

**Stereospecific Preparation and Crystal Structure of *rac-ab*-Dicarbonyl-*f*-methyl-*cd-o*-phenylenebis(dimethylarsine)-*e*-trimethylphosphineiron(II) Tetrafluoroborate**

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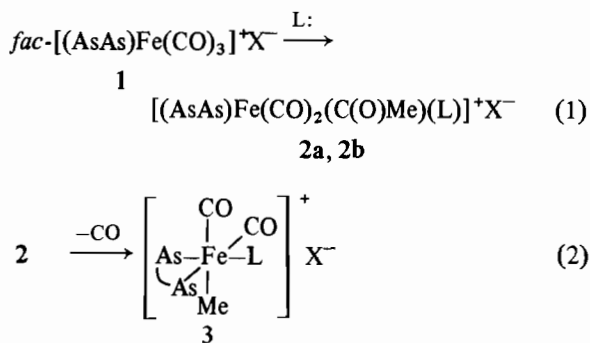
Thermal or photochemically induced CO extrusion of  $h^1$  acyls provides a useful synthetic avenue which leads to a variety of transition metal alkyl complexes [1, 2]. The stereochemical outcome in relation to the central metal for  $d^6$  octahedral  $h^1$  acyls is, in principle, variable but, in spite of the array of possible isomeric alkyl products, a good deal of stereoselectivity is frequently observed [3]. Amongst the 3d metals Mn(I) shows the greatest degree of stereo-control and specifically labeled  $[Mn(Me)(^{13}CO)(CO)_4]$  can be prepared thermally from  $[Mn(^{13}C(O)Me)(CO)_5]$  [4, 5] without appreciable site scrambling. Similarly, Green [6] and Kraihanzel [7, 8] report that a single isomer results from the decarbonylation of  $[Mn(L)(CO)_4(C(O)Me)]$ ,  $[Mn(L)_2(CO)_3(C(O)Me)]$ , or  $[Mn(\bar{L}L)(CO)_3(C(O)Me)]$  (L = Group VA donor). On balance, octahedral Fe(II) acyls also exhibit a high degree of stereo-control at the metal and a single alkyl isomer is formed on CO extrusion from  $[Fe(L)_2(CO)_2(L')(C(O)Me)]$  [9–11] or  $[Fe(\bar{L}L)(CO)_2(L')(C(O)Me)]$  [12, 13] (L' = Group VA donor, halide, or pseudohalide).

In the case of Fe(II) it is not yet altogether clear whether the CO extrusion product distribution reflects kinetic or thermodynamic control. Stereospecific alkyl formation at low temperature [9] or in solvent where geometric isomerization is precluded [12] supports kinetic control. However, the recent observation [11] that two geometrically stable isomeric alkyls form on CO extrusion with concomitant  $I^-$  dissociation from  $[Fe(PMe_3)_2(CO)_2(I)(C(O)Me)]$  under conditions favouring kinetic control indicates that the reaction may not be intrinsically stereospecific and, in keeping with related results in the literature, [8, 11, 14, 15] suggests that the product distribution amongst the 3d metals is a result of

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simple sterically mediated thermodynamic control. We report here some results which expand the synthetic applications and further explore the stereochemical outcome of CO extrusion on  $O_h$   $d^6$  Fe(II).

The cationic acyl  $[(diars)Fe(CO)_2(Ac)(PMe_3)]^+$ , [12] available in good yield as an isomeric mixture of *trans*-Ac,  $PMe_3$ , **2a** and *cis*-Ac,  $PMe_3$ , **2b**<sup>†</sup> from the  $PMe_3$  promoted migratory CO insertion of *fac*- $[(diars)Fe(CO)_3Me]^+$  [15] (cf. eqn. (1)), decarbonylates (cf. eqn. (2)) readily in the solid state at elevated temperature (150 °C, 4 h,  $10^{-3}$  Torr) to give the alkyl **3**<sup>††</sup>.



AsAs = *o*-phenylenebis(dimethylarsine); L =  $PMe_3$ ; X =  $BF_4^-$ ; **2a** = *trans*-Ac,  $PMe_3$ ; **2b** = *cis*-Ac,  $PMe_3$

The sequence (1), (2) can be extended to a larger series of phosphorus donors L: (L =  $P(OMe)_3$ ,  $Ph_nP(OMe)_{3-n}$ , and  $Ph_nPMe_{n-3}$ ) however large cone angles [16] complicate both steps<sup>†††</sup>.

