

ingham, Foster, and Sargeson<sup>2</sup> provided elegant confirmation of the structure of the intermediate. Experiments utilizing <sup>18</sup>O support this theory (Buckingham, *et al.*,<sup>2</sup> and here). An alternate mechanism operates in the case of the *t*-butyl ester complex. This involves formation of the same kind of intermediate, *i.e.*, that containing chelated, carbonyl-oxygen coordi-

nated, ester, but nucleophilic attack occurs at the carbon atom of the alkyl group and it is the alkyl group that is expelled. This mechanism is supported by the results of kinetic studies and oxygen-18 exchange data.

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## Metal Isotope Effect on Metal-Ligand Vibrations.

### I. Phosphine Complexes<sup>1</sup>

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**Abstract:** Far-infrared spectra (600–100 cm<sup>-1</sup>) have been reported for <sup>58</sup>Ni(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, <sup>58</sup>Ni(PEt<sub>3</sub>)<sub>2</sub>Br<sub>2</sub>, <sup>58</sup>Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, <sup>104</sup>Pd(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, <sup>104</sup>Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, and their <sup>62</sup>Ni or <sup>110</sup>Pd analogs. The infrared and Raman spectra of Pd-(PPh<sub>3</sub>)<sub>2</sub>X<sub>2</sub> and Pd(AsPh<sub>3</sub>)<sub>2</sub>X<sub>2</sub> (X = Cl and Br) have also been obtained. Based on the observed isotopic shifts, the Ni-P stretching vibrations have been assigned at *ca.* 274–260 cm<sup>-1</sup> (one band) for *trans*-Ni(PEt<sub>3</sub>)<sub>2</sub>X<sub>2</sub> and at *ca.* 190–160 cm<sup>-1</sup> (two bands) for tetrahedral Ni(PPh<sub>3</sub>)<sub>2</sub>X<sub>2</sub>. Similarly, the Pd-P stretching bands have been assigned at *ca.* 235–232 cm<sup>-1</sup> for *trans*-Pd(PEt<sub>3</sub>)<sub>2</sub>X<sub>2</sub> and at *ca.* 190 cm<sup>-1</sup> for *trans*-Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>.

Recently, a number of infrared studies have been made on metal phosphine complexes.<sup>2–8</sup> The metal-phosphorus stretching frequencies assigned by previous investigators cover a wide frequency range from 460 to 90 cm<sup>-1</sup>. This scattering of frequencies has been attributed to the differences in the nature (1) of the metals (oxidation state, electronic configuration, etc.); (2) of the phosphine ligands PR<sub>3</sub>, where R is CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, or C<sub>6</sub>H<sub>5</sub>; and (3) in the structure of the complex (stereochemistry, coordination number, etc.).<sup>9,10</sup> It should be noted, however, that all the metal-phosphorus stretching bands reported previously have been assigned empirically (or intuitively) without solid experimental evidence. Recently, we have found<sup>11</sup> that the metal isotope technique provides a unique method of assigning the metal-ligand vibrations of a variety of coordination compounds. The purpose of this work is to apply this new technique to the vibrational spectra of metal phosphine complexes and to examine the validity of previous band assignments. In this paper, we report the results ob-

tained for *trans*-Ni(PEt<sub>3</sub>)<sub>2</sub>X<sub>2</sub> (X = Cl and Br), tetrahedral Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, *trans*-Pd(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, *trans*-Pd-(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, and related compounds.

