

## Resonance Raman Spectra of Tetracarbonyldi- $\mu$ -2,2,5,5-tetramethylhex-3-yne-diiron. Stretching Vibration of an Iron-Iron Double Bond<sup>1</sup>

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Resonance Raman spectra have been obtained for  $(t\text{-BuC}_2\text{-}t\text{-Bu})_2\text{Fe}_2(\text{CO})_4$ , in which two di-*tert*-butylacetylene molecules bridge an Fe-Fe bond. A strong band at  $284\text{ cm}^{-1}$  is assigned to Fe-Fe stretching. The relatively high frequency supports the view that the iron atoms are joined by a double bond. Normal-coordinate calculations give a Fe-Fe stretching force constant of  $3.0 \pm 0.4\text{ mdyn/\AA}$ , roughly twice the value for a single Fe-Fe bond. The  $284\text{-cm}^{-1}$  Raman band is in resonance with the first electronic transition, centered at 528 nm. Analysis of the intensities and depolarization ratios indicates, however, that this resonance is weak and that the Raman intensity is dominated by preresonance with higher energy transitions. It is suggested that the latter are metal-metal  $\sigma\text{-}\sigma^*$  and/or  $\pi\text{-}\pi^*$  transitions and that the 528-nm band arises from an iron-acetylene charge-transfer transition. Observation of resonance enhancement for a Raman band at  $531\text{ cm}^{-1}$ , which is assigned primarily to iron-acetylene stretching, supports this view.

### Introduction

An extremely short iron-iron distance,  $2.215\text{ \AA}$ , has recently been observed by Nicholas, *et al.*,<sup>2</sup> in the X-ray crystal structure of their novel compound, tetracarbonyldi- $\mu$ -2,2,5,5-tetramethylhex-3-yne-diiron,  $(t\text{-BuC}_2\text{-}t\text{-Bu})_2\text{Fe}_2(\text{CO})_4$ . The molecular geometry (Figure 1) consists of a basal plane of two iron atoms and four carbonyl groups normal to a plane formed by the four acetylene carbons of the di-*tert*-butylacetylene ligands. Iron-iron single-bond lengths typically vary from  $2.37$  to  $2.77\text{ \AA}$  for organodiiron complexes.<sup>3,4</sup> The  $2.215\text{-\AA}$  separation in  $(t\text{-BuC}_2\text{-}t\text{-Bu})_2\text{Fe}_2(\text{CO})_4$  is consistent with a double iron-iron bond as suggested<sup>2</sup> by the electron count.

We have examined the Raman and infrared spectra of this compound as part of a continuing study of the vibrational spectra of compounds containing metal-metal bonds.<sup>5</sup> Metal-metal stretching vibrations normally give rise to intense and easily identifiable peaks in the Raman spectrum, even in cases where the sample is highly colored, such as  $[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})]_4$ ,<sup>6</sup>  $\text{S}_2\text{Fe}_2(\text{CO})_6$ ,<sup>7</sup> and  $[(\text{C}_5\text{H}_5)\text{FeS}]_4$ .<sup>8</sup> Enhancement due to a resonance Raman effect<sup>9</sup> facilitates observation of the spectrum of these species and also the compound of interest here,  $(t\text{-BuC}_2\text{-}t\text{-Bu})_2\text{Fe}_2(\text{CO})_4$ , which is deep lavender for both solid and solution phases.

### Experimental Section

For highly colored compounds, standard laser Raman techniques using solids or concentrated solutions often fail because of sample decomposition, although good results have recently been obtained with spinning sample holders.<sup>10</sup> An alternative technique is to work with relatively dilute solutions, keeping the light path through the sample to a minimum. We have obtained reliable spectra using transverse excitation of solutions in 1-2-mm diameter capillary tubes.

A crystalline sample of  $(t\text{-BuC}_2\text{-}t\text{-Bu})_2\text{Fe}_2(\text{CO})_4$  was kindly

(1) This investigation was supported by Public Health Service Grant GM 13498 and by National Science Foundation Grant GP 10122.

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provided by Professor Rowland Pettit and Dr. Kenny M. Nicholas. Its electronic spectrum (Figure 2) in benzene solution was recorded using a Cary 14 spectrophotometer. The Raman spectrometer used in this work is equipped with a Coherent Radiation Model 52 Ar<sup>+</sup> laser and a Spectra-Physics He-Ne laser, a Spex Model 1401 double monochromator, and a cooled ITT FW-130 Startracker phototube. The sample solutions were syringed into 1-mm diameter glass capillaries. The concentrations varied from  $3 \times 10^{-3}$  to  $1.2 \times 10^{-2}\text{ M}$ , depending upon the excitation wavelength. Solvents included  $\text{CS}_2$ ,  $\text{CCl}_4$ , benzene, and methylcyclohexane.

Raman intensities were measured by adding a known amount of  $\text{CCl}_4$  to the solution and comparing the intensity of the band of interest to that of the  $\nu_1(\text{A}_1)$  line of  $\text{CCl}_4$ . The concentration of  $\text{CCl}_4$  was 0.1-0.2 M in all cases. At least three spectral scans were made, the peak areas were measured directly with a polar planimeter, and the resulting intensity ratios were averaged and converted to a molar basis.

