

**Figure 2.**  $^{31}\text{P}$  chemical shifts,  $\delta$ , of 0.010 M solutions in tetramethylurea as a function of the concentration of added tetrabutylammonium chloride for (A) triethyl orthophosphate and the tetrabutylammonium salts of (B) the diethyl orthophosphate anion, (C) the monoethyl orthophosphate anion, (D) the orthophosphate anion and (E) the ethylphosphonate anion. The solutions were all adjusted so as to exhibit a pH of 7 when the tetramethylurea was replaced by water.

Our interpretation of the data of Figure 2 is based on the same ideas used in explaining Figure 1. We conclude that there is little effect of the added salt on the chemical shift of either the triethyl or the diethyl orthophosphate since neither of these have associated hydrogen atoms through which the solvent can interact with the  $\text{PO}_4$  groups. The downward change of the chemical shift with added salt for the monoester is then attributed to the added cations disrupting the interaction of the solvent with the proton associated with the  $\text{PO}_4$  groups (presumably through hydrogen bonding). Apparently the upfield change in shift observed for the unesterified orthophosphate upon the salt addition is due to retention of the interaction with the solvent through the very weakly acidic proton plus an increase in magnetic shielding brought about by close approach of the positive ions.

It should be noted in Figure 1 that the chemical shifts corresponding to no additional salt are very close for the sodium and tetramethylammonium cations of all of the phosphate structures except the unesterified orthophosphate, for which it can be seen that the chemical shift of the sodium orthophosphate at pH 7.00 is appreciably lower than that of the tetramethylammonium salt at the same pH. This finding led us to investigate the effect of different countercations on the orthophosphate chemical shift corresponding to pH 7 in aqueous solutions containing 0.010 mol of P/l., with no added chloride or other salt. The results for the various ammonium and alkali metal ions are as follows:  $(\text{CH}_3)_4\text{N}^+$ ,  $-0.61$  ppm;  $\text{NH}_4^+$ ,  $-0.82$  ppm;  $\text{Li}^+$ ,  $-0.71$  ppm;  $\text{Na}^+$ ,  $-1.21$  ppm;  $\text{K}^+$ ,  $-0.62$  ppm;  $\text{Rb}^+$ ,  $-1.66$  ppm;  $\text{Cs}^+$ ,  $-0.77$  ppm. Values were also obtained for two of the alkaline earth metal ions, which were present on a 1:1 molar basis with respect to the phosphorus, with additional tetramethylammonium ion to bring the precursor aqueous solution<sup>10</sup> to pH 7.00. The results are as follows:  $\text{Mg}^{2+}$ ,  $-1.65$  ppm;  $\text{Ca}^{2+}$ ,  $-0.65$  ppm. Unfortunately the strontium and barium phosphates are not sufficiently soluble to have been included in this study. An interesting feature of these findings is the alternation between high and low values of the chemical shift upon going from the

lighter to the heavier alkali metal ions.

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**Registry No.**  $(\text{C}_2\text{H}_5\text{O})_3\text{PO}$ , 78-40-0;  $(\text{C}_2\text{H}_5\text{O})_2\text{PO}_2^-$ , 48042-47-3;  $(\text{C}_2\text{H}_5\text{O})\text{PO}_3^{2-}$ , 57919-10-5;  $\text{PO}_4^{3-}$ , 14265-44-2;  $\text{C}_2\text{H}_5\text{PO}_3^{2-}$ , 16486-09-2;  $\text{Na}$ , 7440-23-5;  $(\text{CH}_3)_4\text{N}^+$ , 51-92-3;  $(t\text{-Bu})_4\text{N}^+$ , 10549-76-5;  $\text{NH}_4^+$ , 14798-03-9;  $\text{Li}$ , 7439-93-2;  $\text{K}$ , 7440-09-7;  $\text{Rb}$ , 7440-17-7;  $\text{Cs}$ , 7440-46-2;  $\text{Mg}$ , 7439-95-4;  $\text{Ca}$ , 7440-70-2;  $^{31}\text{P}$ , 7723-14-0.