### Experimental Section

**Preparation of Compounds.** All the Ni(II) phosphine complexes were prepared according to the methods of Jensen.<sup>12</sup> All the Pd(II) phosphine complexes were prepared according to the methods reported in literature.<sup>13</sup> Metal phosphine complexes containing metal isotopes were prepared on a milligram scale. In each case, metallic nickel or palladium (10–15 mg each) was converted into NiCl<sub>2</sub>·6H<sub>2</sub>O or Na<sub>2</sub>[PdCl<sub>4</sub>]·4H<sub>2</sub>O, respectively, and these salts were treated with the ligands. The purity of each metal isotope was: <sup>58</sup>Ni (99.98%), <sup>62</sup>Ni (99.02%), <sup>104</sup>Pd (89.75%), and <sup>110</sup>Pd (96.98%). All the metal isotopes were purchased from Oak Ridge National Laboratory. Triethylphosphine (PEt<sub>3</sub>) was purchased from Strem Chemicals, Inc., Danvers, Mass. Triphenylphosphine (PPh<sub>3</sub>) and triphenylarsine (AsPh<sub>3</sub>) were purchased from Aldrich Chemical Co., Milwaukee, Wis. The purity of each metal phosphine complex was checked by comparing the spectrum with that reported in literature.

**Spectral Measurements.** Infrared spectra of all the complexes except Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (<sup>58</sup>Ni and <sup>62</sup>Ni) were measured on a Beckman IR-12 (650–200 cm<sup>-1</sup>) and a Hitachi Perkin-Elmer FIS-3 (400–100 cm<sup>-1</sup>) infrared spectrophotometer. The spectra of the remaining complexes were measured on a Beckman IR-11 (600–100 cm<sup>-1</sup>) infrared spectrophotometer. The Nujol mull technique with polyethylene plates was employed in obtaining the spectra of solids. Calibration of the frequency readings was made with 1,2,4-trichlorobenzene and water vapor.

The spectra were run with a scanning speed of 1–2 cm<sup>-1</sup>/min. Reproducibility of the spectra was checked by running the spectra three to five times. The average error in frequency reading was 0.5 cm<sup>-1</sup>.

The Raman spectra of Pd(PPh<sub>3</sub>)<sub>2</sub>X<sub>2</sub> and Pd(AsPh<sub>3</sub>)<sub>2</sub>X<sub>2</sub> (X = Cl or Br) were measured by using a Cary Model 81 Raman spectrophotometer equipped with a He-Ne gas laser source.

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Table I. Infrared Frequencies of Triethylphosphine Complexes Containing Metal Isotopes ( $\text{cm}^{-1}$ )

| $\text{PEt}_3$<br>$\bar{\nu}$ | $^{58}\text{Ni}(\text{PEt}_3)_2\text{X}_2$ |                     | $^{58}\text{Ni}(\text{PEt}_3)_2\text{Br}_2$ |                     | $^{104}\text{Pd}(\text{PEt}_3)_2\text{Cl}_2$ |                     | Band<br>assignment <sup>b</sup> |
|-------------------------------|--|---------------------|---|---------------------|--|---------------------|---------------------------------|
|                               | $\bar{\nu}$                                | $\Delta\bar{\nu}^a$ | $\bar{\nu}$                                 | $\Delta\bar{\nu}^a$ | $\bar{\nu}$                                  | $\Delta\bar{\nu}^a$ |                                 |
| 408 (m)                       | 416.7 (m)                                  | (0.0)               | 413.6 (m)                                   | (1.2)               | 413.0 (m)                                    | (-0.3)              | $\delta$ (CCP)                  |
|                               | 403.3 (vs)                                 | (6.7)               | 337.8 (m)                                   | (10.5) <sup>c</sup> | 358.3 (vs)                                   | (3.4)               | $\nu_a$ (M-X)                   |
| 365 (m)                       | 372.5 (m)                                  | (-0.1)              | 374.0 (m)                                   | (11.1)              | 375.7 (sh)                                   | (-0.3)              | $\delta$ (CCP)                  |
| 330 (m)                       | 329.0 (m)                                  | (-0.5)              | 327.8 (s)                                   | (0.5)               | 330.8 (m)                                    | (0.0)               | $\delta$ (CCP)                  |
|                               | 273.4 (s)                                  | (5.9)               | 265.0 (m)                                   | (4.7) <sup>c</sup>  | 234.5 (s)                                    | (2.5)               | $\nu_a$ (M-P)                   |
| 245 (m)                       | Hidden                                     |                     | Hidden                                      |                     | 272.0 (m, br)                                | (0.0)               | $\delta$ (CCP)                  |
|                               | 200.2 (m)                                  | (0.8)               | 190.4 (s)                                   | (0.7)               | 183.8 (s)                                    | (1.8)               | $\delta$ (CPC)                  |
|                               | 186.5 (sh)                                 | (-0.2)              | 155.1 (m)                                   | (1.5)               | 168.0 (sh)                                   | (-0.5)              | $\delta$ (MX)                   |
|                               | 161.5 (vw)                                 | (-0.5)              | Hidden                                      |                     | 152.0 (vw)                                   | (1.0)               | $\delta$ (MP)                   |
|                               | 106.8 (m, br)                              | (-0.7)              | 106.0 (m)                                   | (-0.4)              | 105.5 (s, br)                                | (0.5)               | ?                               |