Infrared spectra were obtained from Nujol mulls between CsI plates using a Beckman IR-12 spectrophotometer. The absorption frequencies and relative intensities for  $(t\text{-BuC}_2\text{-}t\text{-Bu})_2\text{Fe}_2(\text{CO})_4$  were 1958 (vs), 1922 (vs), 1670 (vw), 1389 (m), 1363 (m), 1230 (w), 1208 (m), 1021 (w), 950 (m), 833 (m), 786 (w), 720 (w), 667 (m), 615 (s), 567 (m), 543 (m), 489 (w), and 438 (m)  $\text{cm}^{-1}$ .

### Results and Discussion

**Assignments.** Figure 3 shows a typical Raman spectrum of  $(t\text{-BuC}_2\text{-}t\text{-Bu})_2\text{Fe}_2(\text{CO})_4$ . An intense band is observed at  $284\text{ cm}^{-1}$ , and three weaker ones are observed at 531, 1925, and  $2001\text{ cm}^{-1}$ . The band at  $1925\text{ cm}^{-1}$  is depolarized, while the others are polarized. No other features could be found, despite the use of various solvents to obtain windows throughout the range  $150\text{-}2200\text{ cm}^{-1}$ . Since we are dealing with resonance Raman scattering (see below), it is not surprising that the vibrational spectrum is incomplete. Only those modes are enhanced which couple to the electronic transitions with which the scattered light is in resonance.

The  $2001\text{-}$  and  $1925\text{-cm}^{-1}$  bands are in the carbonyl stretching region and can be assigned with confidence to the expected  $\text{A}_g$  and  $\text{B}_{2g}$  modes, respectively, of the four carbonyl ligands, under the  $\text{D}_{2h}$  molecular point group. The infrared bands at 1958 and  $1922\text{ cm}^{-1}$  no doubt arise from the two antisymmetric ( $\text{B}_{1u}$  and  $\text{B}_{3u}$ ) modes. The assignment of the  $531\text{-cm}^{-1}$  mode is less definite, but normal-coordinate calculations (see below) suggest that it is a mixture of iron-acetylene stretching and Fe-C-O bending. The intense  $284\text{-cm}^{-1}$  band is almost certainly the Fe-Fe stretching mode of greatest interest here. No other fundamental vibration of  $(t\text{-BuC}_2\text{-}t\text{-Bu})_2\text{Fe}_2(\text{CO})_4$  is expected in the region of this frequency (except possibly deformation modes of the *tert*-butyl groups, which would be very weak). Stretching

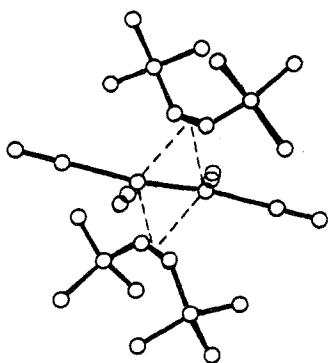


Figure 1. The structure of  $(t\text{-BuC}_2\text{-}t\text{-Bu})_2\text{Fe}_2(\text{CO})_4$  (from ref 2). The dotted lines connect the acetylenic bonds with the iron atoms.

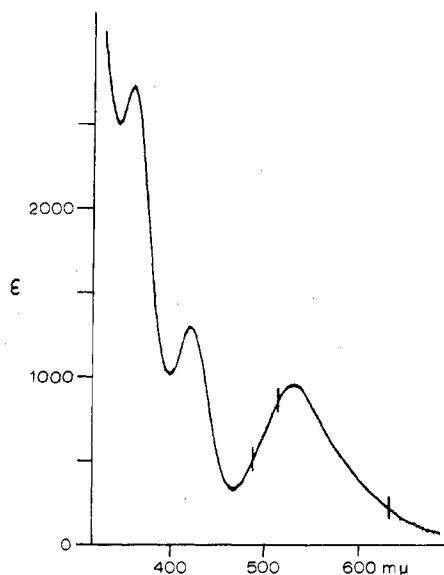


Figure 2. The visible spectrum of  $(t\text{-BuC}_2\text{-}t\text{-Bu})_2\text{Fe}_2(\text{CO})_4$  in benzene. ( $\epsilon$  is the molar extinction coefficient.) Below 300 nm the spectrum rises to a single peak ( $\epsilon = 2.8 \times 10^4$ ) at 247 nm. The vertical bars are drawn at the wavelengths used for Raman excitation: 4880, 5145, and 6328 Å.

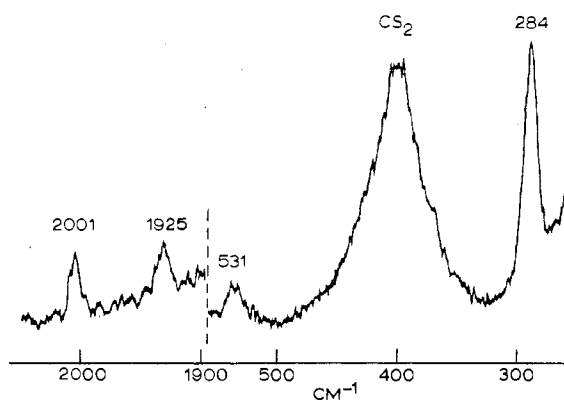


Figure 3. Raman spectrum of  $3 \times 10^{-3} M$   $(t\text{-BuC}_2\text{-}t\text{-Bu})_2\text{Fe}_2(\text{CO})_4$  in  $\text{CS}_2$  with 5145-Å  $\text{Ar}^+$  laser excitation ( $\sim 50$  mW). The band near 400  $\text{cm}^{-1}$  belongs to the solvent. Instrument conditions: slit width 10  $\text{cm}^{-1}$ , scan rate 50  $\text{cm}^{-1}/\text{min}$ , time constant 3 sec.