## References and Notes

- (1) T. Glonek, M. Lunde, M. Mudgett, and T. C. Myers, *Arch. Biochem. Biophys.*, **142**, 508 (1971) [polyphosphate ( $\bar{n} > 175$ ) from *M. lysodeikticus*].
- (2) T. O. Henderson, T. Glonek, R. L. Hilderbrand, and T. C. Myers, *Arch. Biochem. Biophys.*, **149**, 484 (1972) [phosphonates from *Bunodosoma*, Sp].
- (3) T. O. Henderson, T. Glonek, and T. C. Myers, *Biochemistry*, **13**, 623 (1973), [phospholipids and their fragments].
- (4) T. Glonek, T. O. Henderson, A. W. Kruski, and A. M. Scanu, *Biochim. Biophys. Acta*, **348**, 155 (1974) [intact human circulating lipoproteins].
- (5) T. O. Henderson, A. J. R. Costello, and A. Omachi, *Proc. Natl. Acad. Sci. U.S.A.*, **71**, 2487 (1974) [2,3-diphosphoglycerate and adenosine triphosphate within intact human erythrocytes].
- (6) M. Barány, K. Barány, C. T. Burt, T. Glonek, and T. C. Myers, *J. Supramolecular Struct.*, in press [Ebden-Meyerhoff intermediates within intact muscle].
- (7) M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, *Top. Phosphorus Chem.*, **5**, 1 (1967).
- (8) T. Glonek, T. O. Henderson, R. L. Hilderbrand, and T. C. Myers, *Science*, **169**, 192 (1970).
- (9) T. Glonek and J. R. Van Wazer, *J. Magn. Reson.*, **13**, 390 (1974).
- (10) T. Glonek, J. R. Van Wazer, M. Mudgett, and T. C. Myers, *Inorg. Chem.*, **11**, 567 (1972).
- (11) H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).
- (12) J. H. Letcher and J. R. Van Wazer, *J. Chem. Phys.*, **44**, 815 (1966).
- (13) M. Karplus and T. P. Das, *J. Chem. Phys.*, **34**, 1683 (1961).
- (14) K. Moedritzer, *Inorg. Chem.*, **6**, 936 (1967).

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## Raman Spectral Evidence for Trapped Valences in $[(\text{NH}_3)_5\text{Ru-pyr-Ru}(\text{NH}_3)_5]^{5+}$

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Much interest attaches to the electronic structure of the mixed-valence complex  $[(\text{NH}_3)_5\text{Ru-pyr-Ru}(\text{NH}_3)_5]^{5+}$  (pyr = pyrazine) originally prepared and investigated by Creutz and Taube.<sup>2,3</sup> The evidence to date, which includes visible and near-infrared absorption,<sup>2-4</sup> NMR,<sup>5</sup> Mössbauer,<sup>6</sup> and photoelectron<sup>7</sup> spectra, points fairly clearly to a trapped-valence, or class II,<sup>8</sup> formulation, with the two ruthenium centers maintaining their characteristic II and III oxidation states. Vibrational spectroscopy should also be informative in this regard, since metal-ligand and internal ligand vibrational frequencies should differ for Ru(II) and Ru(III) centers. The infrared spectrum is complicated, however, and cannot be interpreted unambiguously.<sup>3</sup>

Raman spectra are frequently easier to interpret, since totally symmetric vibrations can be identified from solution polarization measurements and usually give rise to the most intense Raman bands. We present here a Raman investigation of the isostructural complexes  $[(\text{NH}_3)_5\text{Ru-pyr-Ru}(\text{NH}_3)_5]^{n+}$ ,  $n = 4, 5$ , and 6, henceforth designated as (II,II), (II,III) and (III,III), respectively. The 4+ complex contains two Ru(II) centers, and the 6+ complex contains two Ru(III) centers. The

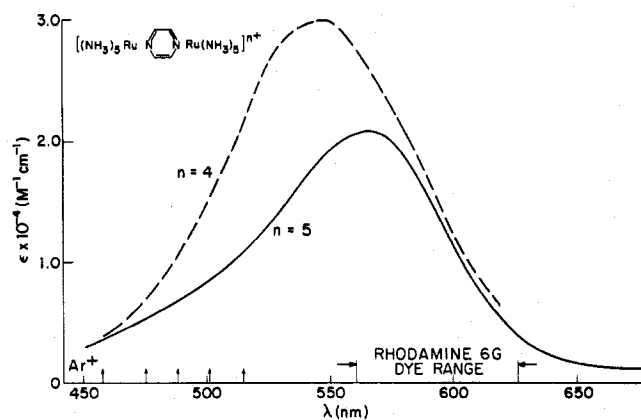


Figure 1. Visible absorption bands of  $[(\text{NH}_3)_5\text{Ru-pyr-Ru}(\text{NH}_3)_5]^{n+}$ ,  $n = 4, 5$ . The  $n = 6$  complex has no visible band. Excitation wavelengths of  $\text{Ar}^+$  ( $\dagger$ ) and Rhodamine 6G dye lasers are indicated.

