mixture was stirred rapidly for 2 h to give a rich, orange-gold solution. The solution was decanted and filtered through Celite on a coarse frit. Tetrahydrofuran was removed from the filtrate by using a rotary evaporator to give a red-orange solid which dissolved readily in 50 mL of benzene. Filtration and slow addition of approximately 100 mL of methanol caused precipitation of a dull orange solid (4.1 g) which was isolated by filtration, washed with methanol, and dried in vacuo. The infrared spectrum of this material revealed ν(NN) absorptions at 1955 and 1970 cm^{-1}. Recrystallization was accomplished by dissolving 1.0 g of this material in 20 mL of THF followed by slow addition of 40 mL of methanol. Filtration, washing with methanol, and drying in vacuo gave 0.5 g of bright orange solid. The infrared spectrum revealed that the band at 1970 cm^{-1} was present as a very weak shoulder on the very intense band at 1955 cm^{-1}. Recrystallization of this material using the above procedure gave 0.4 g of bright orange solid whose infrared spectrum revealed a symmetrical ν(NN) band at 1955 cm^{-1}. A portion of this product was heated to 200 °C by the direct inlet assembly of an EM-600 mass spectrometer. The mass spectrum revealed that THF was present. Anal. Calcd for $Mo(N_2)_2(triphos)(PPh_3)\cdot{}^1/_2THF$, $C_{54}H_{52}MoN_4O_{1/2}P_4$: C, 65.9; H, 5.28; N, 5.69. Found: C, 64.8; H, 5.3; N, 5.7.

Results and Discussion

Two approaches were taken toward the synthesis of bis(dinitrogen) complexes of molybdenum containing mixed ancillary phosphine ligands. The first method involved phosphine ligand displacement in a preformed bis(dinitrogen) complex (e.g., eq 4). The second method was to coordinate

$$trans\text{-}Mo(N_2)_2(PPh_2Me)_4 + dppe \rightarrow Mo(N_2)_2(dppe)(PPh_2Me)_2 + 2PPh_2Me \quad (4)$$

the phosphine ligand(s) prior to or during the reduction step in which dinitrogen became coordinated. Examples of these procedures are shown in eq 5 and 6.

$$MoCl_3(triphos) + PPh_3 \xrightarrow[N_2]{Na/Hg} Mo(N_2)_2(triphos)(PPh_3) \quad (5)$$

$$MoCl_3(THF)_3 + triphos + PPh_3 \xrightarrow[N_2]{Na/Hg} Mo(N_2)_2(triphos)(PPh_3) \quad (6)$$

Synthesis of *trans*-$Mo(N_2)_2(dppe)(PPh_2Me)_2$. The ligand displacement reaction (eq 4) proved to be the most satisfactory method for preparing this compound in high yield. Attempts to prepare this same compound by reduction of $MoCl_3(THF)_3$ with sodium amalgam in the presence of stoichiometric quantities of dppe and PPh_2Me produced a mixture of $Mo(N_2)_2(dppe)_2$, $Mo(N_2)_2(PPh_2Me)_4$, and $Mo(N_2)_2(dppe)(PPh_2Me)_2$. The infrared spectrum of the title compound exhibited a very strong absorption at 1955 cm^{-1} due to ν(NN). In the proton-decoupled phosphorus-31 NMR spectrum the four phosphorus atoms displayed an AA′XX′ spectrum centered at −42.9 ppm.[14] While this work was in progress, this compound was reported in the literature.[15]

Synthesis of *trans*-$Mo(N_2)_2(triphos)(PR_3)$. The reaction of $Mo(N_2)_2(PPh_2Me)_4$ with triphos produced a complex formulated as *trans*-$Mo(N_2)_2(triphos)(PPh_2Me)$ based upon the elemental analysis and infrared spectrum, ν(NN) 1950 cm^{-1}. However, it slowly decomposed at room temperature in the dark both in the solid state and in solution.

