



itant and stoichiometric evolution of carbon monoxide, in agreement with eq. 1, was observed.

Figure 1 shows the IR and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of these solutions. Upon addition of Im-1-Me an infrared band at  $1950\text{ cm}^{-1}$  assigned to the dimer **1** disappeared, while new bands at  $1895(\text{vs})$  and  $1980(\text{m})\text{ cm}^{-1}$  progressively developed. In the presence of an excess of Im-1-Me, the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the THF solution of **1** consists of an AA'XX' multiplet at  $\delta 70.6\text{ ppm}$ , due to **1**, and a new doublet at  $\delta 45.6$  with  $J(\text{Rh}-\text{P}) 116.8\text{ Hz}$ . Other species, such as the free phosphine, were not detected. In agreement with the IR spectra, the doublet signal increased at the expense of the multiplet signal.

In the presence of 35 equimolar amounts of Im-1-Me, the  $^{13}\text{C}$  NMR spectrum of the THF solution of **1**, enriched with  $^{13}\text{CO}$ , at  $-60^\circ\text{C}$  exhibited a doublet at  $\delta 206.6\text{ ppm}$  ( $J(\text{Rh}-\text{C}) 74.0\text{ Hz}$ ) and a double triplet at  $\delta 193.7\text{ ppm}$  ( $J(\text{Rh}-\text{C}) 67.0\text{ Hz}$ ,  $J(\text{P}-\text{C}) 15.0\text{ Hz}$ ), in addition to a multiplet peak at  $\delta 196.5\text{ ppm}$  assigned to  $^{13}\text{CO}$  in **1**. The strong IR band observed at  $1895\text{ cm}^{-1}$  and the  $^{13}\text{C}$  NMR doublet at  $\delta 206.6\text{ ppm}$  are both assigned to the mononuclear rhodate,  $\text{Rh}(\text{CO})_4^-$  [6]. The medium IR band at  $1980\text{ cm}^{-1}$ , and the  $^{31}\text{P}\{^1\text{H}\}$  NMR and  $^{13}\text{C}$  NMR peaks at  $\delta$

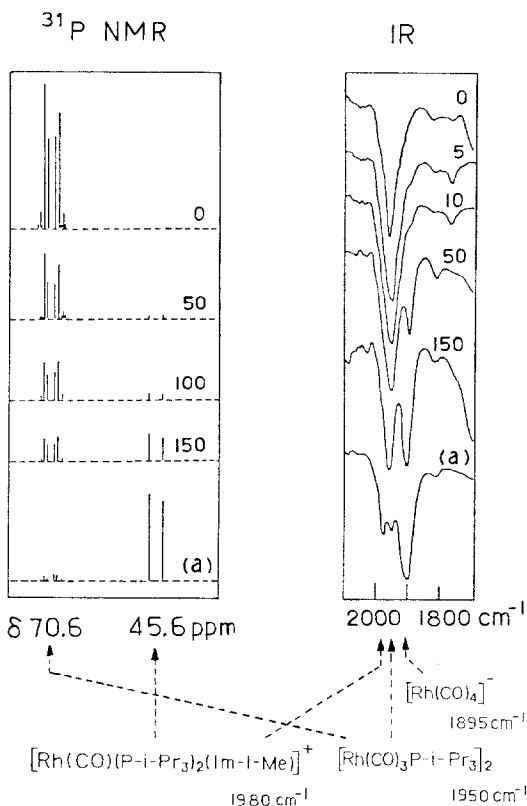


Fig. 1.  $^{31}\text{P}\{^1\text{H}\}$  NMR and IR spectra of a THF solution of  $[\text{Rh}(\text{CO})_3\text{P-}i\text{-Pr}_3]_2$  in the presence of an excess of 1-methylimidazole. The figures in the spectra indicate the amount of added 1-methylimidazole (eq. Rh). (a), 1-methylimidazole solution of  $[\text{Rh}(\text{CO})_3\text{P-}i\text{-Pr}_3]_2$ . Reaction conditions:  $[\text{Rh}(\text{CO})_3\text{P-}i\text{-Pr}_3]_2$  (25 mmol), THF (2.0 ml) and THF- $d_8$  (0.5 ml) at  $25^\circ\text{C}$  under 1 atm (CO).