results are consistent with trapped valences for (II,III) in solution on the vibrational time scale ( $\sim 10^{-13}$  s); at least one pair of vibrational bands can be assigned to separate components from Ru(II) and Ru(III).

### Experimental Section

*p*-Toluenesulfonate salts of the (II,II) and (II,III) ions were kindly provided by Dr. Carol Creutz. (III,III) was prepared from (II,III) by adding excess ceric perchlorate,<sup>3</sup> just prior to running spectra.

Aqueous solutions of (II,II) were prepared using deaerated water, in an argon-filled glovebag. Capillary cells or a spinning cell was filled in the glovebag and sealed. The solutions of (II,III) were prepared in air. Concentrations were determined spectrophotometrically.<sup>3</sup>  $\text{Na}_2\text{SO}_4$  or  $(\text{NH}_4)_2\text{SO}_4$  was sometimes added to a concentration of 1 M as an internal Raman intensity standard.

The spectrometer was based on a Spex 1401 double-grating monochromator and an ITT FW130 phototube with dc amplification. Excitation was provided by a Coherent Radiation Ar ion laser or a Spectra Physics tunable dye laser (Rhodamine 6G), pumped by the Ar ion laser.

Due to the photosensitivity of all three compounds, spectra were run under a variety of conditions. Absorption spectra were obtained before and after recording of the Raman spectra. Both (II,II) and (II,III) underwent a gradual blue shift of the visible absorption band, indicative of aquo substitution.<sup>3</sup> This was not correlated with any noticeable shift in the Raman frequencies; apparently the reaction has no influence on the pyrazine vibrational frequencies. (III,III) rapidly developed a visible band identical with that of (II,III) or (II,II), indicating photoreduction. A consistent body of data was produced by varying time of sample exposure to laser irradiation, incident power, and sample cell and scanning only small portions of the spectrum at one time.

### Results and Discussion

The visible spectrum of (II,II) contains an intense, broad absorption band which extends through the entire range of available laser frequencies, as shown in Figure 1. This absorption is attributable to  $\text{Ru(II)} \rightarrow \text{pyrazine}(d_\pi \rightarrow p_\pi^*)$  charge transfer<sup>3</sup> and should produce resonance enhancement of totally symmetric Raman bands associated with the bridging pyrazine.<sup>9,10</sup> This was indeed found to be the case. The Raman scattering cross section of (II,II) is very high, 0.1 mM solutions producing Raman bands comparable in intensity to the  $\nu_1$  symmetric stretching band of  $\text{SO}_4^{2-}$ , present in 1 M concentration. When the laser frequency was varied, the (II,II) Raman intensities were found to track the absorption band, although measurement of a quantitative excitation profile was rendered difficult by fairly rapid photoaquation,<sup>3</sup> even in the spinning cell.

The resonance Raman spectrum of (II,II) contains only five bands, all polarized. Their frequencies are given in Table I. The band at  $326 \text{ cm}^{-1}$  is assignable to Ru-pyr stretching, while the remaining frequencies correlate with the totally symmetric

Table I. Raman Frequencies ( $\text{cm}^{-1}$ ) and Assignments for  $[(\text{NH}_3)_5\text{Ru-pyr-Ru}(\text{NH}_3)_5]^{n+}$  Complexes

| Assignment <sup>a</sup> | Pyrazine <sup>11,12</sup> | $n = 4$<br>(II,II) | $n = 5$<br>(II,III) | $n = 6$<br>(III,III)                   |
|-------------------------|---------------------------|--------------------|---------------------|--|
| $\nu_{8a}$              | 1578                      | 1593               | 1596                | 1625                                   |
| $\nu_{9a}$              | 1230                      | 1224               | 1234                | 1253                                   |
| $\nu_1$                 | 1015                      | 1084               | 1080                | 1055 <sup>c</sup><br>1033 <sup>c</sup> |
| $\nu_{6a}$              | 596                       | 689                | 701                 | 692                                    |
| $\nu_{\text{Ru-NH}_3}$  |                           | <i>b</i>           | <i>b</i>            | 500                                    |
| $\nu_{\text{Ru-pyr}}$   |                           | 326                | 328                 | ( $\sim 350$ ) <sup>d</sup>            |

<sup>a</sup> See ref 11 for the forms of the pyrazine normal modes.