frequencies for Fe-Fe single bonds are expected around 200  $\text{cm}^{-1}$ . For example in  $\text{S}_2\text{Fe}_2(\text{CO})_6$ , with an Fe-Fe distance of 2.55 Å,<sup>11</sup>  $\nu_{\text{Fe-Fe}}$  has been identified<sup>7</sup> at 191  $\text{cm}^{-1}$ . The substantially higher frequency observed here is consistent with the shortening of the Fe-Fe distance.

Another mode of interest is the  $\text{C}\equiv\text{C}$  stretch of the

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bridging acetylene groups. In free acetylene  $\nu_{\text{C}\equiv\text{C}}$  is 1974  $\text{cm}^{-1}$ , while in disubstituted acetylenes the values range from 2190 to 2260  $\text{cm}^{-1}$ .<sup>12</sup> In all cases the  $\text{C}\equiv\text{C}$  distance is close to 1.20 Å. In  $(\text{C}_2\text{H}_2)\text{Co}_2(\text{CO})_6$ , in which a single acetylene molecule bridges a Co-Co bond,  $\nu_{\text{C}\equiv\text{C}}$  has been identified at 1403  $\text{cm}^{-1}$ ,<sup>13</sup> close to that of the  $\text{A}_u$  excited state of acetylene, for which the  $\text{C}\equiv\text{C}$  distance is 1.388 Å. In  $(t\text{-BuC}_2\text{-}t\text{-Bu})_2\text{Fe}_2(\text{CO})_4$ , the  $\text{C}\equiv\text{C}$  distance is 1.283 Å, halfway between those found in  $(t\text{-BuC}_2\text{-}t\text{-Bu})\text{Pt}(\text{py})\text{Cl}_2$ <sup>14</sup> (1.24 Å, py = pyridine) and  $(\text{PhC}_2\text{Ph})\text{Pt}(\text{Ph}_3\text{P})_2$ <sup>15</sup> (1.32 Å, Ph = phenyl). The  $\text{C}\equiv\text{C}$  stretching frequency for disubstituted acetylenes is  $\sim 2000$   $\text{cm}^{-1}$  in the former type of complex (Pt(II))<sup>16</sup> and  $\sim 1700$   $\text{cm}^{-1}$  in the latter type (Pt(0)).<sup>17</sup> Consequently we might expect  $\text{C}\equiv\text{C}$  stretching frequencies around 1800  $\text{cm}^{-1}$  for  $(t\text{-BuC}_2\text{-}t\text{-Bu})_2\text{Fe}_2(\text{CO})_4$ . There should be two such modes, in-phase ( $\text{A}_g$ , Raman active) and out-of-phase ( $\text{B}_{2g}$ , ir active). The latter mode, which might reasonably involve a low transition dipole moment, may correspond to a very weak band found at 1670  $\text{cm}^{-1}$  in the infrared spectrum. Unfortunately the in-phase mode appears not to be enhanced in our resonance Raman spectra; no trace of it could be found despite a careful search in several solvents.

Several infrared bands are observed below 1400  $\text{cm}^{-1}$  (see Experimental Section) but have not been assigned.

**Force Constants.** An approximate normal-coordinate analysis was carried out in order to estimate the stretching force constant for the iron-iron bond.<sup>18</sup> The usual *FG* matrix method was employed<sup>19</sup> with the aid of Schachtschneider's programs GMAT and FPERT.<sup>20</sup> Only the  $\text{A}_g$  block was calculated, since Fe-Fe stretching only contributes to this block. Molecular parameters were obtained from the reported crystal structure.<sup>2</sup> Inclusion of the *tert*-butyl groups would have made the computation prohibitively and needlessly complicated, so the six methyl groups were neglected. The resulting  $(\text{CC}\equiv\text{CC})_2\text{Fe}_2(\text{CO})_4$  model has nine  $\text{A}_g$  modes, with contributions from Fe-Fe, Fe- $\text{C}_A$  ( $\text{A} = \text{acetylene}$ ), Fe- $\text{C}_O$  ( $\text{O} = \text{carbonyl}$ ),  $\text{C}\equiv\text{O}$ ,  $\text{C}\equiv\text{C}$ , and  $\text{C}-\text{C}$  stretching and Fe- $\text{C}-\text{O}$ ,  $\text{O}-\text{C}-\text{Fe}-\text{C}_O$ , and  $\text{C}-\text{C}\equiv\text{C}$  bending. (Angle bending coordinates within the  $\text{Fe}_2\text{C}_4$  cluster are redundant with the bond stretching coordinates.) The  $\text{C}-\text{C}\equiv\text{C}$  bending mode was also neglected, since it couples little with the modes of interest. Valence force constants were used, and estimated as follows. Force constants for  $\text{C}\equiv\text{O}$  and Fe- $\text{C}_O$  stretchings,  $\text{O}-\text{C}-\text{Fe}-\text{C}_O$  and Fe- $\text{C}-\text{O}$  bendings, and the  $\text{C}\equiv\text{O}$ , Fe- $\text{C}_O$  stretch-stretch interaction were taken from Jones' analysis of  $\text{Fe}(\text{CO})_5$ .<sup>21</sup> For  $\text{C}\equiv\text{C}$  stretching, a force constant, 9.0  $\text{mdyn}/\text{Å}$ , somewhat higher than that used by Iwashita<sup>13</sup> (7.9  $\text{mdyn}/\text{Å}$ ) gave a frequency in the expected region. The value 5.0  $\text{mdyn}/\text{Å}$  for  $F_{\text{C}-\text{C}}$  is typical for C-C single bonds.<sup>12</sup>