<sup>a</sup>  $\Delta\bar{\nu}$  indicates metal isotope shift,  $\bar{\nu}(^{58}\text{Ni}) - \bar{\nu}(^{62}\text{Ni})$  or  $\bar{\nu}(^{104}\text{Pd}) - \bar{\nu}(^{110}\text{Pd})$ . <sup>b</sup>  $\nu_a$ , asymmetric stretch,  $\delta$ ; bending. Ligand vibrations were assigned according to J. H. S. Green, *Spectrochim. Acta*, **24A**, 137 (1966). <sup>c</sup> In  $^{62}\text{Ni}(\text{PEt}_3)_2\text{Br}_2$ , these two bands are overlapped (see Figure 1). Therefore,  $\Delta\bar{\nu}$  values are only approximate.

## Results and Discussion

**Triethylphosphine Complexes.** Triethylphosphine complexes of the type  $\text{M}(\text{PEt}_3)_2\text{X}_2$ , where M is Ni(II) and Pd(II) and X is a halogen, are known to be *trans* square-planar.<sup>12</sup> Thus, one M-X stretching and one M-P stretching (both asymmetric type) vibration should be active in the infrared. Furthermore, both bands should be sensitive to metal isotope substitution.

Figure 1 gives the actual tracing of the spectra of  $^{58}\text{Ni}(\text{PEt}_3)_2\text{X}_2$  (X = Cl and Br) and their  $^{62}\text{Ni}$  analogs. Table I lists the observed frequencies, isotopic shifts, and band assignments. (The bands above  $420\text{ cm}^{-1}$  are not listed here since they are not sensitive to metal isotope substitution.) It is seen that each compound exhibits two bands which give large isotopic shifts relative to others. The band at  $403.3\text{ cm}^{-1}$  of  $^{58}\text{Ni}(\text{PEt}_3)_2\text{Cl}_2$  is clearly due to the Ni-Cl stretching mode, since this band is strong and not present in its bromo analog.<sup>2b,7</sup> Then, the remaining band at  $273.4\text{ cm}^{-1}$  must be assigned to the Ni-P stretching mode. This band persists in  $^{58}\text{Ni}(\text{PEt}_3)_2\text{Br}_2$  at  $265.0\text{ cm}^{-1}$ . Previously, Goggin and Goodfellow<sup>2b</sup> assigned the Ni-P stretching modes of  $\text{Ni}(\text{PEt}_3)_2\text{X}_2$  at  $426\text{--}410\text{ cm}^{-1}$ , and Coates and Parkin<sup>7</sup> assigned the same mode of  $\text{Ni}(\text{PEt}_3)_2\text{Cl}_2$  at  $415\text{ cm}^{-1}$ . These previous assignments must be revised in view of the new results obtained by the metal isotope technique. Although no direct evidence is available, the Ni-P stretching frequencies ( $361\text{--}366\text{ cm}^{-1}$ ) reported by Coates and Parkin<sup>7</sup> for  $\text{Ni}(\text{PMe}_3)_2\text{X}_2$  (X = Cl, Br, and I) seem to be too high.

