

## Preliminary communication

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### <sup>31</sup>P NMR STUDY ON PHOSPHORUS LIGAND EXCHANGE ON BIS(TRIPHENYLPHOSPHINE)-*o*-TOLYLNICKEL(II) BROMIDE

YOSHIYUKI NAKAMURA, KEN-ICHI MARUYA, and TSUTOMU MIZOROKI

*Research Laboratory of Resources Utilization, Tokyo Institute of Technology, O-okayama,  
Meguro-ku, Tokyo 152 (Japan)*

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#### Summary

<sup>31</sup>P NMR spectroscopy has been used to study exchange reactions of bis(triphenylphosphine)-*o*-tolynickel bromide with tertiary phosphines. The observed ligand exchange equilibria are dominated by steric factors.

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$\sigma$ -Arylmetal species of nickel and palladium have been shown to play an important role in organic synthesis such as carbonylation of aryl halides or arylation and oligomerization of olefins. Recently many tertiary phosphine stabilized  $\sigma$ -aryl complexes of nickel [1], palladium [2], and platinum [3,4] have been prepared by oxidative addition of an aryl halide to the tetrakis-(tertiary phosphine)metal(0) complexes, and character of the metal-aryl bonds was elaborated by thermal reactions [5], insertion reactions of carbon monoxide and olefins [5], and <sup>1</sup>H [6] and <sup>19</sup>F NMR studies [7]. In connection with our studies on the role of triphenylphosphine in olefin dimerization catalyzed by the bis(triphenylphosphine)- $\sigma$ -arylnickel(II) halide/boron trifluoride etherate/water system [8], we have undertaken a systematic study of neutral ligand exchange on bis(triphenylphosphine)- $\sigma$ -arylmatal(II) halide complexes (metal = Ni, Pd, or Pt) by <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy. In this communication, we report our results using bis(triphenylphosphine)-*o*-tolynickel(II) bromide.

To a chlorobenzene solution of the nickel complex (0.02 M) under nitrogen at room temperature was added a phosphorus ligand such as P(*o*-C<sub>6</sub>H<sub>4</sub>OMe)<sub>3</sub> (194°), PPhMe<sub>2</sub> (127°), P(*p*-C<sub>6</sub>H<sub>4</sub>OMe)<sub>3</sub> (145°), P(*o*-C<sub>6</sub>H<sub>4</sub>-Me)<sub>3</sub> (194°), P(*p*-C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub> (145°), PPh<sub>2</sub>Me (136°), PPh<sub>3</sub> (145°), P(*p*-C<sub>6</sub>H<sub>4</sub>F)<sub>3</sub> (145°), P(*p*-C<sub>6</sub>H<sub>4</sub>Cl)<sub>3</sub> (145°), P(OMe)<sub>3</sub> (107°), and P(OPh)<sub>3</sub> (128°) (Ph = C<sub>6</sub>H<sub>5</sub>, Me = CH<sub>3</sub>), where the electron donor properties of phosphorus ligands [9] decrease in the order given, and their cone angles as defined by Tolman [10] are shown in parentheses. <sup>31</sup>P-<sup>1</sup>H spectra of the solutions were recorded on a Japan Electron Optics Laboratory PS-100

spectrometer in FT mode (400 to 1000, 2 sec. pulses) at  $-40 \sim -30^\circ\text{C}$  and 40.48 MHz, using 10 mm o.d. tubes. The solutions contained  $\text{C}_6\text{D}_6$  (10%) to provide field-frequency lock, and chemical shifts (ppm) were measured with respect to external triphenylphosphine.

