Contribution from the Department of Industrial Chemistry, Faculty of Engineering, Kumamoto University, Kumamoto 860, Japan, and the Research Institute of Industrial Science, Kyushu University, Fukuoka 812, Japan

Coordination and Reduction of Nitric Oxide on a Cobalt Tetraphenylporphyrin Imidazole Complex

KAZUHIKO TSUJI,[†] MASAHIKO IMAIZUMI,[†] AKIRA OYOSHI,[†] ISAO MOCHIDA,*,[‡] HIROSHI FUJITSU,[‡] and KENJIRO TAKESHITA[‡]

Coordination and reduction of nitric oxide on cobalt tetraphenylporphyrin anchored to imidazole on SiO_2 were studied to obtain basic information for development of a novel catalyst. The complex adsorbed nitric oxide, giving a ν_{NO} band around 1650 cm^{-1}, which is red shifted from that of gaseous nitric oxide. The shift indicates significant activation of nitric oxide promoted by the $d\pi$ orbitals of the cobalt ion, which is influenced through strong π donation from the axially coordinating imidazole ligand. The complex catalytically reduced nitric oxide with hydrogen more effectively than CoTPP on SiO_2. A reaction mechanism based on the trans effect of imidazole for the coordination and activation of nitric oxide was proposed.

Introduction

Since nitric oxide has been recognized as one of the environmental pollutant gases to be removed, a number of its catalytic decompositions and reductions have been proposed.[1] The coordination chemistry of nitric oxide has been also studied with use of transition-metal complexes.[2] Among them, porphyrins of square-pyramidal complexes carrying at their axial positions a basic molecule such as imidazole or pyridine derivatives evoke an interest in the coordination chemistry relating to biological system.[3] The low-valent cobalt complexes (CoTPP) (d$^{6-7}$ configuration) have been demonstrated to activate the coordinating nitric oxide by weakening the nitrogen–oxygen bond through the back-donation of d electrons to the π^* antibonding orbital of the oxide.[4] Thus the oxide can be catalytically reduced with reducing agents such as hydrogen,[5] carbon monoxide,[5c] and ammonia.[6]

The present study reports on the coordination and reduction of nitric oxide on CoTPP linked to imidazole (Co(Im)TPP), which is known to serve as the axial ligand of the heme in the hemoglobin molecule. The electronic configuration of CoTPP effectively modified by the axially coordinating imidazole can be expected to show a superior ability for the coordination (adsorption) and activation of nitric oxide, as suggested by the fact that FeClTPP (d^5 configuration) and NiTPP (d^8 configuration) behaved quite differently on this subject.[5c] A Co(Im)TPP complex that is supported by or linked to silica gel of large surface area may become a large active heterogeneous catalyst owing to the increase of its catalytic effective surface area. The coordination state of nitric oxide is investigated by using FT IR and UV spectroscopies.

Experimental Section

Complex. Cobalt tetraphenylporphyrin (CoTPP) was prepared by Adler's method.[7] Its imidazole complex (Co(Im)TPP) was prepared by stirring equimolar mixtures of CoTPP (500 mg) and imidazole (50 mg, Katayama Kagaku, Guaranteed Reagent) in chloroform for 12 h at room temperature. A purple powder was obtained. In the present study, three kinds of heterogeneous complexes were prepared (formulated as CoTPP(Im)/SiO$_2$, CoTPP(ImMSG), and CoTPP/SiO$_2$; 5 wt % of the complexes were supported on or fixed in these catalysts). CoTPP and CoTPP(Im) supported on SiO$_2$ (CoTPP/SiO$_2$ and CoTPP(Im)/SiO$_2$) were prepared by impregnating the complexes onto silica gel (Wako gel C-100: BET surface area 322 m^2/g) in benzene or chloroform. Ten grams of silica gel (dried at 160 °C for 1 day), 2 g of imidazole, and 3.5 cm^3 or Wacker Silan GE 16 [(chloropropyl)trimethoxysilane] were refluxed in *m*-xylene for 2 h to prepar ImMSG (modified silica gel) according to Basolo and Burwell.[8] A pale yellow precipitate was filtered and washed with dry acetone and benzene several times. The dehydrochlorination of the product was carried out with ethylene oxide at 0 °C. Elemental

analysis of ImMSG (C, 9.90; N, 3.53; H, 1.74) showed that the amount of fixed imidazole on silica gel was 1.25 mmol/g of MSG. To 1 g of ImMSG dispersed in benzene, CoTPP (50 mg) was added and stirred till the red-purple solution became clear, showing complete fixation of CoTPP onto ImMSG. The precipitate was filtered, washed with benzene, and dried. Anal. Calcd for CoTPP(Im): C 13.18; N, 3.78; H, 1.86. Found: C, 12.85; 3.63; H, 1.81.