An infrared study of the reduction of $MoCl_3(triphos)$ (readily prepared from $MoCl_3(THF)_3$ and triphos; see Experimental Section) in the presence of PR_3 (R = Ph, *m*-tolyl, or *p*-tolyl) under dinitrogen with 100% excess of sodium amalgam was carried out. The reactions were monitored with respect to time in an effort to measure the relative rates of formation and the solution stabilities of the dinitrogen complexes. These spectra revealed that the dinitrogen complexes were formed rapidly in all three cases but that, in the case of PPh_3, the complex had superior solution stability. The crude product solution of this complex did not show appreciable decomposition on standing for a period of 7 days at room temperature under dinitrogen. However, isolated yields of pure, recrystallized product were very low. The presence of only one strong NN stretch (1955 cm^{-1}) in the infrared spectrum showed that the two dinitrogen ligands occupy mutually trans positions on the coordination polyhedron.

The corresponding $(p\text{-}MeOC_6H_4)_3P$ complex has also been prepared in low yield and shows a very strong NN stretch at 1962 cm^{-1}.

Protonation of $Mo(N_2)_2(triphos)(PPh_3)$ with anhydrous hydrogen bromide produced ammonia under mild conditions.[16] The reactions of this interesting bis(dinitrogen) complex are under investigation.

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Registry No. *trans*-$Mo(N_2)_2(PPh_2Me)_4$, 33248-03-2; *cis*-$Mo(N_2)_2(PPhMe_2)_4$, 32457-67-3; *trans*-$Mo(N_2)_2(dppe)(PPh_2Me)_2$, 65498-66-0; $MoCl_3(triphos)$, 75365-55-8; *trans*-$Mo(N_2)_2(triphos)(PPh_2Me)$, 75365-56-9; *trans*-$Mo(N_2)_2(triphos)(PPh_3)$, 75420-24-5; $MoCl_3(THF)_3$, 39210-30-5; *trans*-$Mo(N_2)_2(triphos)((p\text{-}MeOC_6H_4)_3P)$, 75365-57-0; $Mo(N_2)_2(dppe)_2$, 25145-64-6.

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(14) The AA′ part of the spectrum is centered at −64.0 ppm and is associated with the phosphorus atoms of the dppe ligands: in $Mo(N_2)_2(dppe)_2$, δ(P) = −65.1 (singlet). The XX′ part of the spectrum is centered at −21.8 ppm and is associated with the phosphorus atoms of the PPh_2Me ligands: in $Mo(N_2)_2(dppe)_2$, δ(P) = −18.8.

(15) Chatt, J.; Pearman, A. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1977**, 2139–2142.

(16) Baumann, J. A.; George, T. A. *J. Am. Chem. Soc.* **1980**, *102*, 6153–6154.

Contribution from the Chemistry Department,
Faculty of Science, Tohoku University, Sendai, 980 Japan

Rotation of Olefins in *trans*(N,olefin)-Bromochloro(η^2-ethylene)platinum(II) Containing Pyridine Derivatives

Sin'ya Miya and Kazuo Saito*

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The kinetic trans effect for the ligand-substitution reactions of Pt(II) has been studied for various ligands but not for the exchange of olefins, despite its importance as an elementary process in transition-metal complex catalysis.[1] We have studied the kinetics of substitution of an olefin for a coordinated olefin molecule with the aid of optical activity and measured the second-order rate constant k_{py} for reaction 1,

$$trans(N,olefin)\text{-}[PtCl_2(4\text{-}X\text{-}py)(S\text{-}mbn)] + dce \text{ or } dmb \rightarrow trans(N,olefin)\text{-}[PtCl_2(4\text{-}X\text{-}py)(dce \text{ or } dmb)] + mbn \quad (1)$$

where mbn, dce, and dmb stand for 2-methyl-2-butene (prochiral), 1,2-dichloroethylene (nonprochiral), and 1,2-dimethyl-2-butene (nonprochiral), respectively, and 4-X-py denotes 4-substituted pyridines.[2] The plot of log k_{py} vs. pK_a of the pyridine bases gave parallel straight lines. We have thus

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(1) Basolo, F.; Pearson, R. G. "Mechanism of Inorganic Reactions", 2nd ed.; Wiley; New York, 1967.

(2) Miya, S.; Kashiwabara, K.; Saito, K. *Inorg. Chem.* **1980**, *19*, 98.

