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## Fluxional Behavior of Some Dinuclear Iron and Cobalt Hexacarbonyl Compounds with Alkylsulfur and Dialkylphosphorus, -arsenic, -germanium, and -tin Bridges

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Received November 4, 1974

AIC40762H

A number of compounds of the general type  $(OC)_3M(\mu-ER_n)_2M(CO)_3$ , in which  $M = Fe$  while  $ER_n$  is  $PMe_2$ ,  $AsMePh$ ,  $AsMe_2$ ,  $SMe$ , or  $SEt$  and  $M = Co$  while  $ER_n = GeMe_2$  or  $SnMe_2$ , have been prepared and their dynamical properties studied by  $^{13}C$  and  $^1H$  NMR spectroscopy at temperatures from  $-130$  to  $+150^\circ$ . The RS-bridged compounds show no evidence of axial-equatorial R group exchange prior to the onset of irreversible thermolysis. All of the phosphino- and arsino-bridged iron compounds show R group exchange with coalescence temperatures in the range  $50$ – $100^\circ$ , while the germlyl- and silylyl-bridged cobalt compounds exhibit R group exchange with coalescence temperatures around  $-55^\circ$ . Interconversion of symmetrical and unsymmetrical isomers of the  $AsMePh$ -bridged iron compound requires a period of many hours at ca.  $150^\circ$  to attain equilibrium. Rapid exchange of nonequivalent carbonyl groups proceeds at very low temperatures in all cases, with coalescence temperatures around  $-70^\circ$ . Thus, there appear to be three essentially independent processes which are, in order of decreasing rate, (1) CO scrambling, (2) axial-equatorial R group exchange in a concerted fashion such that it occurs in both  $ER_2$  groups simultaneously, and (3) axial-equatorial R group exchange in such a way that isomers of an  $ERR'$ -bridged species are interconverted. The low activation energy for process 1 is not inconsistent with observations on many other  $M(CO)_3$ -containing molecules, and the very high activation energy for process 3 is consistent with the need for inversion of the configuration of pyramidal P or As ligands in a bridge-opened intermediate. The mechanism of process 2 remains debatable but it may proceed without bridge opening.

### Introduction

There have been three<sup>2,3</sup> earlier NMR studies of molecules of the type  $(OC)_3M(\mu-ER_2)_2M(CO)_3$ , with  $M = Fe$ ,  $ER_2 = P(CF_3)_2$  or  $P(CH_3)_2$ , and  $M = Co$  and  $ER_2 = Ge(CH_3)_2$ , in each of which stereochemical nonrigidity (fluxionality) was observed. These molecules have structures<sup>4</sup> with nonplanar central rings, which, as shown in Figure 1, results in the two R groups of each  $ER_2$  bridge being nonequivalent. Thus, in their NMR spectra signals for both axial and equatorial R groups should be observed unless there is a sufficiently rapid process which causes them to exchange their environments. In each case just such an exchange process was manifested in the fluorine or proton spectra.

For the  $P(CF_3)_2$ -bridged iron compound<sup>2</sup> the  $^{19}F$  spectra were unsuitable for detailed interpretation due to extensive spin-spin coupling; the coalescence temperature is apparently in the range of  $60$ – $90^\circ$ . For the iron compound with  $P(CH_3)_2$  bridges,<sup>3b</sup> the proton spectra were also complex and the kinetic analysis of the line shape changes was done in too simple an approximation, thus giving incorrect activation parameters; the coalescence temperature was in the neighborhood of  $+70^\circ$ . For the cobalt compound the  $^1H$  spectra from  $-90$  to  $+27^\circ$  showed smooth collapse and coalescence of two methyl signals to one, with a coalescence temperature of ca.  $-55^\circ$ . The simplicity of the spectra here easily allows rigorous kinetic analysis of the line shapes.

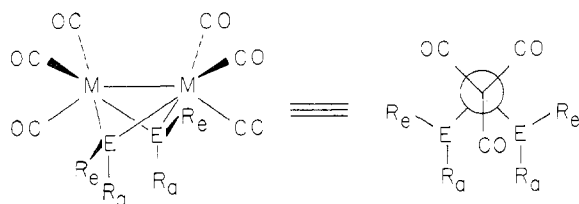
In the report<sup>3a</sup> on  $Co_2(CO)_6(\mu-GeMe_2)_2$  possible mechanisms were briefly considered. There are two broad classes: (1) those in which the bridges remain intact and the site exchange of the R groups occurs by deformations of the coordination geometry about one or both metal atoms; (2) those in which one or both of the  $ER_2$  bridges open up and are then restored in such a way that site exchange occurs. A preference was expressed by Adams and Cotton for a mechanism of type 1 for two reasons.<sup>8</sup> First, neglecting the M–M bond, the metal atoms are five-coordinate and polytopal rearrangements of five-coordinate complexes are well known to be facile. Second, a bridge-opening process leads to an intermediate or transition state containing terminal  $Me_2Ge$  groups for which there was no precedent in stable compounds. If E is Ge or another group 4 element, such a species would be a carbene-like entity, and thus far, complexes which might have been thought to contain them<sup>10</sup> have instead been shown to be stable only when a strong