Characterization of the Catalysts. Diffuse reflectance visible spectra, which are shown in Figure 1, were obtained for the above three catalysts with a Shimadzu UV-202 spectrophotometer. The powdered state of CoTPP(Im) on SiO$_2$ showed the same absorption maxima as those of CoTPP(Im) in benzene solution. Red shifts for both the visible and Soret bands were observed according to the coordination of imidazole. These indicate that SiO$_2$ behaves as a nonpolar solvent like benzene. The same spectra for CoTPP(Im)/SiO$_2$ and CoTPP-(ImMSG) suggest that the degree of dispersion and the electronic effect of imidazole are similar in CoTPP(Im)/SiO$_2$ and CoTPP-(ImMSG).

Adsorption of Nitric Oxide. Adsorption of nitric oxide over the catalysts was measured by volumetric analysis with a glass apparatus (dead volume 33.4 cm^3) connected to a vacuum line and gas reservoirs. After the adsorbent (1 g) was evacuated at a fixed temperature for 30 min, nitric oxide (50 cmHg) was introduced to contact with the adsorbent, monitoring of the uptake being done by means of a mercury manometer.

The introduction of nitric oxide into benzene solution was performed in a quartz cell (1 × 1 × 4 cm), which was connected to the vacuum line with a glass joint. After the benzene solution was degassed by repeating the freezing–pumping–thawing cycle, nitric oxide (1 atm) was introduced into the frozen solution. The spectra were recorded after the solution thawed.

Infrared spectra of the catalysts in KBr disks were recorded with a JEOL FT IR JIR 03-F spectrophotometer.

Catalytic Reaction. The catalytic reaction was performed at 200 and 300 °C with a conventional closed circulating reactor (volume ca. 400 mL, circulation rate 500 mL/min), which was connected to gas reservoirs and a vacuum line. Catalyst weight and partial pressures of NO and H$_2$ were 2 g, 2 cmHg, and 60 cmHg, respectively. Conversion of NO and yields of N$_2$ and N$_2$O were determined with a gas chromatograph, using columns packed with molecular sieve 13X and Porapack-Q, respectively. NH$_3$ was evaluated usually from the

(1) C. Shelef, *Catal. Rev.—Sci. Eng.*, **11**, 1 (1975).
(2) R. Eisenberg and C. D. Meyer, *Acc. Chem. Res.*, **8**, 26 (1975); J. A. McCleverty, *Chem. Rev.*, **79**, 53 (1979).
(3) A. Szabo and L. D. Barron, *J. Am. Chem. Soc.*, **97**, 660 (1975).
(4) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 2nd ed., Wiley-Interscience, New York, 1966, p 747.
(5) (a) I. Mochida, K. Takeyoshi, H. Fujitsu, and K. Takeshita, *Chem. Lett.*, 327 (1976); (b) F. Steinbach and H.-J. Joswig, *J. Catal.*, **55**, 272 (1978); (c) K. Tsuji, H. Fujitsu, K. Takeshita, and I. Mochida, *J. Mol. Catal.*, **9**, 389 (1980); (d) I. Mochida, K. Tsuji, K. Suetsugu, H. Fujitsu, and K. Takeshita, *J. Phys. Chem.*, in press.
(6) P. Gans, *J. Chem. Soc. A*, 943 (1967); S. Naito, *J. Chem. Soc., Chem. Commun.*, 175 (1978).
(7) A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour, and L. Korsakoff, *J. Org. Chem.*, **32**, 476 (1967).
(8) R. L. Burwell, Jr., *CHEMTECH*, 370 (1974).

[†] Kumamoto University.
[‡] Kyushu University.
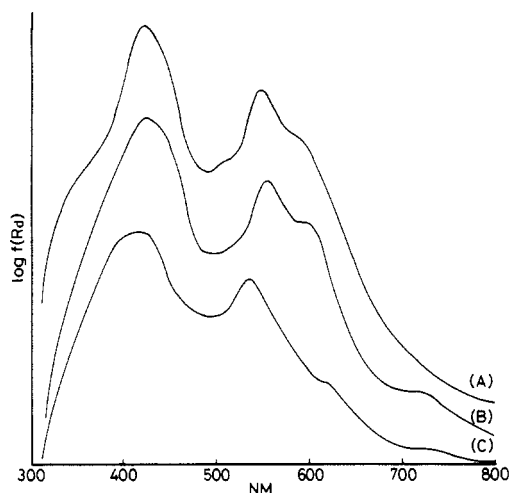
Figure 1. Diffuse reflectance spectra of the catalysts: (A) CoTPP-(ImMSG); (B) CoTPP(Im)/SiO₂; (C) CoTPP/SiO₂. Supporting and fixation ratios of complexes are 5 wt %. Measured by using MgO powder as reference.
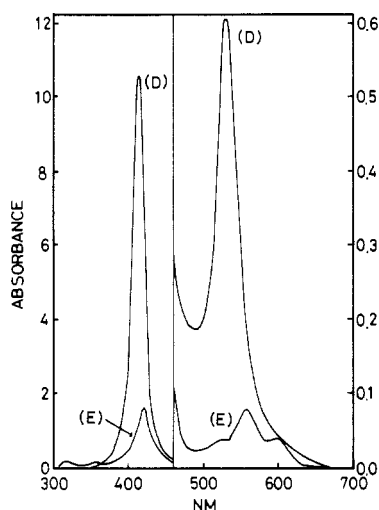