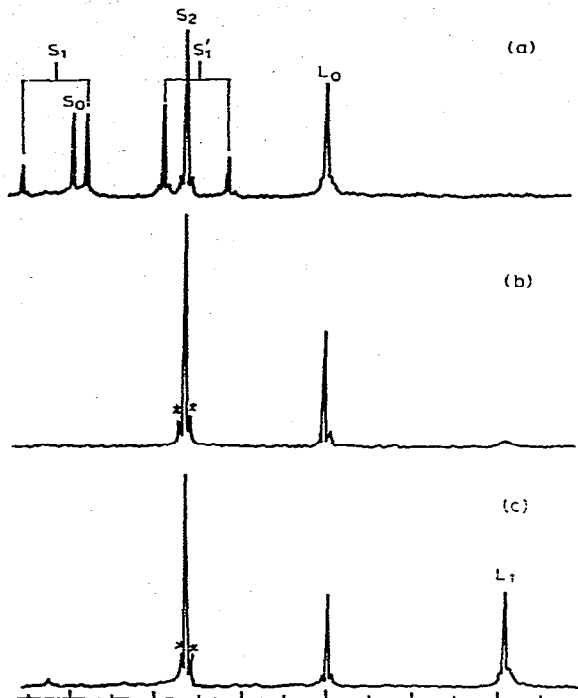
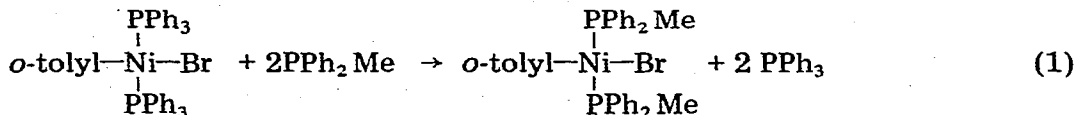


Fig. 1.  $^{31}\text{P}$  NMR of the ligand exchange equilibrium of the nickel complex with  $\text{PPh}_2\text{Me}$  at  $-36^\circ\text{C}$ .  $\text{PPh}_2\text{Me}/\text{Ni-complex} = 1$  (a), 2 (b), 4 (c).

When  $\text{PPh}_2\text{Me}$  was used, eight peaks were observed as shown in Fig. 1, where  $\text{S}_0$  ( $-29.9$  s),  $\text{L}_0$  ( $0.0$  s), and  $\text{L}_1$  ( $+21.1$  s) correspond to *o*-tolyl-Ni( $\text{PPh}_3$ ) $_2$  Br, liberated  $\text{PPh}_3$ , and free  $\text{PPh}_2\text{Me}$ , respectively,  $\text{S}_1$  ( $-32.1$  d:  $^2J(\text{P-P})$  307 Hz) and  $\text{S}_1'$  ( $-15.1$  d:  $^2J(\text{P-P})$  307 Hz) to the  $\text{PPh}_3$  and  $\text{PPh}_2\text{Me}$  of *o*-tolyl-Ni( $\text{PPh}_3$ )( $\text{PPh}_2\text{Me}$ )Br, respectively, and  $\text{S}_2$  ( $-16.5$  s) to *o*-tolyl-Ni( $\text{PPh}_2\text{Me}$ ) $_2$  Br. With 2 or 4 equivalents of  $\text{PPh}_2\text{Me}$  to nickel complex, the peaks,  $\text{S}_1$  and  $\text{S}_1'$ , almost disappeared, and only two peaks,  $\text{S}_2$  and  $\text{L}_0$ , were observed in addition to  $\text{L}_1$ . These spectra show that reaction 1 takes place readily and quantitatively in chlorobenzene at room temperature. When  $\text{PPh}_2\text{Me}$  was replaced by  $\text{PPhMe}_2$ , the exchange also was found to take place



quantitatively. Accordingly, *o*-tolyl-Ni( $\text{PPh}_2\text{Me}$ ) $_2$  Br and *o*-tolyl-Ni( $\text{PPhMe}_2$ ) $_2$ -Br can be easily prepared by mixing *o*-tolyl-Ni( $\text{PPh}_3$ ) $_2$  Br with  $\text{PPh}_2\text{Me}$  or  $\text{PPhMe}_2$  at room temperature.