base, such as pyridine, is coordinated to the Ge or Sn atom, as in  $py \rightarrow Sn(t-Bu)_2Cr(CO)_5$ .<sup>11</sup> If E is a group 5 element, the opening of the bridges would leave each metal atom with only 16 electrons unless a double bond, e.g.,  $R_2P \equiv Fe$ , is postulated in each terminal  $R_2PFe$  group. While there is, perhaps, nothing unreasonable about this, it is without precedent or close analogy and to that extent unlikely.

While no conclusive evidence has yet been reported<sup>8</sup> to determine which general type of mechanism operates in the  $(OC)_3M(\mu-ER_2)_2M(CO)_3$  molecules, there are two subsequent observations which favor the retention of bridges. It has been found<sup>12</sup> that in  $(\eta^5-C_5H_5)Fe(CO)(\mu-CO)(\mu-GeMe_2)Fe(CO)(\eta^5-C_5H_5)$  interconversion of cis and trans isomers attains a rate great enough to cause coalescence of the  $\eta^5-C_5H_5$  and  $CH_3$  NMR signals only at a temperature of ca.  $100^\circ$ . Isomer interconversion in this system can occur only by bridge opening. In the prototype molecule,  $(\eta^5-C_5H_5)_2Fe_2(CO)_4$ , on the other hand, opening and reclosing of bridges are already rapid at  $-80^\circ$ .<sup>13,14</sup> It thus seems clear that while opening and closing of pairs of CO bridges are facile processes, the opening of even one  $Me_2Ge$  bridge is a much less favorable process. It does not seem likely that two such bridges would be opening and closing rapidly at  $-50^\circ$  in  $Co_2(CO)_6(\mu-Me_2Ge)_2$  when a temperature of ca.  $100^\circ$  is required in  $(\eta^5-C_5H_5)_2Fe_2(CO)_3(\mu-Me_2Ge)$  for even one to open.

The spectra of  $Fe_2(CO)_6(\mu-Me_2P)_2$  published by Dessy et al.<sup>3b</sup> show that essentially identical degrees of virtual coupling of the two P atoms (which causes the proton signals to appear as symmetrical triplets) is observed in both the low- and high-temperature limiting spectra. If bridge opening were occurring, it seems likely (though, admittedly, not certain) that a smaller  $J_{PP}$  would characterize the high-temperature spectrum, whereas the insensitivity of  $J_{PP}$  to temperature is to be expected for a mechanism in which the bridge system remains intact.

As the foregoing summary shows, the fluxional behavior of  $(OC)_3M(\mu-R_2E)_2M(CO)_3$  molecules has so far been studied only in a fragmentary way and, despite some suggestive but indirect evidence, the mechanisms involved remain debatable. In order to gain a better understanding of these systems, we have carried out further studies involving (1) additional molecules such as  $Me_2As$ -bridged iron compounds where spectra more amenable to kinetic analysis can be had and



**Figure 1.** Diagrams showing the structures of the  $(OC)_3M(\mu-ER_2)_2M(CO)_3$  molecules and defining the axial ( $R_a$ ) and equatorial ( $R_e$ ) alkyl or aryl groups.

MePhAs-bridged species where the interconversion of geometrical isomers can be studied and (2) the use of carbon-13 NMR so that the behavior of the carbonyl groups can be observed.

### Experimental Section

Volatile reactants were handled in a standard vacuum line. Preparations were carried out and products routinely maintained in a nitrogen atmosphere. However, it may be noted that all of the iron compounds are air stable, even in solution, except at high temperatures. Solvents were thoroughly degassed and in some cases dried over sodium-benzophenone and distilled immediately prior to use. Cobalt carbonyl was purchased from Strem Chemical Co., iron pentacarbonyl from Alfa Inorganics, Inc.,  $Fe_2(CO)_6(SMe)_2$  from Pressure Chemical Co., and benzenearsonic acid from Eastman Organic Chemicals; all were used as received.

Dimethylgermane was prepared by a slight modification of the method of Griffiths.<sup>15</sup> A less elaborate trapping assembly was used and purification was achieved by low-pressure distillations at  $-20^\circ$  and collection of the product in traps at liquid nitrogen temperature. Dimethylstannane was prepared similarly. Methylphenylarsinic acid was prepared from benzenearsonic acid by the method of Cragoe et al.<sup>16</sup> and was reduced to 1,2-dimethyl-1,2-diphenyldiarsine as described by Resor and Wright.<sup>17</sup> Tetramethyldiarsine was prepared either by the method of Auger<sup>18</sup> or from dimethyliodoarsine<sup>19</sup> by treatment with lithium.<sup>20</sup>

Tetramethyldiphosphine was obtained by heating tetramethyldiphosphine disulfide,<sup>21,22</sup> which was purchased from Orgmet, Inc., with tributylphosphine.<sup>21</sup>  $Fe_2(CO)_6(\mu-AsMe_2)_2$  was at first prepared according to the procedure of Hayter,<sup>23</sup> but the procedure described below was found to be superior.