Figure 2. Electronic spectra of cobalt–porphyrin complexes in benzene: (D) CoTPP, 3.48×10^{-5} mol dm⁻³; (E) Co(Im)TPP, 3.22×10^{-5} mol dm⁻³.

difference from mass balance based on nitric oxide; however, occasional analysis was also performed with a column packed with undecan-1-ol/liquid paraffin on Flusin T. Ammonia formed during the reaction was trapped by a small amount of sulfuric acid in the reaction apparatus.

Results

Spectroscopic Studies of NO Adduct in Solution. Electronic spectra of CoTPP (D) and Co(Im)TPP (E) in benzene are shown in Figure 2. The coordination of imidazole to CoTPP caused a red shift of the characteristic bands (Q band, 528 → 550 nm; Soret band, 413 → 421.5 nm) with a new shoulder at 600 nm and a marked decrease of solubility in benzene. The introduction of nitric oxide to CoTPP in benzene after evacuation also resulted in a red shift (Q band, 528 → 540 nm; Soret band, 413 → 415 nm), indicating the formation of the nitrosyl complex of CoTPP (Co(NO)TPP), which was characterized by an intense infrared absorption at 1689 cm⁻¹ assigned to ν_{NO}.[9] In contrast, the introduction of nitric oxide to Co(Im)TPP under the same conditions brought about no change in the spectrum, suggesting that the trans effect of imidazole retards the coordination of nitric oxide to CoTPP. When a Co(Im)TPP crystal that had been in contact with
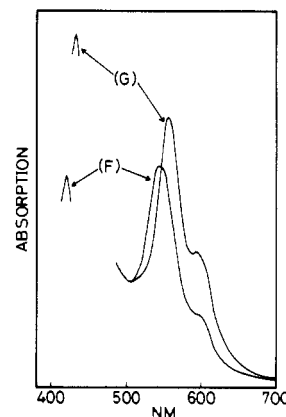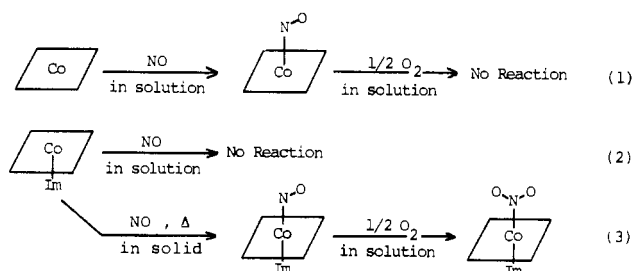
Figure 3. Electronic spectral change in the reaction of Co(Im)-(NO)TPP with air in benzene: (F) after being exposed to NO at 200 °C; (G) after (F) was exposed to air for about 1 week.
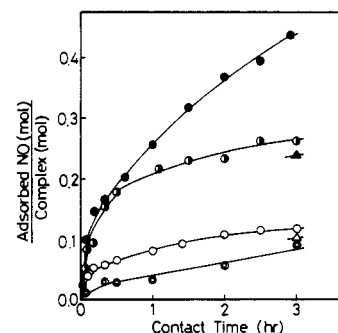
Figure 4. NO adsorption curve for the catalysts: CoTPP(Im)/SiO₂, (O) 28 °C, (◑) 200 °C; CoTPP(ImMSG), (◎) 28 °C, (●) 200 °C; CoTPP/SiO₂, (△) 28 °C, (▲) 200 °C.

Scheme I

nitric oxide at 1 atm and at 200 °C was dissolved in benzene, absorption maxima at 595.5 (sh), 541, and 421.5 nm (Figure 3, spectrum F), which were located between those of Co-(Im)TPP and Co(NO)TPP, were observed, suggesting the formation of a hexacoordinated Co(Im)(NO)TPP species. The spectrum changed gradually in contact with air in benzene, indicating the oxidation of NO ligand to produce Co(Im)-(NO₂)TPP (Figure 3, spectrum G) (This species showed the characteristic IR bands of a nitro group at 1310, 1260, and 820 cm⁻¹, which can be assigned to its ν_{as}, ν_s, and δ, respectively.[10]), although Co(NO)TPP in benzene solution was very stable in air. Thus, the introduction of imidazole to CoTPP as an axial ligand enhanced the reactivity of the coordinated nitrosyl species, although the coordination of nitric oxide was rather retarded. The reactions involved are summarized in Scheme I.