Table I also shows that two bands at  $358.3$  and  $234.5\text{ cm}^{-1}$  of  $^{104}\text{Pd}(\text{PEt}_3)_2\text{Cl}_2$  are relatively sensitive to the  $^{104}\text{Pd}\text{--}^{110}\text{Pd}$  substitution. The former can be assigned safely to the Pd-Cl stretching mode since it is in the appropriate frequency range ( $370\text{--}345\text{ cm}^{-1}$ ).<sup>14</sup> Then, the band at  $234.5\text{ cm}^{-1}$  most probably arises from the Pd-P stretching mode. Previous investigators<sup>2b,3,7</sup> have assigned the Pd-P stretching bands of  $\text{Pd}(\text{PEt}_3)_2\text{X}_2$ - and  $\text{Pd}_2(\text{PEt}_3)_2\text{Cl}_4$ -type complexes at  $450\text{--}380\text{ cm}^{-1}$ . The Pd-P stretching bands of analogous trimethylphosphine complexes have also been assigned at  $380\text{--}340\text{ cm}^{-1}$  by many other investigators.<sup>4-7</sup> Our results show that these frequencies are too high for the Pd(II)-P stretching modes of square-planar complexes.

It should be noted, however, that the magnitude of the observed isotopic shifts is smaller in the Pd(II) than in the Ni(II) complexes mainly because the difference

in reciprocal mass between isotopes is smaller in the former than in the latter. Furthermore, some ligand vibrations may show relatively large isotopic shifts, possibly because of vibrational coupling with metal-ligand stretching modes. In these cases, the distinction between metal-ligand stretching and ligand vibrations cannot be made from the observed metal isotopic shifts alone. A theoretical vibrational analysis or a comparison of infrared spectra among analogous compounds is helpful in making band assignments.

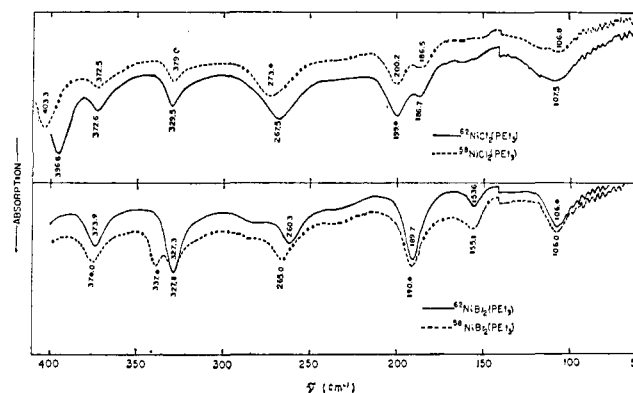


Figure 1. Far-infrared spectra of  $^{58}\text{Ni}(\text{PEt}_3)_2\text{X}_2$  and  $^{62}\text{Ni}(\text{PEt}_3)_2\text{X}_2$  (X = Cl and Br).

Below  $200\text{ cm}^{-1}$ , one expects (1) skeletal bending modes, (2) ligand vibrations newly activated by complex formation, and (3) lattice modes (in the case of solid spectra). As will be shown later, the skeletal bending frequencies are expected to be much less sensitive to metal isotope substitution than the metal-ligand stretching modes. For example, our approximate calculations on  $\text{Ni}(\text{PEt}_3)_2\text{X}_2$  (X = Cl and Br) predict a shift of less than  $2\text{ cm}^{-1}$  for the P-Ni-X bending modes. Thus, it is rather difficult to assign the bending modes from metal isotopic shifts. In Table I, we have proposed band assignments which were predicted from our approximate calculations. The band at  $183.8\text{ cm}^{-1}$  of  $^{104}\text{Pd}(\text{PEt}_3)_2\text{Cl}_2$  gives an isotopic shift of  $1.8\text{ cm}^{-1}$ , which is rather larger for a pure ligand vibration, probably because this ligand vibration couples with the Pd-P stretching mode ( $234.5\text{ cm}^{-1}$ ).

**Triphenylphosphine Complexes.**  $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$  is tetrahedral, whereas  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  is *trans* square-planar.<sup>12</sup> Thus, the former should exhibit two Ni-Cl

(14) D. M. Adams and P. J. Chandler, *Chem. Commun.*, 69 (1966).