A literature method<sup>24</sup> was used to prepare  $Fe_2(CO)_6(SEt)_2$ .

**Preparation of  $Co_2(CO)_6[\mu-(CH_3)_2Ge]_2$ .** Dicobalt octacarbonyl (1.46 g, 4.3 mmol) was dissolved in 55 ml of toluene in a 200-ml three-necked flask equipped with a nitrogen inlet, pressure-equalizing dropping funnel, and magnetic stirrer. Excess  $(CH_3)_2GeH_2$  was dissolved in 10 ml of toluene and placed in the dropping funnel. This was slowly added to the  $Co_2(CO)_8$  solution at room temperature. Gas evolution began promptly and ceased within 15 min, while the color of the solution changed from brown to yellow. After 3 hr of stirring the solution was concentrated to approximately 5 ml, chromatographed over alumina (8%  $H_2O$ ), and eluted with hexane or benzene-hexane mixtures. The solvent was removed under vacuum and the residue recrystallized from pentane-toluene (5:1, v/v) at  $-78^\circ$ , giving 0.75 g (35%) of light yellow crystals, mp  $155.5-157.5^\circ$  (uncor).

Anal. Calcd for  $C_{10}H_{12}Co_2Ge_2O_6$ : C, 24.45; H, 2.44; Co, 24.0. Found: C, 24.8; H, 2.51; Co, 23.5.

The mass spectrum showed a parent ion peak at  $m/e$  490 and a series of peaks corresponding to loss of one to six CO groups. Peaks due to the ions  $(CH_3)_nGe_2Co_2^+$  ( $n = 4-0$ ) were especially prominent. The ir spectrum in the CO stretching region is reported in Table I.

**Preparation of  $Co_2(CO)_6[\mu-(CH_3)_2Sn]_2$ .** The procedure was similar to that just described for the dimethylgermylyl-bridged compound. Dicobalt octacarbonyl (0.27 g, 0.77 mmol) was dissolved in 100 ml of hexane, and  $(CH_3)_2SnH_2$  (0.34 ml, 3.4 mmol) dissolved in 10 ml of hexane was added through the dropping funnel at room temperature. After 0.5 hr the orange solution was concentrated under vacuum to about 20 ml and chromatographed on an alumina (8%  $H_2O$ ) column. The bright yellow product was eluted with hexane and recrystallized in the same manner as the germylyl analog. The yield was 0.05 g (11%); mp  $110^\circ$  dec.

Anal. Calcd for  $C_{10}H_{12}Co_2Sn_2O_6$ : C, 20.59; H, 2.07. Found: C, 19.8; H, 2.60.

The mass spectrum had a parent ion peak at  $m/e$  583 and ion peaks

**Table I.** Infrared Spectra (CO Stretching Bands,  $cm^{-1}$ ) of the Cobalt Compounds<sup>a</sup>

$Co_2(CO)_6(GeMe_2)_2$		$Co_2(CO)_6(SnMe_2)_2$	
2072 s	1984 m	2063 s	1980 s
2035 vs	1964 vw <sup>b</sup>	2025 vs	1974 m
2014 vs	1947 vw <sup>b</sup>	2005 vs	
1994 vs			

<sup>a</sup> Cyclohexane solutions. <sup>b</sup> Presumably  $^{13}C$  satellites.

corresponding to the loss of one to six CO groups. The ions  $(CH_3)_nSn_2Co_2^+$  ( $n = 4-0$ ) were also prominent. The infrared spectrum is reported in Table I.

**Preparation of  $Fe_2(CO)_6[As(CH_3)_2]_2$ .** Tetramethyldiarsine and an excess of iron pentacarbonyl in benzene were heated to  $150^\circ$  for 19 hr. A Carius tube can be used, but a metal bomb (Hoke or Nupro type) is safer. Chromatography on Florisil (100-200 mesh) using benzene as the eluting solvent followed by recrystallization from a benzene-heptane mixture at  $-20^\circ$ , or from hexane at  $-78^\circ$ , gave dark red-orange crystals of the product. The  $^1H$  NMR and ir spectra as well as the melting point were identical with those previously reported<sup>23</sup> for  $Fe_2(CO)_6[As(CH_3)_2]_2$ .