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Table I. Thermodynamic Data for the Olefin Rotation in *trans*(N,olefin)-[PtBrCl(C_2H_4)(4-X-py)]

X	solvent	T,[a] K	$\Delta G^{\ddagger}$, kJ mol^{-1}
CH_3	CD_3NO_2	323 ± 3	66 ± 2[b]
H	CD_3NO_2	328 ± 3	67 ± 2
Cl	$(CD_3)_2CO$	295 ± 3	60 ± 2
CN	$(CD_3)_2CO$	298 ± 3	61 ± 2
CN	CD_3NO_2	300 ± 3	61 ± 2

[a] T = the coalescence temperature. [b] The error resulting from the ambiguity of temperature amounts to ca. 0.5 kJ mol^{-1}. The given error is the overall error.

concluded that the basicity of the pyridine derivatives has a dominating influence for the trans effect on the olefin exchange of Pt(II) complexes. However, such kinetic studies give only overall information. More detailed discussion is needed in which the σ-donating and π-accepting properties of a given base are considered separately. The rotation of a coordinated olefin molecule about an axis defined by the olefin-Pt^{II} σ bond[3] can be closely related to the strength of π bonding. Examination of the temperature-variation profile of NMR signals should give useful information concerning the strength of Pt^{II}–olefin π bonding. We have synthesized new complexes of the type *trans*(N,olefin)-[PtBrCl(C_2H_4)(4-X-py)] (X = CH_3, H, Cl, CN) and recorded the ^1H NMR spectra at various temperatures to observe the coalescence of proton signals due to ethylenic proton.

Experimental Section

Crystals of *trans*(N,olefin)-[PtCl(*S*-pro)(C_2H_4)] (pro = prolinate ion)[4] (4.0 × 10^{-4} mol) were dissolved in HBr (40 cm^3) containing ca. 0.04 mol of NaCl and slowly treated with $(C_6H_5)_4PCl$ (4.5 × 10^{-4} mol) in water (ca. 10 cm^3). The precipitated $(C_6H_5)_4P[PtBr_2Cl(C_2H_4)]$ was filtered off and dried in vacuo. The product (3 × 10^{-4} mol) was dissolved in acetonitrile (ca. 30 cm^3) and treated with the pyridine base (ca. 3 × 10^{-4} mol) and NaCl (3 × 10^{-3} mol) in water (ca. 10 cm^3) with stirring and then with water (30 cm^3). Insoluble *trans*(N,olefin)-[PtBrCl(C_2H_4)(4-X-py)] was precipitated on cooling and was filtered off, washed with water (10 cm^3), and dried in vacuo.

The complexes were dissolved in CD_3NO_2 or $(CD_3)_2CO$ to produce ca. 0.5 mol dm^{-3} solution and submitted to ^1H NMR spectroscopy with Me_4Si as reference, in a JUM-PS-100 (JEOL) apparatus. Anal. Calcd for the 4-cyanopyridine complex, $PtC_8H_8BrClN_2$: C, 21.71; H, 1.82; Br + Cl, 26.06; N, 6.33. Found: C, 21.20; H, 1.74; Br + Cl, 27.28; N, 6.08. Calcd for the pyridine complex, PtC_7H_9BrClN: C, 20.13; H, 2.17; Br + Cl, 27.62; N, 3.35. Found: C, 19.59; H, 2.07; Br + Cl, 28.74; N, 3.15.

Results and Discussion

Synthesis. The observed C, H, and N contents of the new complexes were slightly smaller than the calculated values, while that of the total halogen was greater. Repeated recrystallization did not give samples of higher purity. The presence of *trans*(N,olefin)-[$PtBr_2(C_2H_4)$(4-X-py)] is possible. The IR absorption of the products gives peaks at 214 and 231 cm^{-1} in the Pt^{II}–Br vibration region (185–250 cm^{-1} [5]). If *cis*-dibromo complex was present, two Pt–Br vibrations should be observed on top of the aimed complex. The ^1H NMR signal of the olefin protons gives three peaks, two strong and one weak, at around 5 ppm vs. Me_4Si at low temperature, each being accompanied by a satellite due to ^{195}Pt. The strong peaks coalesce on a rise of temperature, but the weak peak remains unchanged. All these facts indicate that the product was contaminated by *trans*(N,olefin)-[$PtBr_2(C_2H_4)$(4-X-py)], whose content was estimated to be ca. 15% for all the products from the integrated ^1H NMR peak intensity. Since this impurity does not affect the coalescence of the strong peaks, the product was used for the study.