With these force constants fixed,  $F_{\text{Fe-Fe}}$  was adjusted to calculate the 284- $\text{cm}^{-1}$  frequency. A value of 3.44  $\text{mdyn}/\text{Å}$

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Table I. Sample Normal-Coordinate Calculation for  $(t\text{-BuC}_2\text{-}t\text{-Bu})_2\text{Fe}_2(\text{CO})_4$  ( $A_g$  Block Only)

$A_g$ normal mode		Potential energy distribution <sup>a</sup>							
Calcd	Obsd	C≡O	C≡C	C-C	Fe-C <sub>A</sub> <sup>b</sup>	Fe-C-O	Fe-C <sub>O</sub> <sup>b</sup>	Fe-Fe	C-Fe-C
2001	2001	99							
1828			69	27	4				
898			31	55	14				
597				5	31	43	13	16	12
531	531			10	57	33	1	3	4
459				2	2	8	70	21	
284	284					2	17	67	1
98						14		4	82

Valence Force Constants, mdyn/Å		
Stretching	Stretch-stretch interaction	
C≡O	16.06 <sup>c</sup>	Fe-C <sub>O</sub> , C≡O
C≡C	9.00	Fe-C <sub>O</sub> , Fe-C <sub>A</sub>
C-C	5.00	Fe-Fe, Fe-C <sub>O</sub>
Fe-C <sub>A</sub>	2.20	Fe-Fe, Fe-C <sub>A</sub>
Fe-C <sub>O</sub>	2.40	
Fe-Fe	2.68 <sup>c</sup>	

<sup>a</sup> Per cent contribution to the potential energy from the force constants for the indicated coordinates. <sup>b</sup> C<sub>A</sub> = acetylene carbon; C<sub>O</sub> = carbonyl carbon. <sup>c</sup> These force constants were varied to fit the observed frequencies. The others were held fixed.

was required, and the potential energy distribution showed a substantial degree of mixing between the Fe-Fe and Fe-C<sub>O</sub> coordinates, the latter contributing 20% to the 284-cm<sup>-1</sup> mode. The mixing produces a considerable uncertainty in the Fe-Fe force constant estimate. Introduction into the calculation of a reasonable Fe-Fe, Fe-C<sub>O</sub> interaction force constant, 0.2 mdyn/Å, resulted in a 20% reduction of  $F_{\text{Fe-Fe}}$  to 2.76 mdyn/Å. Introduction of Fe-Fe, Fe-C<sub>A</sub> and Fe-C<sub>O</sub>, Fe-C<sub>A</sub> interaction force constants had little further effect on  $F_{\text{Fe-Fe}}$ . They did, however, increase the contribution of the Fe-C<sub>A</sub> coordinate to the 531-cm<sup>-1</sup> mode (*vide infra*). Table I contains the results of a calculation with what we judge to be the most reasonable set of force constants. In view of the paucity of data, they should be viewed as no more than illustrative.

These calculations indicate that the Fe-Fe force constant is  $3.0 \pm 0.4$  mdyn/Å. Despite this uncertainty, the estimate of  $F_{\text{Fe-Fe}}$  provides satisfying confirmation of the suggestion that  $(t\text{-BuC}_2\text{-}t\text{-Bu})_2\text{Fe}_2(\text{CO})_4$  contains a Fe=Fe double bond. For two molecules with Fe-Fe single bonds,  $\text{S}_2\text{Fe}_2(\text{CO})_6$ <sup>7</sup> and  $[\text{CpFeCO}]_4$ ,<sup>6</sup> approximate calculations have given force constant estimates of 1.3 mdyn/Å, about half the value found in this study. We note that the diatom approximation<sup>18</sup> applied to the 284-cm<sup>-1</sup> Fe-Fe stretching frequency gives an estimate of only 1.4 mdyn/Å for  $F_{\text{Fe-Fe}}$ . The error is much greater than usual for metal-metal bonds<sup>18</sup> and is another consequence of the extensive mixing with Fe-C<sub>O</sub> vibrations, due to the enhanced Fe-Fe bond strength.

#### Resonance Enhancement and the Electronic Spectrum.

Relative molar intensities and depolarization ratios are listed in Table II for the Raman bands in the spectrum excited with 5145-Å radiation. The intense Fe-Fe stretching band at 284 cm<sup>-1</sup> could also be measured with 4880- and 6328-Å excitation. These three laser frequencies span the lowest electronic absorption band, as shown in Figure 2. It is clear from the molar intensities that the 284-cm<sup>-1</sup> vibrational mode is in resonance with the first electronic transition, centered at 528 nm.