Adsorption of Nitric Oxide over Catalysts. In spite of no spectroscopic evidence for the coordination of nitric oxide molecule to the Co(Im)TPP complex in solution, the adsorption of the gas on the silica-supported imidazole complex was

(9) W. R. Scheidt and J. R. Hoard, *J. Am. Chem. Soc.*, **95**, 8281 (1973).

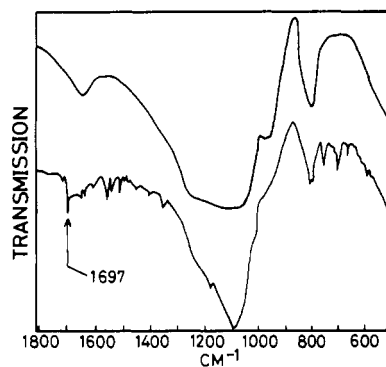(10) S. G. Clarkson and F. Basolo, *Inorg. Chem.*, **12**, 1528 (1973).

Figure 5. IR spectrum of an adsorbed NO species: (lower) CoTPP/SiO₂-NO; (upper) SiO₂ (blank).

measurable by volumetric analysis.

The molar ratios of adsorbed NO (50 cmHg of NO was introduced) to supported porphyrin complex (CoTPP/SiO₂, CoTPP(Im)/SiO₂, and CoTPP(ImMSG)) at room temperature and 200 °C were plotted against the contact time (Figure 4). The ratios of the three catalysts at room temperature increased regularly with time to reach the same value after 3 h, although the initial rates were different, suggesting the imidazole influences kinetically the coordination of nitric oxide to the supported complex. At 200 °C, the adsorption rate was remarkably enhanced and the molar ratios after 3 h were 2–5 times those at room temperature, although the ratio reached 1 with a longer contact time at both temperatures regardless of the catalysts. The high adsorption rate of CoTPP(ImMSG) after 1 h should be noted, although it may be indifferent to its catalytic activity. NO was not adsorbed on SiO₂ itself.

When a gas mixture of nitric oxide (2 cmHg) and hydrogen (60 cmHg) was introduced over the imidazole-containing catalysts at 200 °C, molar ratios of nearly 1 (1.07 with CoTPP(Im)/SiO₂ and 0.84 with CoTPP(ImMSG)) were achieved within 5 h, and no reduction product was detected.

IR Spectra of the Adsorbed NO Species over Catalysts. After the three catalysts mentioned above were fully evacuated, nitric oxide (1 atm) was introduced and left in contact with them for 1 week at room temperature. The supporting ratio of the complexes was raised to 30 wt % in order to observe the IR bands easily, although the fixation ratio in CoTPP-(ImMSG) was still 5 wt % because of difficulty in achieving a higher degree of the fixation ratio.

Figure 5 shows the spectra of the CoTPP/SiO₂ plus NO system (lower) and SiO₂ (upper) in the region 1800–600 cm⁻¹. Gaseous NO showed a band at 1876 cm⁻¹. Among absorption bands due to the complex and the support, a new sharp absorption peak at 1697 cm⁻¹ was observable, which should be assigned to the stretching of adsorbed nitric oxide.

For CoTPP(Im)/SiO₂ and CoTPP(ImMSG), definite absorption derived from the adsorbed nitric oxide was difficult to find in the above region by simple inspection; however, the broad band of SiO₂ centered at 1635 cm⁻¹ may obscure its absorption band. Figure 6 shows FT IR spectra of CoTPP-(Im)/SiO₂ (upper) and the CoTPP(Im)/SiO₂ plus NO system (lower) after computational averaging. A new peak at 1650 cm⁻¹ (lower spectrum) was observable, differing from 1635 cm⁻¹ (upper spectrum). The introduction of nitric oxide to CoTPP(ImMSG) produced a new peak at 1643 cm⁻¹ revealed by the same technique. Such a peak may be assigned to the stretching band of adsorbed nitric oxide, which was shifted to lower frequency by the influence of imidazole at the trans position.

Catalytic Reduction of Nitric Oxide with Hydrogen. The catalytic activities of CoTPP and CoTPP(Im) in reducing NO on silica gel with hydrogen into molecular nitrogen, nitrous oxide, and ammonia are summarized in Table I. The con-
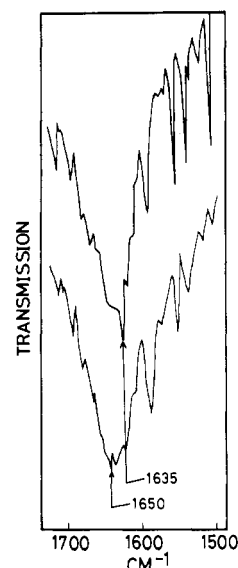

Figure 6. FT IR spectrum of an adsorbed NO species: (lower) CoTPP(Im)/SiO₂-NO; (upper) CoTPP(Im)/SiO₂.