**Preparation of  $Fe_2(CO)_6[P(CH_3)_2]_2$ .** Tetramethyldiphosphine and an excess of iron pentacarbonyl in benzene were heated to  $140^\circ$  for 24 hr in either a metal bomb or an evacuated Carius tube. Chromatography on Florisil using petroleum ether (bp  $30-60^\circ$ ) and recrystallization from a mixture of dichloromethane and hexane afforded orange crystals of the product which was identified<sup>23</sup> by its  $^1H$  NMR and ir spectra and its melting point.

**Preparation of  $Fe_2(CO)_6[As(CH_3)(C_6H_5)]_2$ .** 1,2-Dimethyl-1,2-diphenyldiarsine (1-2 g, 3-6 mmol) and an excess of iron pentacarbonyl (2-4 g, 10-20 mmol) were heated for 2-3 days at  $150-160^\circ$  in a metal bomb or a evacuated Carius tube. From the resulting dark brown reaction mixture the benzene and excess iron pentacarbonyl were removed under reduced pressure. The solid, orange residue was dissolved in petroleum ether or hexane and chromatographed on a Florisil column. The hydrocarbon solvents eluted a light orange band; addition of ether (5%) to the hydrocarbon solvent then eluted a deeper orange band. Each fraction was evaporated to dryness and the solid residue was recrystallized by chilling petroleum ether or hexane solutions. From the first band, orange crystals of the anti isomer (0.1-0.2 g, 5%) were obtained and from the second band orange crystals of the syn isomer (0.5-1.2 g, 33%) were obtained. Both products were identified by comparison of their spectra with those previously reported.<sup>25</sup>

**Carbon-13 Enrichments.** Enrichment, to 20-40%, with  $^{13}CO$  was achieved by stirring the compound in hexane under a  $^{13}CO$  atmosphere while simultaneously irradiating. As an example,  $Fe_2(CO)_6(AsMe_2)_2$  (200 mg) in 150 ml of hexane with 150 ml of  $^{13}CO$  (90%) in a Pyrex flask was irradiated for 20 hr with a Hanovia 140-W low-pressure lamp, to give approximately 10% enrichment. The CO was vented, and the flask was cooled to  $-196^\circ$  and refilled with 90%  $^{13}CO$ . After another 20 hr of stirring and irradiation the extent of enrichment was about 21% by ir.

**Recording of NMR Spectra.** Instruments used at the University of British Columbia were Varian T-60, HA-100, XL-100, and CFT-20 spectrometers. Temperature variations were studied with the HA-100 and XL-100 instruments using a Varian V-4343 variable-temperature unit calibrated against an ethylene glycol standard. At Texas A&M University a Varian HA-100 spectrometer equipped with the V-4343 variable-temperature unit and calibrated against both methanol and ethylene glycol was used for proton spectra. The  $^{13}C$  spectra were recorded on a JEOL PFT 100/Nicolet 1080 Fourier transform spectrometer operating at 25.035 MHz. To each sample used for  $^{13}C$  spectra approximately 0.5 mg of tris(acetylacetonato)chromium(III) was added to decrease  $T_1$ . Such a small amount was used to avoid undesirable broadening of the lines at low temperatures, which we have observed in other cases.<sup>33</sup>

### Results

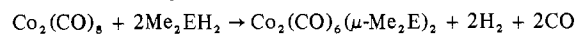
**The  $Co_2(CO)_6(EMe_2)_2$  Compounds.** Two new compounds are reported:  $Co_2(CO)_6(\mu-Me_2E)_2$  with  $E = Ge$  and  $Sn$ . They are obtained by reactions of the hydrides  $(CH_3)_2EH_2$  with  $Co_2(CO)_8$ . The reactions cause gas evolution. We have not attempted to identify these gases, but on the assumption that

Table II. Kinetic Results for Methyl Proton Site Exchange in the  $M_2(CO)_6(EMe_2)_2$  and  $Fe_2(CO)_6(AsMePh)_2$  Compounds<sup>a</sup>

M	ER <sub>2</sub>	T <sub>c</sub> , °K	log A	E <sub>a</sub> , kcal mol <sup>-1</sup>	ΔG <sub>298</sub> <sup>‡</sup> , kcal mol <sup>-1</sup>	ΔH <sup>‡</sup> , kcal mol <sup>-1</sup>	ΔS <sup>‡</sup> , cal mol <sup>-1</sup> deg <sup>-1</sup>	Solvent
Co	GeMe <sub>2</sub>	228 (3)	13.9 (5)	12.9 (5)	11.4 (5)	12.4 (5)	3.5 (12)	CF <sub>2</sub> Cl-CH <sub>2</sub> Cl <sub>2</sub> , 2:1, v/v
Co	SnMe <sub>2</sub>	228 (3)	13.2 (5)	12.5 (5)	12.0 (5)	12.0 (5)	0.0 (13)	CF <sub>2</sub> Cl-CH <sub>2</sub> Cl <sub>2</sub> , 1:1, v/v
Fe <sup>b</sup>	AsMe <sub>2</sub>	347 (2)	12.4 (6)	16.7 (6)	17.2 (6)	16.1 (6)	-3.7 (15)	C <sub>6</sub> H <sub>6</sub>
Fe <sup>c</sup>	AsMe <sub>2</sub>	344 (3)	11.7 (5)	15.5 (5)	17.0 (5)	14.8 (5)	-7.6 (10)	PhCOOMe
Fe	PMe <sub>2</sub>	347 (3)	11.8 (6)	15.7 (6)	17.0 (6)	15.0 (6)	-6.6 (12)	C <sub>6</sub> H <sub>6</sub>
Fe <sup>d</sup>	AsMePh	373 (4)	12.4 (9)	18.0 (9)	18.5 (9)	17.4 (9)	-3.8 (15)	C <sub>6</sub> H <sub>6</sub>