**Enhancement Factors.** The magnitude of the resonance enhancement can be gauged from estimates of bond polarizability derivatives. The measured Raman intensities can be converted to mean molecular polarizability derivatives  $\bar{\alpha}'_Q$  in the usual manner<sup>22</sup> (see Table II). The latter can be

(22) R. E. Hester in "Raman Spectroscopy," H. A. Szymanski, Ed., Plenum Press, New York, N. Y., 1967, Chapter 4.

Table II. Raman Intensities and Depolarization Ratios for  $(t\text{-BuC}_2\text{-}t\text{-Bu})_2\text{Fe}_2(\text{CO})_4$ 

$\nu$ , cm <sup>-1</sup>	$\lambda_0$ , Å	Solvent	$\rho_1$ <sup>b</sup>	$R_{\text{mol}}$ <sup>c</sup>	$\bar{\alpha}'_Q$ , Å <sup>2</sup>
284	4880	Benzene	0.35	54	1.70
	5145	Benzene	0.55	178	2.19
	6328	Benzene	0.13	12	0.99
531	5145	Benzene	0.35	40	
1925	4880	CCl <sub>4</sub>	0.70		
	5145	CCl <sub>4</sub>	0.84	29	
2001	5145	CS <sub>2</sub>	0.20	29	

<sup>a</sup> Exciting wavelength. <sup>b</sup> Depolarization ratio for linearly polarized light. <sup>c</sup> Molar intensity of the indicated  $(t\text{-BuC}_2\text{-}t\text{-Bu})_2\text{Fe}_2(\text{CO})_4$  band, relative to the  $\nu_1$  CCl<sub>4</sub> band.  $R_{\text{mol}} = I_2 M_1 / I_1 M_2$ ;  $I$  = intensity,  $M$  = molarity, 1 = CCl<sub>4</sub>, 2 =  $(t\text{-BuC}_2\text{-}t\text{-Bu})_2\text{Fe}_2(\text{CO})_4$ . <sup>d</sup>  $(\bar{\alpha}'_Q)^2 = R_{\text{mol}}[\nu_1/\nu_2]^4 (\Delta\nu_2/\Delta\nu_1) \{ [1 - \exp(-hc\Delta\nu_2/kT)] / [1 - \exp(-hc\Delta\nu_1/kT)] \} (1 + \rho_1)(3 - 4\rho_2)/(1 + \rho_2)(3 - 4\rho_1) (\bar{\alpha}'_{Q_1})^2$  (see ref 22).

expressed in terms of bond polarizability derivatives,  $\bar{\alpha}'_u$ , via the equation<sup>22</sup>

$$\bar{\alpha}'_{Q_i} = \sum_j \sqrt{N_j} l_{ij} \bar{\alpha}'_u$$

where  $N_j$  is the number of bond stretching coordinates,  $u$ , in the symmetry coordinate  $S_j$  and  $l_{ij}$  is the eigenvector element connecting  $S_j$  with the normal coordinate  $Q_i$ . For the 284-cm<sup>-1</sup> mode, the normal-coordinate analysis shows that the only significant contributors to the eigenvector are Fe-Fe and Fe-C<sub>O</sub> stretching. The elements are  $l_{\text{Fe-Fe}} = 0.1085$  and  $l_{\text{Fe-C}_O} = 0.0585$ . These values are not very sensitive to the choice of force constants in the analysis. For Fe-C<sub>O</sub>,  $N_j = 4$  and, if we assume that  $\bar{\alpha}'_{\text{Fe-C}_O} = 2.15 \text{ Å}^2$  which is the value of the Cr-C<sub>O</sub> bond polarizability derivative in  $\text{Cr}(\text{CO})_6$ ,<sup>23</sup> then the contribution of Fe-C<sub>O</sub> stretching to  $\bar{\alpha}'_Q$  is  $0.25 \text{ Å}^2$ . For  $\bar{\alpha}'_{\text{Fe-Fe}}$  we estimate a value of  $\sim 2.9 \text{ Å}^2$ . This estimate derives from  $\bar{\alpha}'_{\text{Mn-Mn}} = 3.70 \text{ Å}^2$  in  $\text{Mn}_2(\text{CO})_{10}$ <sup>24</sup> by application of the  $\delta$ -function potential equation,<sup>25</sup> which predicts that

$$\bar{\alpha}'_{\text{Fe-Fe}} = \bar{\alpha}'_{\text{Mn-Mn}} \left( \frac{\chi_{\text{Fe}}}{\chi_{\text{Mn}}} \right)^{1/2} \left( \frac{Z_{\text{Mn}}}{Z_{\text{Fe}}} \right) \left( \frac{(n/2)_{\text{Fe-Fe}}}{(n/2)_{\text{Mn-Mn}}} \right) \times \left( \frac{r_{\text{Fe-Fe}}}{r_{\text{Mn-Mn}}} \right)^3$$

(23) A. Terzis and T. G. Spiro, *Inorg. Chem.*, 10, 643 (1971).