Table I. Catalytic Activities of CoTPP and Its Derivatives for NO Reduction with H₂ at 300 °C

catalyst	NO complex, mmol	conv, %	product yield, %[b]		
			N₂	N₂O	NH₃[c]
CoTPP(Im)/SiO₂	0.135	79.8	13.7 (17)	13.7 (17)	52.4 (66)
CoTPP(ImMSG)	0.135	77.6	19.6 (25)	12.2 (16)	45.8 (59)
CoTPP/SiO₂	0.149	36.0	5.6 (15)	9.4 (26)	21.0 (59)
CoTPP[a]	1.491	19.4	2.6 (13)	5.6 (29)	11.2 (58)

[a] In ref 5c. [b] Numbers in parentheses are selectivity. Selectivity = (product yield)/(NO conversion). [c] Yield NH₃ = conversion NO − yield (N₂ + N₂O).

Table II. Electronic Spectra of M(LL')TPP[a]

complex	abs band, nm		ref
	Q	Soret	
CoTPP	528	412	this work
Co(Im)TPP	599, 559	424	this work
Co(NO)TPP	580 (sh), 540	415	this work
Co(Im)(NO)TPP	595.5 (sh), 541	421.5	this work
CoClTPP[b]	575 (sh), 541	425.5	17
ZnTPP	588, 549.5	422.5	14
Zn(Im)TPP	606, 566	431	14

[a] Solvent is benzene unless otherwise noted. L = none, NO, and Cl⁻; L' = none and Im (imidazole). [b] Measured in methanol.

version of nitric oxide and the product distribution were almost the same over CoTPP(Im)/SiO₂ (supported catalyst) and CoTPP(ImMSG) (fixed catalyst). Their catalytic activities were more than twice that of the CoTPP/SiO₂ catalyst. The amounts of converted NO molecule per CoTPP(Im) molecule on SiO₂ within 5 h were 40 times that per CoTPP molecule in its crystal form. The product distribution was almost the same over all catalysts listed in Table I with slightly higher selectivity of molecular nitrogen over imidazole complexes.

Discussion

Electronic Interaction of CoTPP with Axial Ligands. Table II summarizes the absorption maxima of metallotetraphenylporphyrins carrying one or two axial ligands. Only the monoimidazole adduct of CoTPP, which showed red shifts in both the Q and Soret bands as reported by Ibers et al.[11] and Scheidt et al.,[12] was formed even with excess base, because

(11) R. G. Little and J. A. Ibers, *J. Am. Chem. Soc.*, **96**, 4452 (1974).

Table III. Stretching Frequencies of Adsorbed (Coordinated) NO Species

adsorbed NO species	ν_{NO}, cm^{-1}	ref
NO (gaseous)	1876	
(ON)CoTPP/SiO$_2$	1697	this work
(ON)CoTPP	1689	9
(ON)CoTPP(Im)/SiO$_2$	1650	this work
(ON)CoTPP(ImMSG)	1643	this work
(ON)Co(dmgH)$_2$	1641	15a
trans-(ON)CoCl(en)$_2{}^+$	1611	15b
(ON)Co(NH$_3$)$_5{}^{2+}$	1610	15c

the supply of the electrons in d$_\pi$ orbitals into two axial ligands may destabilize the axial bonding to coordinating imidazole molecules. No spectral change was observed when an excess of pyridine was added to CoTPP in benzene probably because its π-donating ability is poorer than that of imidazole in spite of their similar σ-donor strengths.[13] Valentine et al.[14] reported similar red shifts of the electronic spectra of ZnTPP under the influence of various axial ligands containing imidazole due to the π-electron transfer from the axial bases to the porphyrin ring via Zn ion. The red shift observed with the introduction of imidazole to CoTPP may be explained in a similar manner.

It is known that the nitrosyl group coordinated to CoTPP withdraws the π electron from the central metal, forming the complex designated as Co^{III}(NO$^-$)TPP,[9,15] in a similar manner as O$_2{}^-$ does in the oxygen adduct.[16] The NO adduct showed a red shift in its spectrum compared to that of the original complex. A very similar spectrum was observed for Co^{III}-ClTPP in methanol,[17] suggesting that the spectral red shift of the complexes containing the anionic ligands (NO$^-$ and Cl$^-$) is attributable to the formal oxidation of cobalt ion (II → III).