<sup>a</sup> Numbers in parentheses are estimated errors occurring in the least significant digit recorded. <sup>b</sup> Results from the University of British Columbia. <sup>c</sup> Results from Texas A&M University. <sup>d</sup> Unsymmetrical isomer.

they are mixtures of H<sub>2</sub> and CO the preparative reactions could be described by



The expected sawhorse arrangement of six CO ligands with overall molecular symmetry of C<sub>2v</sub> means that there should be five infrared-active CO stretching modes and the results (Table I) are in good accord with this.

Proton NMR spectra of Co<sub>2</sub>(CO)<sub>6</sub>(GeMe<sub>2</sub>)<sub>2</sub> at various temperatures from -90 to +30° have already been published.<sup>3a</sup> The pattern of line shape changes over this temperature range has been analyzed by fitting computed spectra for various rates to the observed spectra at various temperatures. The results in terms of both the Arrhenius and the Eyring equations are given in Table II. The previously mentioned<sup>3a</sup> approximate E<sub>a</sub> value (15 ± 1 kcal mol<sup>-1</sup>) is superseded by the value given here.

The behavior of the proton NMR spectrum of Co<sub>2</sub>(CO)<sub>6</sub>(SnMe<sub>2</sub>)<sub>2</sub> is almost identical with that of its germanium analog. The single line in the fast-exchange limit is at 1.01 ppm (rather than 1.20 ppm for the Ge compound) downfield from TMS and shows small satellite resonances with  $J(^{117}Sn-H) \approx J(^{119}Sn-H) = 42.5$  Hz. The activation parameters for this compound are also given in Table II.

**The Fe<sub>2</sub>(CO)<sub>6</sub>(EMe<sub>2</sub>)<sub>2</sub> Compounds and Fe<sub>2</sub>(CO)<sub>6</sub>(AsMePh)<sub>2</sub>.** These are all known compounds which were identified by comparison with literature data. For the PMe<sub>2</sub>- and AsMe<sub>2</sub>-bridged compounds, the proton spectra are very similar to those for the cobalt compounds, except that the processes of collapse occur at considerably higher temperatures. Again, the line shapes have been used to evaluate the Arrhenius and Eyring parameters of activation, with the results given in Table II. In the study done on Fe<sub>2</sub>(CO)<sub>6</sub>(AsMe<sub>2</sub>)<sub>2</sub> at Texas A&M University calculated line shapes for various rate constants were fitted to observed spectra, while at the University of British Columbia the procedure of Gutowsky and Holm<sup>26</sup> for exchange between two equally populated sites was employed. The two sets of results agree quite well. The PMe<sub>2</sub>-bridged compound had more complex spectra because of coupling to the phosphorus nuclei. Phosphorus-decoupled spectra were therefore recorded for the purpose of rate measurements and the activation parameters evaluated by the Gutowsky-Holm procedure.

In the case of the AsMePh-bridged compound, the proton NMR spectra in the methyl region at various temperatures are shown in Figure 2 for the unsymmetrical isomer. Evidently, this is the only isomer present in the freshly prepared solution which has not been heated (see below). The separate resonances for the axial and equatorial methyl groups are seen at room temperature. When the solution is heated, broadening becomes evident at about 50°, and as the temperature increases further, the two peaks collapse and merge into a singlet, which is still broad at 122°. The coalescence temperature is about 100°, i.e., some 26° higher than for the EMe<sub>2</sub>-bridged compounds. A line shape analysis gives the results shown in Table II. It appears that it is mainly a greater enthalpy of activation which is responsible for the higher coalescence temperature.