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Here  $\chi$  is the Pauling electronegativity,  $Z$  is the effective nuclear charge (taken as the atomic number minus the number of inner-shell electrons),  $n/2$  is the bond order (1 for Mn-Mn and 2 for Fe-Fe), and  $r$  is the internuclear distance (2.92 Å for Mn-Mn<sup>26</sup> and 2.215 Å for Fe-Fe<sup>2</sup>). The contribution of the Fe-Fe coordinate to the 284-cm<sup>-1</sup> mode  $\bar{\alpha}'_Q$  is then  $2.9 \times 0.1088 = 0.31$ , whence  $\bar{\alpha}'_Q = 0.25 + 0.31 = 0.56$ . This estimate may be compared with the  $\bar{\alpha}'_Q$  values listed in Table II, which are obtained from the intensity measurements at the different exciting wavelengths.

We see that the resonance enhancement factor is rather modest: about 3.8 for 5145-Å excitation, which is near the center of the electronic absorption band, and about 1.8 for 6328-Å excitation. If the 284-cm<sup>-1</sup> Raman band were in resonance with *only* the 528-nm electronic transition, then we would expect an enhancement factor of 18.4 at 6328 Å, according to the theory developed by Albrecht and Hutley<sup>27</sup> for preresonance enhancement ( $F_A$  term frequency dependence<sup>28</sup>). If the 284-cm<sup>-1</sup> vibration couples the 528-nm transition to another of the visible or ultraviolet transitions ( $F_B$  term dependence<sup>28</sup>), then the expected enhancement factor at 6328 Å would be 5-9. On the other hand, if the band were in resonance only with the strong ultraviolet band at 247 nm ( $F_A$  term dependence), the expected enhancement factor would be 1.6 at 6328 Å and 2.0 at 5145 Å. We conclude therefore that resonance with the 528-nm transition does not dominate the Raman intensity of the 284-cm<sup>-1</sup> mode and that resonance with higher energy transitions is at least as important.

**Depolarization Ratios.** This line of reasoning is supported by the depolarization ratios, which show an unusual variation with the excitation frequency. Resonance with a single electronic transition enhances a single element of the Raman scattering tensor<sup>27</sup> (e.g.,  $\alpha'_{zz}$  for a z-polarized electronic transition), and if the element dominates the intensity, then the depolarization ratio,  $\rho_1$ , approaches 1/3 at resonance. The value of 0.55 observed with the near-resonance 5145-Å laser line is significantly larger than 1/3 and requires that more than one scattering tensor element contribute significantly.

The molecular symmetry of (*t*-BuC<sub>2</sub>-*t*-Bu)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>4</sub> is  $D_{2h}$ . In this point group totally symmetric vibrations ( $A_g$ ) have scattering tensors with diagonal elements only:  $\alpha'_{xx}$ ,  $\alpha'_{yy}$ , and  $\alpha'_{zz}$ . The depolarization ratio<sup>22</sup> can be shown to have the form

$$\rho_1 = \frac{1}{3} \frac{\alpha'_{xx}{}^2 + \alpha'_{yy}{}^2 + \alpha'_{zz}{}^2 - \alpha'_{xx}\alpha'_{yy} - \alpha'_{xx}\alpha'_{zz} - \alpha'_{yy}\alpha'_{zz}}{\alpha'_{xx}{}^2 + \alpha'_{yy}{}^2 + \alpha'_{zz}{}^2 + \frac{2}{3}\alpha'_{xx}\alpha'_{yy} + \frac{2}{3}\alpha'_{xx}\alpha'_{zz} + \frac{2}{3}\alpha'_{yy}\alpha'_{zz}}$$

(26) M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, **4**, 1140 (1965).

(27) A. C. Albrecht and M. C. Hutley, *J. Chem. Phys.*, **55**, 4438 (1971).

(28) According to Albrecht and Hutley,<sup>27</sup> the Raman intensity may be proportional to either  $F_A^2$  or  $F_B^2$  where  $F_A = \nu^2(\nu_e^2 + \nu_0^2)/(\nu_e^2 - \nu_0^2)^2$  and  $F_B = 2\nu^2(\nu_e\nu_s + \nu_0^2)/(\nu_e^2 - \nu_0^2)(\nu_s^2 - \nu_0^2)$ . Here  $\nu_0$  is the exciting frequency,  $\nu$  is the Raman-shifted frequency,  $\nu_0 - \Delta\nu$ , and  $\nu_e$  and  $\nu_s$  are resonant electronic transition frequencies. The A term describes the frequency dependence if the resonant vibrational mode is coupled to a single electronic transition, while the B term applies if a mode is enhanced by virtue of mixing two electronic transitions. Resonance enhancement can be described<sup>29</sup> by  $\bar{\alpha}'_Q = f(\bar{\alpha}'_Q)_0$  where  $(\bar{\alpha}'_Q)_0$  is the nonresonance ( $\nu_0 = 0$ ) classical limit and  $f$  is the enhancement factor. Substitution into the intensity equation<sup>22</sup> of  $F_A$  or  $F_B$  gives  $f = \nu_e^2 F_A/\nu^2 = \nu_e^2(\nu_e^2 + \nu_0^2)/(\nu_e^2 - \nu_0^2)^2$  or  $f = \nu_e\nu_s F_B/2\nu^2 = \nu_e\nu_s(\nu_e\nu_s + \nu_0^2)/(\nu_e^2 - \nu_0^2)(\nu_s^2 - \nu_0^2)$ .

(29) T. C. Streckas and T. G. Spiro, *J. Raman Spectrosc.*, in press.