With triphenylphosphine derivatives having substituents X (X = OMe,

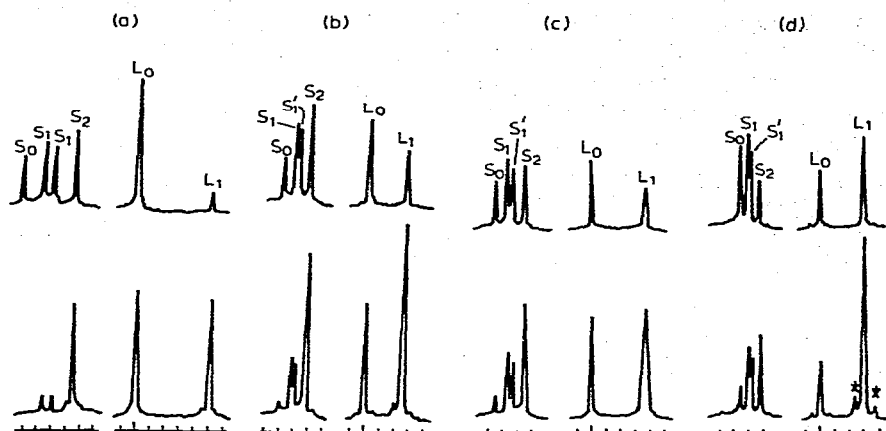


Fig. 2.  $^{31}\text{P}$  NMR of the ligand exchange equilibria of the nickel complex with  $\text{P}(p\text{-C}_6\text{H}_4\text{X})_3$  at  $-36^\circ\text{C}$ .  $\text{P}(p\text{-C}_6\text{H}_4\text{X})_3/\text{Ni-complex} = 2$  (upper), or 4 (lower). (a)  $\text{P}(p\text{-C}_6\text{H}_4\text{OMe})_3$ :  $S_0$  ( $-30.1$  s),  $L_0$  ( $0.0$  s),  $S_1$  ( $-28.7$  s),  $S_1'$  ( $-28.0$  s),  $S_2$  ( $-26.5$  s), and  $L_1$  ( $+5.2$  s). (b)  $\text{P}(p\text{-C}_6\text{H}_4\text{Me})_3$ :  $S_0$  ( $-29.9$  s),  $L_0$  ( $0.0$  s),  $S_1$  ( $-29.1$  s),  $S_1'$  ( $-28.9$  s),  $S_2$  ( $-28.1$  s), and  $L_1$  ( $+2.6$  s). (c)  $\text{P}(p\text{-C}_6\text{H}_4\text{F})_3$ :  $S_0$  ( $-29.9$  s),  $L_0$  ( $0.0$  s),  $S_1$  ( $-29.0$  s),  $S_1'$  ( $-28.7$  s),  $S_2$  ( $-27.8$  s), and  $L_1$  ( $+3.7$  s). (d)  $\text{P}(p\text{-C}_6\text{H}_4\text{Cl})_3$ :  $S_0$  ( $-29.9$  s),  $L_0$  ( $0.0$  s),  $S_1$  ( $-29.3$  s),  $S_1'$  ( $-29.2$  s),  $S_2$  ( $-28.6$  s), and  $L_1$  ( $+3.0$  s). \* Satellite with  $^{13}\text{C}$ .

Me, Cl, or F) at the *para*-position, ligand exchange also took place at room temperature as shown in Fig. 2. Peaks of mono- and di-substituted complexes were observed near that of the starting complex; the outer wing lines of the AB patterns of the mono-substituted complexes were too weak to observe.