**Table II.** Infrared Frequencies of Triphenylphosphine Complexes Containing Metal Isotopes (cm<sup>-1</sup>)

| PPh <sub>3</sub><br>$\bar{\nu}$ | <sup>58</sup> Ni(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> |                     | <sup>104</sup> Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> |                     | Band assignment <sup>b</sup>   |
|---------------------------------|--|---------------------|---|---------------------|--|
|                                 | $\bar{\nu}$  | $\Delta\bar{\nu}^a$ | $\bar{\nu}$   | $\Delta\bar{\nu}^a$ |  |
| 513 (s)                         | 522 (vs)   | (0.0)               | 522.2 (vs)  | (0.1)               | $\gamma$ vibration   |
| 499 (s)                         | 499 (vs)   | (0.0)               | 510.1 (vs)  | (0.1)               |  |
| 492 (s)                         | 490 (sh)   | (0.0)               | 501.4 (s)   | (0.3)               |  |
| 431 (m)                         | 448 (sh)   | (0.0)               | 457.4 (m)   | (0.3)               | $t$ vibration or<br>$\nu$ (P-Ph)   |
| 420 (m)                         | 440 (m)  | (0.0)               | 438.1 (m)   | (-0.4)              |  |
| 410 (sh)                        | 420 (vw)   | (0.0)               | 424.8 (w)   | (0.0)               |  |
| 398 (w)                         | 399 (vw)   | (0.0)               | 396.1 (vw)  | (0.0)               | $w$ vibration<br>$\nu_a$ (M-Cl)<br>$\nu_s$ (M-Cl)  |
|                                 | 341.2 (s)  | (5.0)               | 360.3 (s)   | (4.3)               |  |
|                                 | 305.0 (m)  | (1.7)               |   |                     |  |
| 272 (vw)                        |  |                     | 278.4 (w)   | (0.0)               | $x$ vibration  |
| 254 (w)                         | 263.5 (vw)   | (-0.3)              | 263.1 (w)   | (-0.7)              |  |
| 248 (w)                         | 248.9 (w)  | (-0.5)              | 253.8 (w)   | (0.6)               |  |
| 216 (w)                         | 225.6 (w, sh)  | (-0.2)              | 233.9 (w)   | (-0.1)              | $u$ vibration or<br>$\delta$ (Ph-P-Ph)   |
| 198 (w)                         | 217.5 (w)  | (0.5)               | 223.3 (w)   | (0.2)               |  |
| 187 (w)                         | 204.4 (w)  | (1.0)               | 206.0 (w)   | (1.5)               |  |
|                                 | 189.6 (w)  | (2.1)               | 191.2 (m)   | (4.2)               | $\nu_a$ (M-P)<br>$\nu_s$ (M-P),<br>$\delta$ (Ni-Cl)<br>$\delta$ (Pd-Cl) or<br>$\delta$ (Pd-P)<br>? |
|                                 | 164.0 (vw)   | (2.4)               |   |                     |  |
|                                 |  |                     | 155.0 (vw)  | (2.5)               |  |
|                                 |  |                     | 143.0 (vw)  | (0.5)               |  |
|                                 | 110.5 (m)  | (0.5)               | 118.5 (m)   | (0.4)               |  |

<sup>a</sup>  $\Delta\bar{\nu}$  indicates metal isotope shift:  $\bar{\nu}(^{58}\text{Ni}) - \bar{\nu}(^{62}\text{Ni})$  or  $\bar{\nu}(^{104}\text{Pd}) - \bar{\nu}(^{110}\text{Pd})$ . <sup>b</sup>  $\nu_a$ , asymmetric stretch;  $\nu_s$ , symmetric stretch;  $\delta$ , bending. Ligand vibrations were assigned according to K. Shobatake, C. Postmus, J. R. Ferraro, and K. Nakamoto, *Appl. Spectrosc.*, **23**, 12 (1969).