<sup>b</sup> Unobserved. <sup>c</sup> Assigned to Fermi resonance; see text.

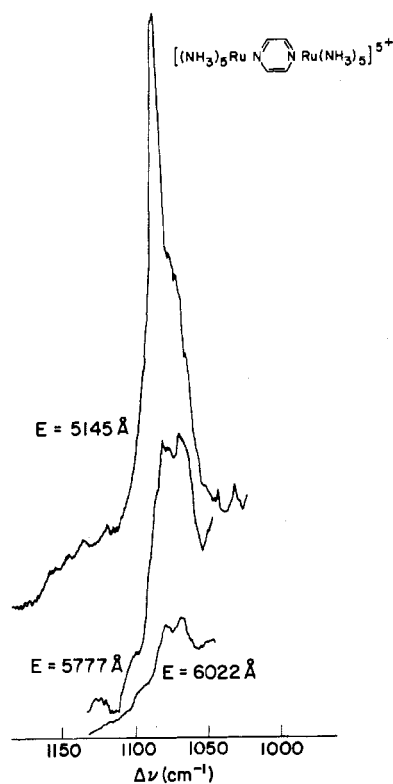
<sup>d</sup> Unobserved; estimated from the assigned Fermi interaction.

vibrations of free pyrazine<sup>11,12</sup> (leaving aside the C-H stretching mode). The shifts in frequency reflect the combined effects of  $\sigma$  bonding to Ru(II),  $\pi$  back-donation, and coupling with  $\nu_{\text{Ru-pyr}}$ . Similar shifts have been observed for bridging pyrazine in stannic halide complexes.<sup>13</sup>

The visible spectrum of (III,III) does not display intense absorption, and the Raman spectrum is not resonance enhanced, much higher concentrations of (III,III) being required to obtain a spectrum. At the same time photoreduction of (III,III) to (II,III) and (II,II) is facile,<sup>3</sup> and resonance-enhanced bands of photoproducts are readily apparent. This interference was minimized by adding excess ceric perchlorate, using laser frequencies in the red region, and recording spectra rapidly. Nevertheless, it was only possible to identify the most intense bands in the (III,III) Raman spectrum, all of which are polarized. They include a band at  $502 \text{ cm}^{-1}$ , assignable to Ru-NH<sub>3</sub> stretching, by comparison with  $\nu_{\text{RuNH}_3}$  ( $500 \text{ cm}^{-1}$ ) in  $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ .<sup>14</sup> The remaining frequencies again correlate with the totally symmetric vibrations of free pyrazine (see Table I), except that two bands, 1033 and  $1055 \text{ cm}^{-1}$ , are observed in the region where  $\nu_1$  is expected. We assign this doublet to Fermi resonance between  $\nu_1$  and the combination of  $\nu_{6a}$  and  $\nu_{\text{Ru-pyr}}$ . A somewhat analogous Fermi resonance has been observed for biphenyl.<sup>15</sup> A band assignable to  $\nu_{\text{Ru-pyr}}$  was not observed in the (III,III) spectrum but the Fermi resonance condition requires a value close to  $350 \text{ cm}^{-1}$ , about  $25 \text{ cm}^{-1}$  above the corresponding (II,II) frequency. This is consistent with the somewhat higher effective charge expected for Ru(III).