There has been no report on six-coordinated nitrosylcobalt porphyrin formulated as CoL(NO)P, where L and P denote neutral bases and porphyrins, respectively, although FeTPP and MnTPP are known to form six-coordinated complexes such as Fe(1-MeIm)(NO)TPP and Mn(4-MePy)(NO)TPP, respectively.[18] By the introduction of imidazole, it becomes hard for CoTPP to coordinate nitric oxide kinetically as indicated by difficulty in the formation of the Co(Im)(NO)TPP species under relatively low pressure of nitric oxide at room temperatures. This phenomenon suggests the similarity of nitric oxide to carbon monoxide[19] rather than molecular oxygen[20,21] in terms of coordination ability to the five-coordinated porphyrins since no six-coordinated carbonylcobalt porphyrin has been reported.

It is clear that the axial site of the CoTPP complex is most affected by the strong π-donating properties of imidazole. The oxidation of NO ligand in Co(Im)(NO)TPP seems similar to that of Co(Schiff base)(NO)L reported by Clarkson and Basolo.[10] The same manner was shown in Scheme I for the Co(Im)(NO)TPP complex with oxygen in solution. Imidazole
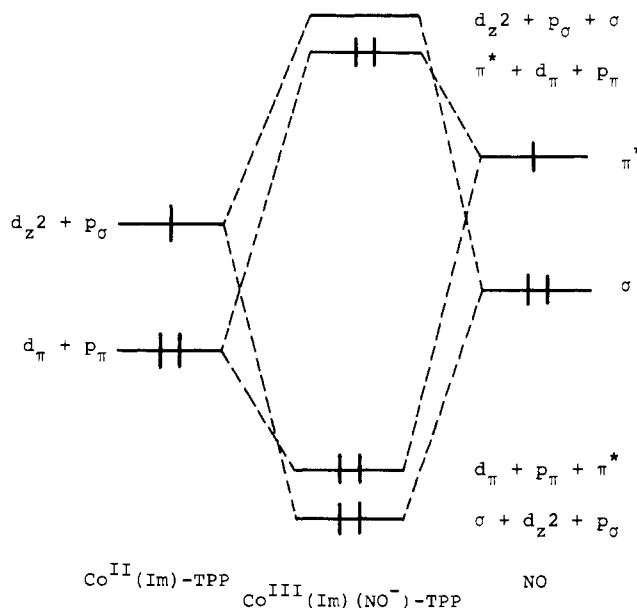
(12) W. R. Scheidt, *J. Am. Chem. Soc.*, **96**, 90 (1974); P. N. Dewer, P. Madura, and W. R. Scheidt, *ibid.* **96**, 5293 (1974).
(13) F. F. Walker, *J. Am. Chem. Soc.*, **95**, 1150 (1973).
(14) M. Nappa and J. S. Valentine, *J. Am. Chem. Soc.*, **100**, 5075 (1978).
(15) (a) M. Tamaki, I. Masuda, and K. Shinra, *Bull. Chem. Soc. Jpn.*, **45**, 171 (1972); (b) D. A. Snyder and K. L. Weaver, *Inorg. Chem.*, **9**, 2760 (1970); (c) D. Hall and A. A. Taggart, *J. Chem. Soc.*, 1359 (1965).
(16) B. M. Hoffman, D. L. Diemente, and F. Basolo, *J. Am. Chem. Soc.*, **92**, 61 (1970); F. A. Walker, *ibid.*, **92**, 4235 (1970); B. B. Wayland and M. E. Abd-Elmageed, *ibid.*, **96**, 4809 (1974); F. A. Walker, *J. Magn. Reson.*, **15**, 201 (1974).
(17) T. Sakurai, K. Yamamoto, H. Naito, and N. Nakamoto, *Bull. Chem. Soc. Jpn.*, **49**, 3042 (1976).
(18) P. L. Piciulo, G. Rupprecht, and W. R. Scheidt, *J. Am. Chem. Soc.*, **96**, 5293 (1974).
(19) B. B. Wayland and D. Mohajer, *J. Am. Chem. Soc.*, **93**, 5295 (1971).
(20) D. V. Stynes, H. C. Stynes, B. R. James, and J. A. Ibers, *J. Am. Chem. Soc.*, **95**, 1796 (1973).
(21) M. J. Carter, D. P. Pillema, and F. Basolo, *J. Am. Chem. Soc.*, **96**, 392 (1974); A. Dedieu and A. Veillard, *Theor. Chim. Acta*, **36**, 231 (1975).

Figure 7. Electronic configuration of interacting Co(Im)TPP complex with NO molecule: d$_\pi$ designates d$_{xz}$ and d$_{yz}$ of cobalt ion; p$_\sigma$ and p$_\pi$ come from imidazole.