**Table III.** Infrared and Raman Frequencies of Triphenylphosphine and Triphenylarsine Complexes of Palladium in Natural Abundance (cm<sup>-1</sup>)

| Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> |          | Pd(PPh <sub>3</sub> ) <sub>2</sub> Br <sub>2</sub> |             | Pd(AsPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> |             | Pd(AsPh <sub>3</sub> ) <sub>2</sub> Br <sub>2</sub> |          | Band assignment <sup>a</sup>                                     |
|--|----------|--|-------------|---|-------------|---|----------|--|
| Ir   | Raman    | Ir   | Raman       | Ir  | Raman       | Ir  | Raman    |  |
| 530 (sh)   | 533 (m)  | 530 (sh)   | 530 (m)     | 475 (s)   | 476 (sh)    | 478 (vs)  | 476 (vw) | $\gamma$ vibration   |
| 522 (vs)   | 520 (sh) | 523 (vs)   | 520 (sh)    | 467 (s)   | 465 (m)     | 466 (vs)  | 464 (w)  |  |
| 510 (vs)   | 508 (w)  | 510 (vs)   | 508 (w)     |   |             |   |          |  |
| 501 (s)  | 494 (w)  | 499 (s)  | 496 (w)     |   |             |   |          |  |
| 457 (m)  | 456 (sh) | 458 (m)  | 454 (sh)    | 336 (s)   | 336 (s, br) | 339 (s)   | 336 (s)  | $t$ vibration or<br>$\nu$ (P-Ph) or<br>$\nu$ (As-Ph)             |
| 438 (m)  | 440 (m)  | 436 (m)  | 436 (m)     | 328 (s)   |             | 329 (s)   | 325 (sh) |  |
| 424 (m)  | 428 (sh) | 425 (sh)   | 426 (sh)    |   |             |   |          |  |
| 396 (w)  | 398 (w)  | 397 (vw)   | 399 (vw)    | 399 (vw)  | 399 (w)     | 400 (vw)  | 399 (vw) | $w$ vibration<br>$\nu$ (Pd-halogen)                              |
| 360 (s)  | 304 (s)  | 286 (m)  | 188 (vs)    | 360 (s)   | 308 (s)     | 282 (m)   | 191 (vs) |  |
| 278 (w)  |          | 282 (sh)   |             | 257 (vw)  | 264 (m)     | 258 (vw)  | 260 (m)  | $x$ vibration  |
| 263 (w)  | 258 (w)  | 263 (w)  | 258 (br, w) | 240 (m)   | 239 (m)     | 239 (w)   | 241 (m)  |  |
| 253 (w)  |          | 255 (w)  |             |   |             |   |          |  |
| 233 (w)  | 228 (w)  | 237 (w)  | 232 (w)     | 218 (sh)  |             | 228 (w)   |          | $u$ vibration or<br>$\delta$ (Ph-P-Ph) or<br>$\delta$ (Ph-As-Ph) |
| 223 (w)  |          | 217 (w)  |             | 208 (sh)  | 209 (m, br) | 206 (sh)  | 205 (sh) |  |
| 206 (w)  | 199 (w)  | 205 (w)  | 203 (sh)    | 202 (m)   | 187 (m)     | 194 (m)   | 185 (vw) |  |
| 191 (m)  | 155 (m)  | 185 (m)  | 150 (m)     | 180 (m)   | 132 (m)     | 180 (vs)  | 130 (vs) | $\nu$ (Pd-P) or $\nu$ (Pd-As)                                    |
| 155 (vw)   |          | 152 (vw)   |             | 149 (vw)  |             | 150 (vw)  |          | $\delta$ (Pd-X) or<br>$\delta$ (Pd-P)                            |
| 143 (vw)   | 135 (sh) | 142 (vw)   | 135 (vw)    | 135 (vw)  |             | 125 (vw)  |          |  |
| 118 (m, br)  |          | 108 (m)  | 100 (sh)    | 105 (m, br)   |             | 106 (sh)  |          |  |

<sup>a</sup> Ligand vibrations were assigned according to the reference given in footnote *b* of Table II.

