzene but insoluble in light petroleum. *Anal.* Calcd for $C_{63}H_{64}P_3N_2CO$: C, 75.59; H, 6.44; N, 2.80. Found: C, 75.57; H, 6.76; N, 2.93.

Hydridonitrogentris(diphenylethylphosphine)cobalt, $CoHN_2[(C_6H_5)_2C_2H_5P]_3$, hydridonitrogentris(tri-*n*-butylphosphine)cobalt, $CoHN_2[(C_4H_9)_3P]_3$, and hydridonitrogentris(triethylphosphine)cobalt, $CoHN_2[(C_2H_5)_3P]_3$, were obtained as oils, soluble in benzene, toluene, and petroleum ether. All attempts to obtain them in a pure form were unsuccessful. The infrared spectra of these nitrogen complexes of cobalt show a very sharp absorption at 2000–2100 cm^{-1} assignable to an N≡N stretching vibration (Table I). With the increase of the electron-donating power of a ligand, the N≡N stretching frequency was shifted to a lower position as known in the case of carbonyl complexes of transition metals. In these infrared spectra no characteristic absorption due to a Co—H stretching vibration was found, but nmr spectra of these nitrogen complexes show an absorption band at τ 29–31. This band was a quartet with the intensity ratios 1:3:3:1; the coupling constant between the phosphorus-31 nucleus (spin $^1/_2$) and the hydridic hydrogen nucleus was 50 cps (Table II). These results were so similar to the results of $CoHN_2[P(C_6H_5)_3]_3$ that the structures of these four complexes seem to be analogous to that of $CoHN_2[P(C_6H_5)_3]_3$.

TABLE I

INFRARED SPECTRA OF $CoHN_2L_3$

L	ν(N≡N), cm^{-1}	Solvent
$(C_6H_5)_3P$	2088	Benzene
$(p\text{-}CH_3C_6H_4)_3P$	2073	Benzene
$(C_6H_5)_2C_2H_5P$	2060	Toluene
$(n\text{-}C_4H_9)_3P$	2032	Toluene
$(C_2H_5)_3P$	2033	Toluene

TABLE II

NMR SPECTRA OF $CoHN_2L_3$

L	τ	J_{PH}, cps	Solvent
$(C_6H_5)_3P$	29	50	THF
$(C_6H_5)_2C_2H_5P$	30	50	Toluene
$(n\text{-}C_4H_9)_3P$	31	50	Toluene
$(C_2H_5)_3P$	31	50	Toluene

The hydrido complexes $CoH[(C_6H_5)_2HP]_4$ and $CoH[(C_6H_5)_2CH_3P]_4$ are orange, crystalline solids. The former is soluble in benzene, toluene, and ether. *Anal.* Calcd for $C_{48}H_{45}P_4Co$: C, 71.65; H, 5.64. Found: C, 71.36; H, 5.77. The latter is sparingly soluble in these solvents. *Anal.* Calcd for $C_{52}H_{53}P_4Co$: C, 72.55; H, 6.21. Found: C, 72.73; H, 6.60. These complexes are both diamagnetic, and the nmr spectrum of $CoH[(C_6H_5)_2HP]_4$ shows a quintet at τ 29.3. The infrared spectra of $CoH[(C_6H_5)_2HP]_4$ and $CoH[(C_6H_5)_2CH_3P]_4$ show a broad absorption at 1910 and 1950 cm^{-1}, respectively, assignable to a Co–H stretching vibration.

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