If only one element is important  $\rho_1 \approx 1/3$ . Positive contributions from one or both of the other elements produce  $\rho_1 < 1/3$ , while negative contributions produce  $\rho_1 > 1/3$ . We require, therefore, that at 5145 Å, at least two elements be of comparable importance and that they be opposite in sign. It follows that at least two electronic transitions, of *different* polarization, are involved in resonance enhancement. Conceivably these two transitions could be in the same absorption band, but then we would expect  $\rho_1$  to vary slowly and monotonically through the absorption band. The fact that  $\rho_1$  instead reaches a maximum near the band center requires that the second and stronger resonant transition be at a higher frequency.

**Nature of the Electronic Transitions.** An understanding of resonance enhancement rests on a proper interpretation of the electronic spectrum. A thorough analysis of the electronic spectrum of a molecule as complicated as (*t*-BuC<sub>2</sub>-*t*-Bu)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>4</sub> is not presently feasible, but some useful inferences can plausibly be made. It can be anticipated that a metal-metal stretching mode will be strongly enhanced by resonance with a transition involving the metal-metal bonding and antibonding orbitals. The band at 528 nm is too low in energy and too weak ( $\epsilon 10^3$  l. mol<sup>-1</sup> cm<sup>-1</sup>) for such a transition. In Mn<sub>2</sub>(CO)<sub>10</sub> the  $\sigma$ - $\sigma^*$  metal-metal transition has been assigned to a strong band ( $\epsilon 2 \times 10^4$ ) at 340 nm.<sup>30</sup> The metal-metal bond in (*t*-BuC<sub>2</sub>-*t*-Bu)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>4</sub> is much shorter than in Mn<sub>2</sub>(CO)<sub>10</sub>, and the  $\sigma$ - $\sigma^*$  transition will be at correspondingly higher energy. The intense band ( $\epsilon 2.8 \times 10^4$ ) observed in the ultraviolet spectrum at 247 nm is a good candidate for this transition. Inasmuch as the molecule has a Fe=Fe double bond, there should also be a  $\pi$ - $\pi^*$  metal-metal transition, probably at somewhat lower energy. The band at 357 nm ( $\epsilon 2.7 \times 10^3$ ) is a plausible candidate for this transition. Contributions from Fe  $\rightarrow$  CO charge-transfer transitions are also likely for the ultraviolet bands. In Fe(CO)<sub>5</sub> these transitions are found at and above 244 nm.<sup>29</sup>

The likeliest candidates for the two visible absorption bands of (*t*-BuC<sub>2</sub>-*t*-Bu)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>4</sub> are Fe  $\rightarrow$  acetylene charge-transfer transitions. The acetylene ligands each have two  $\pi^*$ -antibonding orbitals which can accept metal electrons. In the molecular frame they are oriented parallel and perpendicular to the metal-metal bond. The parallel pair form one linear combination which can interact with a filled iron orbital ( $d_{xy}$  if the Fe-Fe axis is taken as  $z$ ) and one which cannot. The perpendicular pair do likewise. Consequently there are two empty molecular orbitals, based on the acetylene  $\pi^*$  orbitals, which do not interact with any filled iron orbitals, and are therefore available for low-energy charge-transfer transitions. Transition of these two orbitals from any of the available donor orbitals would be  $x$  or  $y$  polarized, while the Fe-Fe transitions, either  $\sigma$ - $\sigma^*$  or  $\pi$ - $\pi^*$ , would be  $z$  polarized.

Consequently, we suggest that the dominant element in the Raman scattering tensor for the 284-cm<sup>-1</sup> mode is  $\alpha'_{zz}$ , enhanced by preresonance with metal-metal electronic transitions which lie in the ultraviolet. Superimposed on this in the region of the 528-nm charge-transfer absorption band is resonance enhancement of either  $\alpha'_{xx}$  or  $\alpha'_{yy}$ . In view of the very different electronic processes involved it is not altogether surprising that the signs of the two tensor elements are different. At resonance with the 528-nm transition,  $\rho_1$  reaches a maximum value, near 0.55, and then decreases toward 1/3, the value characteristic of  $\alpha'_{zz}$  alone, as the excitation energy is increased. Resonance with an Fe  $\rightarrow$  acetylene charge-transfer

(30) R. A. Levenson, H. B. Gray, and G. P. Ceasar, *J. Amer. Chem. Soc.*, **92**, 3653 (1970).

transition would also account for the enhanced Raman intensity of the  $531\text{-cm}^{-1}$  mode, for which the major contribution is from Fe-C<sub>A</sub> stretching.

Relatively far below resonance, at  $6328\text{ \AA}$ , the depolarization ratio of the  $284\text{-cm}^{-1}$  mode is appreciably less than  $1/3$ . This means that one of the elements  $\alpha'_{xx}$  or  $\alpha'_{yy}$  must have the same sign as  $\alpha'_{zz}$  (see eq 1) and consequently, in view of

the above analyses, that  $\alpha'_{xx}$  and  $\alpha'_{yy}$  must differ in sign.