If the odd electron on (II,III) is completely delocalized, giving equivalent Ru centers on the vibrational time scale, then the Raman spectrum of (II,III) should display a set of frequencies intermediate between those of (II,II) and (III,III). If the Ru centers are inequivalent, then each of the pyrazine frequencies, save one, should double, one set of frequencies being close to (II,II) and the other being close to (III,III) (some frequency shift is expected due to coupling between the two ends of the complex). The situation is complicated, however, by the effects of resonance enhancement. The visible spectrum of (II,III) has an absorption band with about half the intensity of the (II,II) band (see Figure 1), assignable to charge transfer from the Ru(II) end of the complex.<sup>3,4</sup> Accordingly, resonance enhancement is expected for Raman bands associated primarily with the Ru(II) center but not with those associated primarily with the Ru(III) center. Indeed, the Raman spectrum of (II,III) is very similar to that of (II,II), with slight shifts in frequency, and intensities characteristic of resonance enhancement.

However, the (II,III) spectrum contains an additional polarized band, at  $1070 \text{ cm}^{-1}$ , which does not appear in the



**Figure 2.** The 1080- and 1070-cm<sup>-1</sup> features of the Raman spectrum of [(NH<sub>3</sub>)<sub>5</sub>Ru-pyr-Ru(NH<sub>3</sub>)<sub>5</sub>]<sup>5+</sup>, obtained with a spinning cell, at various excitation wavelengths, *E*.

(II,II) spectrum. With excitation in the middle of the absorption band, this Raman feature appears as a shoulder on the intense 1080-cm<sup>-1</sup> ( $\nu_1$ ) band. As the excitation is moved to the low-energy side of the absorption band, the 1080-cm<sup>-1</sup> band loses intensity rapidly, while the 1070-cm<sup>-1</sup> band intensity change is much less. The effect is shown in Figure 2; with 6022-Å excitation the 1070-cm<sup>-1</sup> band is actually stronger than the 1080-cm<sup>-1</sup> band. Clearly the 1080-cm<sup>-1</sup> band is enhanced via the Ru(II) → pyr charge-transfer transition, but the 1070-cm<sup>-1</sup> band is not. Therefore, the 1070-cm<sup>-1</sup> band is assignable to the  $\nu_1$  component arising from the Ru(III) end of the complex.

The Fermi resonance observed for this fundamental in (III,III) is not seen in the (II,III) spectrum although the weakness of the 1070-cm<sup>-1</sup> band makes it difficult to preclude another, still weaker, component. It is plausible, however, that the increase of the  $\nu_1$  frequency to 1070 cm<sup>-1</sup> from ~1044 cm<sup>-1</sup> in (III,III) significantly weakens the Fermi interaction. Other components assignable to the Ru(III) center should also appear in the off-resonance (II,III) spectrum, but the great disparity between resonance-enhanced and non-resonance-enhanced bands has so far precluded their observation.

Table I summarizes our assignments of the observed Raman features, on the assumption that the trapped-valence formulation of (II,III) is valid. Direct evidence for this formulation consists of the one band, 1070 cm<sup>-1</sup>, attributable to Ru(III), and the resonance enhancement and close frequency correspondence to (II,II) of the bands assignable to Ru(II).

**Registry No.** [(NH<sub>3</sub>)<sub>5</sub>Ru-pyr-Ru(NH<sub>3</sub>)<sub>5</sub>]<sup>4+</sup>, 26253-76-9; [(NH<sub>3</sub>)<sub>5</sub>Ru-pyr-Ru(NH<sub>3</sub>)<sub>5</sub>]<sup>5+</sup>, 35599-57-6; [(NH<sub>3</sub>)<sub>5</sub>Ru-pyr-Ru(NH<sub>3</sub>)<sub>5</sub>]<sup>6+</sup>, 38900-60-6.

#### References and Notes

- (1) This investigation was supported by National Science Foundation Grant GP41008X.
- (2) C. Creutz and H. Taube, *J. Am. Chem. Soc.*, **91**, 3988 (1969).
- (3) C. Creutz and H. Taube, *J. Am. Chem. Soc.*, **95**, 1086 (1973).
- (4) B. Mayoh and P. Day, *J. Am. Chem. Soc.*, **94**, 2885 (1972).