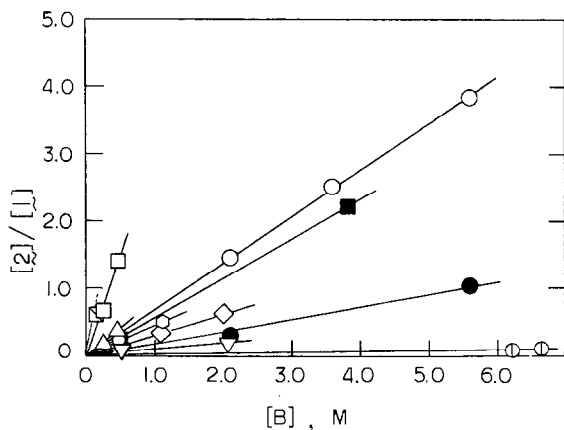


Fig. 2. Plot of concentration ratio,  $[2]/[1]$ , as a function of concentration of base: in DMI as solvent. (□) triazole; (◻) imidazole; (○) 1-methylimidazole; (Δ) 1,2-dimethylimidazole; (◇) benzimidazole; (▽) 1-methylbenzimidazole; (◊) 4-dimethylaminopyridine; (⊕) pyridine; in THF solvent, (■) imidazole; (●) 1-methylimidazole. Reaction conditions:  $[\text{Rh}(\text{CO})_3\text{P-}i\text{-Pr}_3]_2$ , 0.2 mmol, solvent, 8 ml, 20 °C, 1 atm (CO).

45.6(d) and 193.7(dt) ppm, respectively, were assigned to the cation  $[\text{trans-Rh}(\text{CO})(\text{P-}i\text{-Pr}_3)_2(\text{Im-1-Me})]^+$ . The  $^{31}\text{P}$  coupling to  $^{103}\text{Rh}$  ( $J(\text{Rh-P})$  116.8 Hz) is consistent with the four-coordinate square planar structure of rhodium(I) complexes with two phosphines *trans* to each other [7]. The double triplet pattern of the  $^{13}\text{C}$  resonance also supports this structure. Further support for these assignments is provided by the IR and  $^{31}\text{P}$  NMR data of the cationic complex  $[\text{Rh}(\text{CO})(\text{P-}i\text{-Pr}_3)_2(\text{Im-1-Me})]^+\text{BPh}_4^-$  (**3**), prepared independently\*, which shows absorption at  $1990\text{ cm}^{-1}$  and  $\delta$  46.8(d) ppm ( $J(\text{Rh-P})$  116.0 Hz). Thus all data seem to support the presence of the homonuclear ion pair  $[\text{trans-Rh}(\text{CO})(\text{P-}i\text{-Pr}_3)_2(\text{Im-1-Me})]^+[\text{Rh}(\text{CO})_4]^-$  (**2a**) in the solution.

When the solution was slightly pressurized by carbon monoxide, the intensities of the  $^{31}\text{P}$  NMR signals due to **2a** decreased, while those of the dimer complex **1** increased. Use of the  $^{31}\text{P}$  NMR data enabled us to determine the concentrations of **1** and **2a**. A plot of the ratio  $[2a]/[1]$  as a function of the concentration of free Im-1-Me gives a straight line which passes through the origin (Fig. 2).

$$[2a]/[1] = K(1/[\text{CO}]) \cdot [\text{B}]$$

These results strongly suggest the reversibility of reaction 1.

We investigated the effect of a variety of nitrogen bases other than Im-1-Me on reaction 1. The IR and  $^{31}\text{P}$  NMR spectra and the conductivity of the solution, showed that **1** is converted into the ion pair **2** in the presence of an excess of base in THF. Heterocycles such as triazoles, imidazoles, and 4-aminopyridines were found to be the most effective. The equilibrium constants,  $K$  in eq. 1 for each base, measured in DMI at 25 °C and calculated from the slope of the lines depicted in Fig. 2, decrease in the order; triazole ( $> 4.0$ ), imidazole (3.57)  $>$  1,2-dimethylimidazole (0.98)  $\sim$  1-methylimidazole (0.88)  $>$  4-dimethylaminopyridine

\* **3** was prepared by a procedure similar to that for  $[\text{Rh}(\text{CO})(\text{P-}i\text{-Pr}_3)_2(\text{pyridine})]^+\text{BPh}_4^-$ ; see T. Yoshida, T. Okano, Y. Ueda and S. Otsuka, *J. Am. Chem. Soc.*, 103 (1981) 3411.

(0.61) > benzimidazole (0.39 > 1-methylbenzimidazole (0.15) > pyridine (0.01). Sterically hindered 2,4,6-collidine did not cause disproportionation. Aliphatic amines, such as triethylamine, diethylamine, and 1-methylpyrrolidine, with high  $pK_a$  values, yielded unidentified species which gave  $^{31}\text{P}$  NMR doublets around  $\delta$  50 ppm with  $J(\text{Rh-P})$  127 Hz but showed no IR absorption due to  $\text{Rh}(\text{CO})_4^-$ . Thus, nucleophilic attack of the base on the rhodium center, rather than simple acid–base interaction, seems to direct the disproportionation reaction of **1**. Finally, it was found that in marked contrast to the ready reaction of **1**, that Im-1-Me, under similar conditions, does not induce disproportionation of  $[\text{Co}(\text{CO})_3\text{P-n-Bu}_3]_2$  [8].

**Acknowledgement.** This is part of the ‘C<sub>1</sub> Chemistry Project’, a National Research & Development Program of the Agency of Industrial Science and Technology, Ministry of International Trade and Industry (M.I.T.I.), Japan. The authors would like to thank their fellow researchers in this project.

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