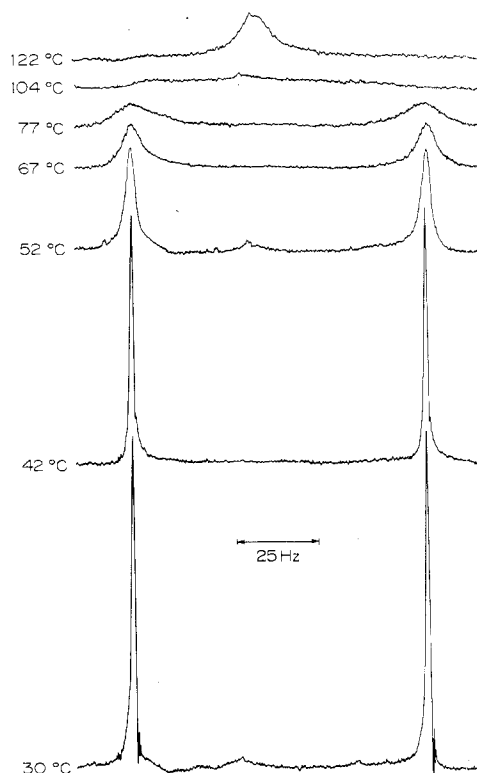


Figure 2. The <sup>1</sup>H NMR spectra of the methyl groups of the unsymmetrical isomer of Fe<sub>2</sub>(CO)<sub>6</sub>(AsMePh)<sub>2</sub> at various temperatures.

A solution of the symmetrical isomer, which has the two methyl groups in equatorial positions in the crystal (by analogy with the unpublished results of J. R. Huntsman and L. F. Dahl on the phosphorus analog), is independent of temperature at all temperatures below 100°. This presumably means that the stability of the other symmetrical isomer, in which both methyl groups are axial, is so low that no observable quantity is present in this temperature range.

The behavior of the AsMePh-bridged molecules at higher temperatures was studied. When a benzene solution of the unsymmetrical form is heated to 150° for 15 hr, an equilibrium mixture of this and the symmetrical isomer with equatorial methyl groups, in a molar ratio of 1:6, is established. The same equilibrium is established starting with the symmetric isomer after 90 hr at 150°.

Finally, we turn to the <sup>13</sup>C spectra of the Fe<sub>2</sub>(CO)<sub>6</sub>(EMe<sub>2</sub>)<sub>2</sub> compounds. In the AsMe<sub>2</sub>-bridged compound the room temperature <sup>13</sup>C spectrum in the carbonyl region consists of a single sharp line at 212.9 ppm (downfield from TMS), while that of the PMe<sub>2</sub>-bridged compound is a triplet ( $J_{P-C} \approx 6.0$  Hz) at 212.7 ppm. For the arsenic compound the signal remains narrow (ca. 2.8 Hz at half-height) until at about -45° broadening can first be observed. The signal continues to broaden and finally separates into two signals in an intensity ratio of 1:2, at 213.9 and 211.3 ppm, which are well separated at -90° and narrow to ca. 2.8 Hz at half-height by about

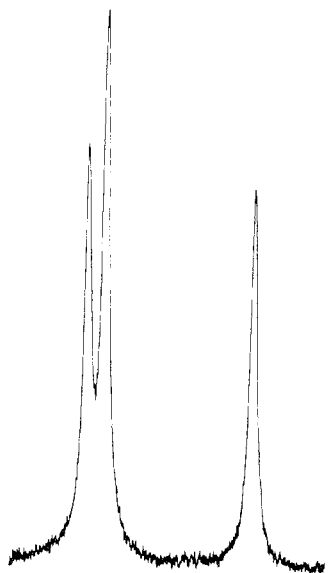


Figure 3. The  $^1\text{H}$  NMR spectrum of  $\text{Fe}_2(\text{CO})_6(\text{SCH}_3)_2$  at  $30^\circ$ : solvent,  $\text{C}_6\text{D}_6\text{Br}$ ; lock signal,  $\text{CCl}_2\text{HCCl}_2\text{H}$ .

$-105^\circ$ . The coalescence temperature is  $-79 \pm 4^\circ$ . By computer fitting, the following kinetic activation parameters have been evaluated:  $\log A = 12.9$  (5),  $E_a = 9.9$  (4)  $\text{kcal mol}^{-1}$ ,  $\Delta H^\ddagger = 9.4$  (4)  $\text{kcal mol}^{-1}$ ,  $\Delta S^\ddagger = -0.5$  (20)  $\text{cal mol}^{-1} \text{deg}^{-1}$ ,  $\Delta G_{298}^\ddagger = 9.7$  (7)  $\text{kcal mol}^{-1}$ .

For the  $\text{PMe}_2$ -bridged compound the observations are more complex because of the similar values of  $J_{\text{P-C}}$  and the chemical shift difference. From the spectrum at  $-100^\circ$  we estimate  $J_{\text{P-C}} = 10.0$  and  $2.8$  Hz (for an average of  $6.4$  Hz, in fair agreement with the value  $6.0$  Hz in the fast-exchange limit) and the chemical shift difference is ca.  $5.8$  Hz. No attempt has been made to analyze these spectra to obtain activation parameters. It is evident that the rate of site exchange of the CO groups in this compound is very nearly the same as in the  $\text{AsMe}_2$  homolog.