- (5) J. H. Elias and R. Drago, *Inorg. Chem.*, **11**, 415 (1972).
- (6) C. Creutz, M. L. Good, and S. Chandra, *Inorg. Nucl. Chem. Lett.*, **9**, 171 (1973).
- (7) P. H. Citrin, *J. Am. Chem. Soc.*, **95**, 6472 (1973).
- (8) M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, **10**, 247 (1967).
- (9) A. C. Albrecht and M. C. Hutley, *J. Chem. Phys.*, **55**, 4438 (1971).
- (10) B. P. Gaber, V. Miskowski, and T. G. Spiro, *J. Am. Chem. Soc.*, **96**, 6868 (1974).
- (11) R. Lord, A. Marston, and F. Miller, *Spectrochim. Acta*, **9**, 113 (1957).
- (12) J. D. Simmons and K. K. Innes, *J. Mol. Spectrosc.*, **14**, 190 (1967).
- (13) M. Goldstein and W. D. Unsworth, *Spectrochim. Acta, Part A*, **27**, 1055 (1971).
- (14) W. P. Griffith *J. Chem. Soc. A*, 899 (1966).
- (15) A. Bree, C. Y. Pang, and L. Rabenck, *Spectrochim. Acta, Part A*, **27**, 1293 (1971).

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#### Protonation of the Metal-Metal Bond in [ $\mu$ -(SCH<sub>3</sub>)Fe(CO)<sub>2</sub>L]<sub>2</sub> Complexes (L = P(CH<sub>3</sub>)<sub>3-x</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>x</sub>). Experimental Evidence of the Variation of Nucleophilicity of the Metal-Metal Bond with Donor Properties of Phosphorus Ligands

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A recent publication on the protonation of the metal-metal bond in dinuclear complexes<sup>1</sup> prompts us to report our observations on the protonation of [ $\mu$ -(SCH<sub>3</sub>)Fe(CO)<sub>2</sub>L]<sub>2</sub> compounds. Although these compounds have been known for a long time,<sup>2</sup> a reexamination of the behavior of [ $\mu$ -(SCH<sub>3</sub>)Fe(CO)<sub>3</sub>]<sub>2</sub> toward phosphines has only recently appeared.<sup>3</sup> Furthermore, except for the action of halogens on [ $\mu$ -(SR)Fe(CO)<sub>2</sub>L]<sub>2</sub>,<sup>4</sup> no study has been made of the reactivity of these compounds containing a metal-metal bond toward electrophilic reagents.

We have therefore investigated the behavior of [ $\mu$ -(SCH<sub>3</sub>)Fe(CO)<sub>2</sub>L]<sub>2</sub> complexes toward a proton. An important difference having appeared in the behavior of complexes when L = P(CH<sub>3</sub>)<sub>3</sub> or P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>, we have, for this reason, extended the study of the reactivity toward a proton to the series with L = P(CH<sub>3</sub>)<sub>3-x</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>x</sub> (x = 0-3). For these complexes the proposed structure is that in which the ligands L are trans to the metal-metal bond and the SCH<sub>3</sub> have the syn-endo position.<sup>3</sup>

#### Experimental Section

All of the reactions have been done under a nitrogen atmosphere. The ligands P(CH<sub>3</sub>)<sub>3</sub>,<sup>5</sup> P(CH<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>),<sup>6</sup> and P(CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub><sup>6</sup> have been prepared following literature methods. P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> and [ $\mu$ -(SCH<sub>3</sub>)Fe(CO)<sub>3</sub>]<sub>2</sub> are of commercial origin and have been used without further purification.

The syntheses of [ $\mu$ -(SCH<sub>3</sub>)Fe(CO)<sub>2</sub>L]<sub>2</sub> compounds have been performed according to published procedures<sup>3</sup> with slight modifications. Infrared spectra were recorded on a Perkin-Elmer 225 and NMR spectra were obtained with a Varian A-60A.

**Protonation of [ $\mu$ -(SCH<sub>3</sub>)Fe(CO)<sub>2</sub>P(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub> (I) and [ $\mu$ -(SCH<sub>3</sub>)Fe(CO)<sub>2</sub>P(CH<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>)]<sub>2</sub> (II).** We have applied the procedure used by Green et al.<sup>7</sup> to protonate ( $\pi$ -C<sub>6</sub>H<sub>6</sub>)MoL<sub>3</sub> complexes. To a solution of 0.5 g of complexes I or II in 20 ml of ethanol was added 5 ml of concentrated hydrochloric acid. The solution was stirred for 10 min, giving a pale orange solution. Then a few drops of a saturated aqueous ammonium hexafluorophosphate solution was added. A yellow-orange powder precipitated which was collected, washed