and two Ni-P stretching, whereas the latter should exhibit one Pd-Cl and one Pd-P stretching band in the infrared. Table II gives the observed frequencies and isotopic shifts for <sup>58</sup>Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> and <sup>104</sup>Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>. Only the four bands at 341.2, 305.0, 189.6, and 164.0 cm<sup>-1</sup> of the Ni complex are relatively sensitive to the <sup>58</sup>Ni-<sup>62</sup>Ni substitution. The former two bands are assigned to the Ni-Cl stretching modes since they are relatively strong and absent in the bromo analog. Then the latter two bands must be assigned to the Ni-P stretching modes. These assignments are in complete

agreement with those previously made by Bradbury, *et al.*<sup>8</sup>

In <sup>104</sup>Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, two bands at 360.3 and 191.2 cm<sup>-1</sup> show exceptionally large isotopic shifts by the <sup>104</sup>Pd-<sup>110</sup>Pd substitution. The former is in the region of terminal Pd-Cl stretching frequencies<sup>14</sup> and assigned safely to this mode. Then it is reasonable to assign the latter to the Pd-P stretching mode. Previously, Goodfellow, *et al.*,<sup>3</sup> assigned the bands at 450 and 428 cm<sup>-1</sup> of Pd<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>4</sub> to the Pd-P stretching modes. These bands may be assignable to the vibrations of the triphenylphosphine ligand.

Based on the results obtained above, we have assigned the infrared and Raman spectra of *trans*-Pd(PPh<sub>3</sub>)<sub>2</sub>X<sub>2</sub> and *trans*-Pd(AsPh<sub>3</sub>)<sub>2</sub>X<sub>2</sub> (X = Cl and Br) containing the metal of natural abundance. Table III lists the observed frequencies and band assignments. Previously, Park and Hendra<sup>6</sup> assigned the M-X and M-P stretching vibrations of analogous trimethylphosphine and trimethylarsine complexes. Our M-X frequencies shown in Table III are very close to those reported by Park and Hendra.<sup>6,15</sup> However, our Pd-PPh<sub>3</sub> (190–150 cm<sup>-1</sup>) and Pd-AsPh<sub>3</sub> (180–130 cm<sup>-1</sup>) stretching frequencies are markedly lower than their Pd-PMe<sub>3</sub> (360–340 cm<sup>-1</sup>) and Pd-AsMe<sub>3</sub> (280–260 cm<sup>-1</sup>) stretching frequencies, respectively.

**Approximate Normal Coordinate Analysis.** In the previous sections, we have assigned the M-P and M-X stretching bands based on the observed isotopic shifts. It is, therefore, desirable to compare them with theoretical isotopic shifts calculated from normal coordinate analysis. Since the M(PEt<sub>3</sub>)<sub>2</sub>X<sub>2</sub>-type molecule is too complex to carry out a rigorous treatment, we have adopted a *trans* planar MY<sub>2</sub>X<sub>2</sub> model assuming that the PEt<sub>3</sub> ligand is a single atom having the mass of PEt<sub>3</sub>. Evidently, such an approximate calculation provides only a rough measure of theoretical isotopic shifts. Even so, the results are sufficient to show that the magnitudes of the observed isotopic shifts are at least reasonable.

Table IV compares the theoretical and observed isotopic shifts of *trans*-Pd(PEt<sub>3</sub>)<sub>2</sub>X<sub>2</sub> (X = Cl and Br) due to

(15) In ref 6, there seem to be obvious errors in designation of vibrational modes: In Table II,  $\nu_1$  and  $\nu_2$  represent the M-P or M-As stretching, whereas  $\nu_3$  and  $\nu_4$  denote the M-halogen stretching modes.