**Registry No.** (*t*-BuC<sub>2</sub>-*t*-Bu)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>4</sub>, 40269-58-7.

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## Iron(II), Cobalt(II), and Nickel(II) Complexes with the Open-Chain, Tetradentate Ligand Hexaphenyl-1,4,7,10-tetraphosphadecane. Singlet Ground-State Five-Coordinated Iron(II) Complexes

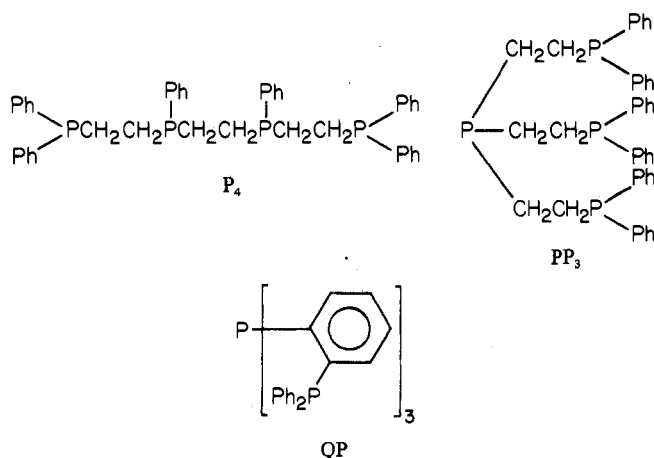
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Several five-coordinate metal(II) complexes with the open-chain tetradentate ligand hexaphenyl-1,4,7,10-tetraphosphadecane (P<sub>4</sub>) having the general formula [MLX]BPh<sub>4</sub> (M = Fe, Co, Ni; X = Cl, Br, I) were prepared and characterized. Spectral and X-ray information suggest a square-pyramidal geometry for all the complexes. The cobalt(II) and nickel(II) complexes are low spin. The magnetic properties of the iron(II) complexes are consistent with a spin equilibrium between a singlet ground state and a thermally accessible low-lying triplet state. For purposes of comparison we also prepared the [Fe(PP<sub>3</sub>)Br]BPh<sub>4</sub> complex, where PP<sub>3</sub> is the ligand tris(2-diphenylphosphinoethyl)phosphine. The thiocyanate complexes Fe(L)(NCS)<sub>2</sub> (L = P<sub>4</sub>, PP<sub>3</sub>) are diamagnetic and probably have a pseudooctahedral geometry.

### Introduction

Phosphorus is the most nucleophilic donor atom known and thus five-coordinate metal complexes containing it as donor atom have ground states of the lowest possible spin multiplicity.<sup>1</sup> Excluding the set P<sub>5</sub> the most nucleophilic sets are of the type P<sub>4</sub>X (X = halogen or pseudohalogen) which in general involve phosphorated tetradentate ligands. The ligands of this type which have been used to date are tris(*o*-diphenylphosphinophenyl)phosphine (QP),<sup>2</sup> tris(2-diphenylphosphinoethyl)phosphine (PP<sub>3</sub>),<sup>3</sup> both of which have a tripod structure, and the open-chain ligand hexaphenyl-1,4,7,10-tetraphosphadecane (P<sub>4</sub>) (I).<sup>3</sup> With bivalent 3d



metal ions these ligands give five-coordinate complexes

[M(P<sub>4</sub>X)]<sup>+</sup>; the cobalt(II) and nickel(II) complexes are all low-spin. So far iron(II) complexes have only been prepared with the first two ligands. They are found to have approximately trigonal-bipyramidal geometry and a triplet ground state. All other known five-coordinate complexes of iron(II) have less than four phosphorus atoms in the donor set and either have a quintuplet ground state<sup>4</sup> or are involved in a <sup>5</sup>E ⇌ <sup>3</sup>A equilibrium.<sup>5</sup> On the other hand on the basis of theoretical considerations it appears that, if it is possible for a five-coordinate iron(II) complex to exist in a singlet ground state, this will occur when the geometry is approximately square pyramidal (C<sub>4v</sub> symmetry or less) and when the donor atom set has a maximum overall nucleophilicity.

Since it seemed probable that with the open-chain ligand P<sub>4</sub> five-coordinate complexes having a square-pyramidal structure would be obtained, we decided to see if we could prepare five-coordinate iron(II) complexes with this ligand. We now report that, in spite of previous failures to prepare them, five-coordinate iron(II) complexes can be prepared with the ligand P<sub>4</sub>. They have the general formula [Fe(P<sub>4</sub>-X)]BPh<sub>4</sub> (X = halogen) and in some cases crystallize with CH<sub>2</sub>Cl<sub>2</sub> of crystallization. The analogous complexes of cobalt(II) and nickel(II) were also prepared.

All the complexes were characterized and their physical properties studied by the usual methods.

Previously only four-coordinated square-planar complexes of nickel(II) with ligand P<sub>4</sub> were reported.<sup>3</sup>

### Experimental Section

The ligands P<sub>4</sub> and PP<sub>3</sub> were obtained from the Pressure Chemical Co. All the solvents used were reagent grade. The iron(II) complexes were all prepared and stored under nitrogen.

**Preparation of the Complexes Fe(P<sub>4</sub>)X(BPh<sub>4</sub>), X = Cl, Br, I.** A solution of anhydrous FeX<sub>2</sub> (1 mmol) in absolute ethanol was added to a solution of the ligand (1 mmol) in methylene chloride (20 ml).

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(3) R. B. King, R. N. Kapoor, M. S. Saran, and P. N. Kapoor, *Inorg. Chem.*, **10**, 1851 (1971).