The  $^{13}\text{C}$  spectra were measured on solutions in  $\text{CH}_2\text{Cl}_2$  or  $\text{CH}_2\text{Cl}_2\text{-CHClF}_2$  with  $\text{CD}_2\text{Cl}_2$  (10%) as an internal deuterium lock and  $\text{CS}_2$  (15%) as an internal reference.

**$\text{Fe}_2(\text{CO})_6(\text{SR})_2$  Compounds.** For  $\text{Fe}_2(\text{CO})_6(\text{SMe})_2$ , we were unable to observe any exchange of methyl groups between the axial and equatorial sites. The spectrum at room temperature, Figure 3, indicates that both the unsymmetrical isomer and one of the symmetrical isomers (we cannot tell which one) are present in a molar ratio of about 3:2 and that no exchange processes are occurring. The possibility that the *axax* and *eqeq* forms of the symmetrical isomer might be rapidly interconverting so as to give only a single line for both symmetrical isomers seems unlikely since the resulting single line would be expected to occur roughly halfway between the two lines for the unsymmetrical isomer rather than close to one of them. Moreover, it is not reasonable to expect that the rearrangement process requisite to averaging the *axax* and *eqeq* isomers could be extremely rapid while, at the same temperature (ca.  $30^\circ$ ), the comparable process within the unsymmetrical (*axeq*) isomer would be extremely slow. It is important to note that all three lines in Figure 3 have the same width.

As the temperature was raised, broadening of all three lines became noticeable at about  $80^\circ$ . However, this broadening was irreversible and is due to decomposition. Thus, we have been unable to observe the site-exchange process for the methyl groups of  $\text{Fe}_2(\text{CO})_6(\text{SMe})_2$ .

Because of the poor solubility of the  $\text{SMe}$ -bridged compound we did not attempt to use it for low-temperature studies of carbonyl scrambling. Instead, the  $\text{SEt}$ -bridged analog was prepared and examined. It shows a single  $^{13}\text{C}$  line at  $209.2$

ppm at  $25^\circ$ . This begins to broaden at about  $-20^\circ$  and reaches maximum width at  $-66 \pm 3^\circ$ . By  $-80^\circ$  three resonances of equal intensities are observed and these become sharp below  $-90^\circ$ . They occur at  $210.8$ ,  $209.1$ , and  $208.0$  ppm. The observation of three equally intense lines is consistent with the presence of only the unsymmetrical (*axeq*) isomer, the same one that was observed in the crystalline compound by X-ray diffraction.<sup>5</sup> These  $^{13}\text{C}$  spectra were measured on a solution in 2-methyltetrahydrofuran with  $\text{CD}_2\text{Cl}_2$  (10%) as an internal deuterium lock and  $\text{CS}_2$  (15%) as an internal reference.

### Discussion

In all four of the  $\text{M}_2(\text{CO})_6(\text{EMe}_2)_2$  compounds, the two structurally distinct types of methyl group, axial and equatorial (cf. Figure 1), undergo site exchange. At lower temperatures, separate resonances are observed for the two types and at higher temperatures only a single sharp resonance is seen. For the cobalt compounds this process has a lower activation energy than for the iron compounds, as indicated in Table II. There are two entries for  $\text{Fe}_2(\text{CO})_6(\text{AsMe}_2)_2$ , based on wholly independent experimental data and analysis thereof in the two laboratories. The comparison is of interest in giving a realistic idea of the actual uncertainties in such measurements and kinetic analyses. The differences between pairs of corresponding parameters are between 0.6 and 1.6 times the sums of the estimated errors. This suggests that in an individual case of this sort, where carefully made measurements are analyzed by nonapproximate methods and the results fitted by a least-squares procedure, the true uncertainties may be somewhat larger, but not by more than a factor of 2, than the calculated esd's.

The difference in activation enthalpies of ca.  $3.0$   $\text{kcal mol}^{-1}$  between the mean for the two cobalt compounds ( $12.2$   $\text{kcal mol}^{-1}$ ) and the mean of the three measurements on the iron compounds ( $15.3$   $\text{kcal mol}^{-1}$ ) is not large, but, coupled with a difference in  $\Delta S^\ddagger$  values which works in the same direction, it leads to a very striking difference in the coalescence temperatures, of roughly  $100^\circ$ . Thus, the difference in the raw experimental observations is more striking than the differences between the numbers derived from them by analysis.

It is not evident whether any, or if so what, difference in mechanism is implied by the differences in activation parameters, especially the  $\Delta S^\ddagger$  values which are ca.  $+2$  and  $-6$   $\text{cal mol}^{-1} \text{deg}^{-1}$  for the Co and Fe compounds, respectively. Since the difference of ca.  $8$  eu has a normal uncertainty of ca.  $3$  eu, it is unlikely, in our view, that it bespeaks any qualitative difference in mechanism.