**Table IV.** Comparison of Theoretical and Observed Isotopic Shifts for *trans*-Ni(PEt<sub>3</sub>)<sub>2</sub>X<sub>2</sub> (cm<sup>-1</sup>)

|  | Theoretical      |                   | Observed         |                   |
|--|------------------|-------------------|------------------|-------------------|
|  | <sup>68</sup> Ni | $\Delta\bar{\nu}$ | <sup>68</sup> Ni | $\Delta\bar{\nu}$ |
| Ni(PEt <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> |                  |                   |                  |                   |
| Ni-Cl stretch                                      | 402.4            | 7.2               | 403.3            | 6.7               |
| Ni-P stretch                                       | 270.8            | 7.3               | 273.4            | 5.9               |
| Ni-Cl bend   | 189.5            | 0.0               | 186.5            | -0.2              |
| Ni-P bend  | 168.2            | 1.7               | 161.5            | -0.5              |
| Ni(PEt <sub>3</sub> ) <sub>2</sub> Br <sub>2</sub> |                  |                   |                  |                   |
| Ni-Br stretch                                      | 340.9            | 8.6               | 337.8            | 10.5 <sup>a</sup> |
| Ni-P stretch                                       | 265.9            | 7.5               | 265.0            | 4.7               |
| Ni-Br bend   | 141.0            | 0.1               | 155.1            | 1.5               |
| Ni-P bend  | 147.1            | 0.5               | <i>b</i>         |                   |

<sup>a</sup> See footnote *a* of Table I. <sup>b</sup> Hidden by the neighboring band.

<sup>68</sup>Ni-<sup>62</sup>Ni substitution. The molecular parameters used were: Ni-Cl, 2.30; Ni-Br, 2.40; Ni-P, 2.25 Å.<sup>16</sup> The four angles around the Ni atoms were assumed to be 90°. The potential energy was expressed by using the Urey-Bradley field.<sup>17</sup> The following set of force constants was found to be satisfactory: *K* (stretching), 1.35 for Ni-Cl, 1.25 for Ni-Br, and 0.75 for Ni-P; *H* (bending), 0.11; *F* (repulsive), 0.13 (all in units of m dyn/Å). The results shown in Table IV indicate that (1) the magnitude of the observed isotopic shifts is close to that expected theoretically and (2) the isotopic shifts for bending modes are less than 2 cm<sup>-1</sup> in these cases.

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## Metal Isotope Effect on Metal-Ligand Vibrations. II. Tris Complexes of 2,2'-Bipyridine and 1,10-Phenanthroline<sup>1,2</sup>

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**Abstract:** The far-infrared spectra (500–150 cm<sup>-1</sup>) of the isotopic pairs have been obtained for the [Fe(bipy)<sub>3</sub>]<sup>2+</sup> (<sup>54</sup>Fe and <sup>57</sup>Fe), [Ni(bipy)<sub>3</sub>]<sup>2+</sup> and [Ni(phen)<sub>3</sub>]<sup>2+</sup> (<sup>68</sup>Ni and <sup>62</sup>Ni), and [Zn(bipy)<sub>3</sub>]<sup>2+</sup> and [Zn(phen)<sub>3</sub>]<sup>2+</sup> (<sup>64</sup>Zn and <sup>68</sup>Zn) ions. Based on the observed isotopic shifts, the Fe-N, Ni-N, and Zn-N stretching bands have been assigned at 375–360, 300–240, and 240–175 cm<sup>-1</sup>, respectively.

The infrared spectra of tris complexes of 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen) with the first-row transition metals have been studied by several investigators. Schilt and Taylor<sup>3</sup> and Inskeep<sup>4</sup> studied the infrared spectra of these compounds in the

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(3) A. A. Schilt and R. C. Taylor, *J. Inorg. Nucl. Chem.*, **9**, 211 (1959).

(4) R. G. Inskeep, *ibid.*, **24**, 763 (1962).

regions from 2000 to 600 and 2000 to 250 cm<sup>-1</sup>, respectively, and Clark and Williams<sup>5</sup> extended the infrared measurements down to 60 cm<sup>-1</sup>. As noted by these investigators, the bands observed in the high-frequency region are mainly due to the ligand vibrations slightly perturbed by coordination and cannot be correlated to the nature of the metal. On the other hand, the spectra below 500 cm<sup>-1</sup> are different for each metal involved. Attempts have been made to assign the metal-nitrogen (M-N) stretching vibrations in this region. Inskeep<sup>4</sup>

(5) R. J. H. Clark and C. S. Williams, *Spectrochim. Acta*, **23A**, 1055 (1967).