Scheme II
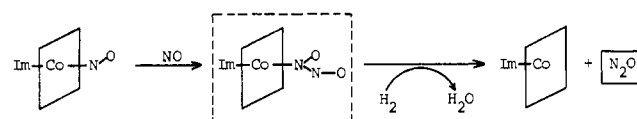
is known to promote the oxygen-uptake abilities of cobalt deuteroporphyrin IX dimethyl ester and Schiff base complexes.[21]

Effect of Imidazole on the Reactivity of a Nitrosyl Group Coordinated to CoTPP. The extent of activation of the coordinated nitric oxide (lengthening of the N–O bond) can be discussed directly by use of the infrared spectra. Table III summarizes the stretching frequency of the adsorbed nitric oxide on the present catalysts together with those of some cobalt nitrosyl complexes. Gaseous nitric oxide shows a characteristic intense band at 1876 cm^{-1}. It has been postulated that the lower frequency of the coordinated nitric oxide relative to that of gaseous nitric oxide indicates that the ligand takes a bent form in the M–N–O linkage. For nitrosyl ligand coordinated to CoTPP on SiO$_2$ ν_{NO} is 8 cm^{-1} higher than ν_{NO} for the unsupported Co(NO)TPP. The ligands in the imidazole-containing catalysts show the band lower by 50 cm^{-1} than that of Co(NO)TPP/SiO$_2$, indicating a higher activation of nitric oxide by strong π donation of imidazole through d$_\pi$-bonding orbitals of the cobalt ion.[21]

The nitrosyl groups in the other complexes listed in Table III show a lower ν_{NO} than that of the corresponding TPP complexes of the same coordination number, suggesting that TPP ligand is rather unfavorable for the activation of nitric oxide compared with dmgH, en, and NH$_3$. This may be because TPP competes to a larger extent with nitrosyl ligand for the π electron provided from the cobalt ion[9] than other ligands. One can expect the most elongated N–O bond in *trans*-[(ON)Co(Im)(NH$_3$)$_4{}^{2+}$]; however, one should also take other factors into consideration when exploring the more active catalyst, for example, the stability or activation of reductant.

Mechanistic Consideration of the Reduction of Nitric Oxide with Hydrogen over the Imidazole-Containing Catalysts. In a previous paper, we proposed a tentative reaction scheme for the reduction of nitric oxide with hydrogen over metalloporphyrins.[5c] The product distribution over the imidazole-containing catalysts in the present study, which is comparable

to that over CoTPP/SiO$_2$ and CoTPP, suggests a similar reaction scheme.

The adsorption of nitric oxide may be rather difficult as shown in the UV spectroscopy study of it in solution on CoTPP(Im); however, its activation will be more pronounced once it adsorbs. Such situations will be explained in terms of simple molecular orbitals as illustrated in Figure 7, where the orbitals interacting scarcely with nitric oxide are ignored. The orbitals composed of d$_{z^2}$ + p$_\sigma$ + p$_{\sigma'}$ and π^* + d$_\pi$ + p$_\pi$ are related to the coordination and activation of nitric oxide, respectively. When the electronic density of these orbitals increases with the strong σ- and π-donating abilities of imidazole, the coordination of NO may be hindered but the activation

is enhanced by a strenghthening of the anionic nature of adsorbed nitric oxide. The electronic configuration (Figure 7) after the electron transfer into the π MO (π^* + dπ + pπ, major contribution of π^* NO) from the σ-MO (d$_{z^2}$ + pσ + σ) indicates a formal structure of Co^{III}ImNO$^-$.

An alternative route leading to nitrous oxide (Scheme II) may contribute to a certain extent. Such a reaction between the adsorbed NO and a gaseous NO may be probable because imidazole promotes the oxidation of a cobalt–nitrosyl complex by molecular oxygen.

Contribution from the Department of Chemistry,
University of Western Ontario, London, Canada N6A 5B7

Reactions of Binuclear Hydridoplatinum Complexes with Alkynes

RICHARD J. PUDDEPHATT* and MARY A. THOMSON

Reaction of the binuclear hydride [Pt$_2$H$_2$(μ-H)(μ-dppm)$_2$]PF$_6$ (I) (dppm = Ph$_2$PCH$_2$PPh$_2$) with alkynes, RC≡CR, in dichloromethane solution gives [Pt$_2$Cl(*cis*-CR=CHR)(μ-RCCR)(μ-dppm)$_2$] (II), R = CF$_3$ or CO$_2$Me, and H$_2$. In donor solvents (S = MeCN, PhCN, or acetone) the reaction gives only [Pt$_2$H(S)(μ-RCCR)(μ-dppm)$_2$]PF$_6$ (III), which can be converted to [Pt$_2$HCl(μ-RCCR)(μ-dppm)$_2$] (IV) or [Pt$_2$Cl$_2$(μ-RCCR)(μ-dppm)$_2$] (V) by reaction with NaCl or HCl, respectively, and to II by reaction with RCCR in CH$_2$Cl$_2$ solution (R = CF$_3$). 3,3,3-Trifluoropropyne reacts with I to give [Pt$_2$(CCCF$_3$)$_2$(μ-CF$_3$CCH)(μ-dppm)$_2$]. The compounds are characterized by ^{1}H, ^{19}F, and ^{31}P NMR spectroscopy, and the sequence of reactions by which the compounds are formed is determined.