For the unsymmetrical isomer of  $\text{Fe}_2(\text{CO})_6(\text{AsMePh})_2$  site exchange of axial and equatorial methyl groups also occurs, with activation parameters only slightly different from those in the  $\text{AsMe}_2$ -bridged compound. For the  $\text{SMe}$ -bridged compound, no axial-equatorial site exchange was observed up to about  $80^\circ$  where decomposition became rapid enough to terminate the experiment.

### Conclusions

(1) The first conclusion which emerges from this study is that the site exchange of axial and equatorial substituents on the bridging groups in molecules of this type is a fairly general process but is subject to considerable variation in the ease with which it occurs. In the  $\text{SMe}$ -bridged compound the combination of a high activation energy and low thermal stability prevents its becoming observable on the NMR time scale.

(2) No information can be obtained concerning the manner in which CO groups may be obliged to undergo site exchange while the R group site exchange occurs. As pointed out earlier,<sup>3a</sup> such information could (depending on what the relationship might be) provide some help in selecting a mechanism for the R group site exchange process. However,

we have found that CO scrambling by itself becomes rapid even at temperatures where R group site exchange is still too slow to detect. Thus, when the temperatures required for detectable effects of R group site exchange on the NMR spectra are reached, independent CO scrambling is so rapid that any additional contribution introduced as an integral part of the R group site exchange process is unobservable.

(3) The final point to consider is the fact that interconversion of the symmetrical and unsymmetrical isomers of  $\text{Fe}_2(\text{CO})_6(\text{AsMePh})_2$  is far slower than axial-equatorial site exchange within each type of isomer. It seems certain that the interconversion of symmetrical and unsymmetrical isomers can only occur by a pathway that includes bridge opening. However, in addition to bridge opening, two other steps are essential. There must be a rotation by  $\pi$  about the M-E bond and the pyramidal configuration at E must be inverted. Either or both of these steps are likely to have high activation energies. If the M-E bond is a pure  $\sigma$  bond, then inversion of the  $\text{FeAsMe}_2$  on  $\text{FePMe}_2$  pyramidal configurations should have the high (ca. 30 kcal mol<sup>-1</sup>) activation energies characteristic of arsines and phosphines generally.<sup>27</sup> To the extent that the pyramidal configuration at As or P might be flattened by use of the lone pair in a  $p\pi \rightarrow d\pi$  bond to the metal atom, a rotational barrier about the M...E bond would become important. Thus, a high activation energy for the isomerization reaction is to be expected, even if the barrier to bridge opening itself is low. This means that the great difference in the rates of axial-equatorial exchange of R groups on the one hand and isomer interconversion on the other does not constitute evidence against (or for) a bridge-opening mechanism for the R group site exchange process. The disappointing fact is that none of the experiments described in this report has provided direct evidence as to the mechanism of the latter process.

(4) Undoubtedly the most important new results obtained are those which show that carbonyl scrambling is a remarkably facile process in these molecules. While rapid scrambling of CO groups within  $\text{Fe}(\text{CO})_3$  moieties has been observed in a number of other cases,<sup>28-32</sup> it was not obvious that the circumstances in these molecules are such as to permit rapid scrambling.

**Acknowledgment.** The work at the University of British Columbia was supported by the National Research Council of Canada through an operating grant (to W.R.C.) and scholarships (to L.M.), and the work at Texas A&M University was supported by the National Science Foundation under Grant No. 33142X.

**Registry No.**  $\text{Co}_2(\text{CO})_6(\text{GeMe}_2)_2$ , 41550-24-7;  $\text{Co}_2(\text{CO})_6(\text{SnMe}_2)_2$ , 54678-21-6;  $\text{Fe}_2(\text{CO})_6(\text{AsMe}_2)_2$ , 15525-09-4;  $\text{Fe}_2(\text{CO})_6(\text{PMe}_2)_2$ , 14871-43-3;  $\text{Fe}_2(\text{CO})_6(\text{AsMePh})_2$ , 54712-54-8;  $\text{Fe}_2(\text{CO})_6(\text{SMe})_2$ , 14878-96-7;  $\text{Fe}_2(\text{CO})_6(\text{SEt})_2$ , 15634-62-5;  $(\text{CH}_3)_2\text{GeH}_2$ , 1449-64-5;  $(\text{CH}_3)_2\text{SnH}_2$ , 2067-76-7; dicobalt octacarbonyl, 10210-68-1; tetramethyldiarsine, 471-35-2; tetramethyldiphosphine, 3676-91-3; 1,2-dimethyl-1,2-diphenyldiarsine,

23396-46-5; iron pentacarbonyl, 13463-40-6.

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