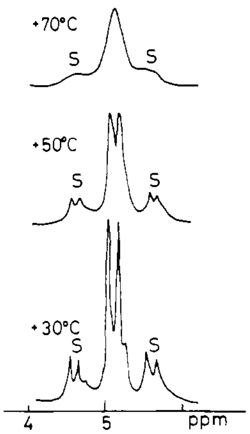

Figure 1. Temperature-variation profile of the ethylene proton signal of *trans*(N,olefin)-[PtBrCl(C_2H_4)(4-X-py)] in CD_3NO_2 (S = satellite due to ^{195}Pt; protons on the pyridine ring give peaks in the region from 7 to 9 ppm vs. Me_4Si).

Rotation of the Ethylene. The temperature-variation profile (Figure 1) should reflect the rotation of ethylene without being accompanied by the dissociation of the complex, because the satellite due to ^{195}Pt is always observed regardless of the temperature. The $\Delta G^{\ddagger}$ values were calculated by $\Delta G^{\ddagger} = -RT \ln (\Delta\nu\pi h/2^{1/2}kT)^3$ ($\Delta\nu$ = chemical shift of the coalescence peak) and are shown in Table I. The $\Delta G^{\ddagger}$ for the 4-cyanopyridine complex does not change in CD_3NO_2 and $(CD_3)_2CO$, and the solvent effect does not seem significant.

The $\Delta G^{\ddagger}$ values are in a rather narrow range and give very modest change for the complexes with different 4-substituted pyridine ligands. However, there seems to be an overall trend that the $\Delta G^{\ddagger}$ decreases with decrease in pK_a of the substituted pyridines. Those ligands with electron-drawing 4-cyano and 4-chloro substituents should withdraw the d_π electron of Pt^{II} more than those with electron-donating substituents do, so that the π-electron density between Pt^{II} and ethylene becomes less to make the rotation about the Pt^{II}–ethylene axis easier. Our observation indicates that the extent of such an influence is very small. Albright et al. suggested that the rotational barrier was not affected by the Pt^{II}–olefin π-bond strength much on the basis of molecular orbital calculation.[6] All these facts give support to our previous conclusion that the σ-donating ability of the pyridine derivatives is important in determining the trans effect upon the exchange reaction of the olefin ligand.

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Registry No. *trans*-(N,olefin)-[PtCl(*S*-pro)(C_2H_4)], 32697-41-9; *trans*-(N,olefin)-[PtBrCl(C_2H_4)(4-CH_3-py)], 75443-48-0; *trans*-(N,olefin)-[PtBrCl(C_2H_4)(py)], 75443-49-1; *trans*-(N,olefin)-[PtBrO(C_2H_4)(4-Cl-py)], 75400-15-6; *trans*-(N,olefin)-[PtBrCl(C_2H_4)(4-NC-py)], 75400-16-7; $(C_6H_5)_4P[PtBr_2Cl(C_2H_4)]$, 75443-50-4; *trans*-(N,olefin)-[$PtBr_2(C_2H_4)$(4-CH_3-py)], 57595-06-9; *trans*-(N,olefin)-[$PtBr_2(C_2H_4)$(py)], 57589-31-8; *trans*-(N,olefin)-[$PtBr_2(C_2H_4)$(4-Cl-py)], 75400-17-8; *trans*-(N,olefin)-[$PtBr_2(C_2H_4)$(4-NC-py)], 75400-18-9.

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(3) Ashley-Smith, J.; Douek, I.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1974**, 128 and references therein. Boucher, H.; Bosnich, B. *Inorg. Chem.* **1977**, *16*, 717.

(4) Fujita, J.; Konya, K.; Nakamoto, K. *Inorg. Chem.* **1970**, *9*, 2794.

(5) Adams, D. M.; Chatt, J.; Geratt, J.; Westland, A. D. *J. Chem. Soc.* **1964**, 734.

(6) Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801.