There has been great interest in the chemistry of binuclear and polynuclear platinum complexes, partly because there can be a resemblance between this chemistry and reactions that have been proposed to occur at a platinum surface in heterogeneous catalytic processes.[1-7] One of the best known catalytic reactions is the hydrogenation of alkenes and alkynes, and reactions of binuclear platinum hydrides with unsaturated reagents might be expected to give useful models for individual steps in the proposed catalytic cycles. For this reason we have studied reactions of the hydride[8] [Pt$_2$H$_2$(μ-H)(μ-dppm)$_2$]PF$_6$, dppm = Ph$_2$PCH$_2$PPh$_2$, with alkenes and alkynes. This paper gives results for reactions with alkynes bearing electronegative substituents. There have been many studies of related reactions with mononuclear platinum hydrides, particularly by Clark and co-workers, and the mechanisms are understood in some detail.[9,10] However, we know of no previous studies of reactions of alkynes with binuclear platinum hydrides.[11] A

preliminary account of parts of this work has been published.[12]

Results

Synthesis of New Compounds. A summary of many of the reactions studied is given in Scheme I. The characterization of the complexes will be discussed separately, and only the syntheses will be given here.

The first product to be isolated in pure form was IIa formed as very pale yellow crystals by reaction of excess hexafluorobut-2-yne, C$_4$F$_6$, with I in dichloromethane solution. Formally, this reaction involves loss of two hydrogen atoms from I, cis insertion of one alkyne into the remaining Pt–H bond, addition of a second alkyne between the two Pt atoms, and abstraction of Cl$^-$ from the solvent. The presence of chloride in the product was unexpected but was clearly indicated by the mass spectrum and elemental analysis; the chloride was easily displaced by iodide to give IIe.

The sequence of reactions by which IIa is formed is clearly of interest, and we have investigated this problem.

Reactions with other alkynes show that electronegative substituents are necessary on the alkyne in order to observe any reaction. Thus acetylene, but-2-yne, and diphenylacetylene failed to react with I in dichloromethane at temperatures up to 70 °C. However, the dimethyl ester of acetylenedicarboxylic acid did react with I to give IIb in fair yield, along with ill-characterized oligomers of the alkyne, which could be separated from the desired IIb by column chromatography. In this reaction a gas was evolved immediately on mixing the reagents, and this was identified as H$_2$ by gas chromatography. Quantitative analysis gave yields of 60–80% of H$_2$; this is at least as high as the isolated yield of IIb but may indicate that a side reaction not involving H$_2$ elimination from I also occurs. Hydrogen was identified as a product (GC) in the reaction giving IIa, but quantitative analysis was not attempted in this case.

(1) Boag, N. M.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1980**, 1281.
(2) Boag, N. M.; Green, M.; Howard, J. A. K.; Stone, F. G. A.; Wadepohl, H. *J. Chem. Soc., Dalton Trans.* **1981**, 862.
(3) Vranka, R. G.; Dahl, L. F.; Chini, P.; Chatt, J. *J. Am. Chem. Soc.* **1968**, *91*, 1574.
(4) Taylor, N. J.; Chieh, P. C.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* **1975**, 448.
(5) Albinati, A.; Carturan, G.; Musco, A. *Inorg. Chim. Acta* **1976**, *16*, L3.
(6) Boag, N. M.; Green, M.; Howard, J. A. K.; Spencer, J. L.; Stansfield, R. F. D.; Thomas, M. D. O.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1980**, 2182.
(7) Manojlovic-Muir, Lj.; Muir, K. W.; Solomun, T. *J. Organomet. Chem.* **1979**, *179*, 479.
(8) Brown, M. P.; Puddephatt, R. J.; Rashidi, M.; Seddon, K. R. *J. Chem. Soc., Dalton Trans.* **1978**, 516.
(9) Attig, T. G.; Clark, H. C.; Wong, C. S. *Can. J. Chem.* **1977**, *55*, 189.
(10) Thorn, D. L.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 2079.
(11) Binuclear platinum hydrides have been reported by: Tulip, T. H.; Yamagata, T.; Yoshida, T.; Wilson, R. D.; Ibers, J. A.; Otsuka, S. *Inorg. Chem.* **1979**, *18*, 2239. Clark, H. C.; Goel, A. B.; Goel, R. G.; Ogini, W. O. *J. Organomet. Chem.* **1978**, *157*, C16. Bracher, G.; Grove, D. M.; Pregosin, P. S.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 155. Minghetti, G.; Banditelli, G.; Bandini, A. L. *J. Organomet. Chem.* **1977**, *139*, C80.

(12) Puddephatt, R. J.; Thomson, M. A. *Inorg. Chim. Acta* **1980**, *45*, L281.