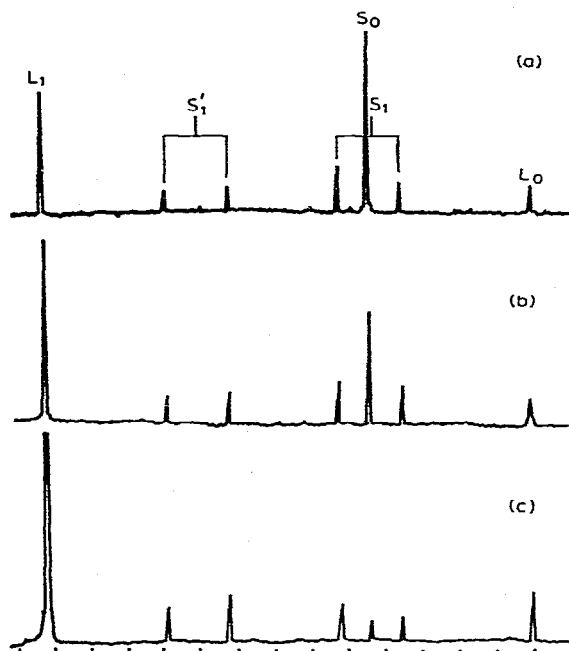


Fig. 3.  $^{31}\text{P}$  NMR of the ligand exchange equilibrium of the nickel complex with  $\text{P}(\text{OC}_6\text{H}_5)_3$  at  $-36^\circ\text{C}$ .  $\text{P}(\text{OC}_6\text{H}_5)_3/\text{Ni-complex} = 1$  (a), 2 (b), or 10 (c).  $S_0$  ( $-29.2$  s),  $L_0$  ( $0.0$  s),  $S_1$  ( $-29.0$  d:  $^2J(\text{P-P})$  453 Hz),  $S_1'$  ( $-105.4$  d:  $^2J(\text{P-P})$  453 Hz),  $L_1$  ( $-132.8$  s).

The assignments of these peaks were confirmed by their relative intensities, and by the  $^1\text{H}$  NMR spectra of the *o*-tolyl ligands. No ligand exchange, however, was observed with the sterically crowded ligands,  $\text{P}(o\text{-C}_6\text{H}_4\text{Me})_3$  and  $\text{P}(o\text{-C}_6\text{H}_4\text{OMe})_3$ , even at higher temperature ( $40^\circ\text{C}$ ). This result stands in significant contrast to those with the sterically less crowded ligands mentioned above. The most plausible explanation for these results is that the ligand exchange equilibria on *o*-tolyl-Ni( $\text{PPh}_3$ ) $_2$ Br are predominantly controlled by steric factors, as in phosphorus ligand exchange on zerovalent nickel complexes reported by Tolman [10a], although electronic factors cannot be neglected as shown in Fig. 2.

Trimethyl phosphite ( $-147.2$  s) readily exchanged with the nickel complex at room temperature to give mono- ( $-28.7$  d:  $^2J(\text{P-P})$  437 Hz,  $-120.7$  d:  $^2J(\text{P-P})$  437 Hz) and di-substituted complexes ( $-121.5$  s), along with two species which show peaks ( $-29.2$  s and  $-171.8$  s). These presumably correspond to [*o*-tolyl- $\text{PPh}_3$ ]Br and  $\text{Ni}[\text{P}(\text{OMe})_3]_4$ , respectively. On the other hand, triphenyl phosphite gave only a mono-substituted complex; subsequent substitution to give *o*-tolyl-Ni[ $\text{P}(\text{OPh})_3$ ] $_2$ Br was not observed even in the presence of a large excess of the phosphite as shown in Fig. 3. This difference may be also controlled mainly by steric factors.

## References

- 1 M. Hidai, T. Kashiwagi, T. Ikeuchi and Y. Uchida, *J. Organometal. Chem.*, **30** (1971) 279.
- 2 P. Fitton and E.A. Rick, *J. Organometal. Chem.*, **28** (1971) 287.
- 3 D.H. Gerlach, A.R. Kane, G.W. Parshall, J.P. Jesson and E.L. Muettterties, *J. Amer. Chem. Soc.*, **93** (1971) 3543.
- 4 N. Kawata, T. Mizoroki and A. Ozaki, *Bull. Chem. Soc. Japan.*, **47** (1974) 1807.
- 5 S. Otsuka, A. Nakamura, T. Yoshida, M. Naruto and K. Ataka, *J. Amer. Chem. Soc.*, **95** (1973) 3180.
- 6 R.G. Miller, R.D. Stauffer, D.R. Fahey, and D.R. Pannell, *J. Amer. Chem. Soc.*, **92** (1970) 1511.
- 7 G.W. Parshall, *J. Amer. Chem. Soc.*, **96** (1974) 2360.
- 8 K. Maruya, N. Kawata, T. Mizoroki and A. Ozaki, *Bull. Chem. Soc. Japan.*, **45** (1972) 2255; **47** (1974) 413; **47** (1974) 2003.
- 9 C.A. Tolman, *J. Amer. Chem. Soc.*, **92** (1970) 2953.
- 10 (a) C.A. Tolman, *J. Amer. Chem. Soc.*, **92** (1970) 2956; (b) C.A. Tolman, W.C. Seidel and L.W. Gosser, *J. Amer. Chem. Soc.*, **96** (1974) 53.