Spectroscopic and analytical data<sup>††</sup> for the alkyl complex obtained from the solid state thermolysis of **2** (L =  $PMe_3$ ) are fully in accord with the formation of one of the four possible geometric isomers [17]. Two strong CO stretching frequencies observed at 2008 and 1965  $cm^{-1}$  in the infrared spectrum along with four nonequivalent As–Me signals in the  $^1H$  NMR spectrum are consistent with an all-*cis* geometry. A small  $^4J$  to  $^3P$  clearly observed for two of the four nonequivalent As–Me resonances suggests that  $PMe_3$

<sup>†</sup> No  $^4J$  couplings between  $^3P$  and the As–Me groups were resolvable in the  $^1H$  NMR spectrum of **2b**. We therefore (cf. ref. [15]) assign an all-*cis* geometry with  $PMe_3$  *cis* to both As atoms.

<sup>††</sup> Analysis. Calculated for  $C_{16}H_{28}As_2BF_4FeO_2P$ : C, 33.37; H, 4.90. Found: C, 33.39; H, 4.76. M.p. 170 °C (sealed  $N_2$  filled cap.). IR ( $CH_2Cl_2$ ): 2008, 1965  $cm^{-1}$  ( $\nu_{CO}$ ).  $^1H$  NMR ( $CD_2Cl_2$ ): –0.54 ppm (d,  $J = 7.5$  Hz, 3, FeMe), 1.70 ppm (d,  $J = 9.7$  Hz, 9, PMe), 1.73 ppm (s, 3, AsMe), 1.78 ppm (d,  $J = 0.4$  Hz, 3, AsMe), 1.80 ppm (s, 3, AsMe), 1.82 ppm (d,  $J = 0.5$  Hz, 3, AsMe), 7.75 ppm (m, 4,  $C_6H_4$ ).  $^31P$  NMR ( $CD_2Cl_2$ ) 19.98 ppm (Rel. to ext. 85%  $H_3PO_4$ ).

<sup>†††</sup> A mechanistic study of the CO extrusion reaction for this series is underway. Full details, including preparation and characterization, will be published elsewhere.

is *cis* to two As–Me sites and *trans* to the remaining two sites as in structure 3.

A single crystal X-ray study of 3 (L = PMe<sub>3</sub>) confirmed the spectroscopic results and allowed unambiguous stereochemical assignment as the title compound [18].

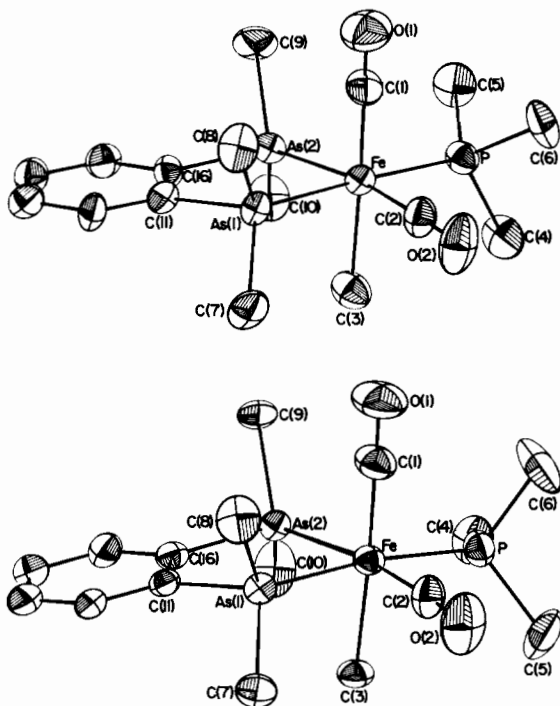


Fig. 1. ORTEP drawing of 3, molecules A and B. Selected bond distances (Å) for molecule A [molecule B]: Fe–As(1), 2.337(2) [2.335(2)]; Fe–As(2), 2.360(2) [2.364(2)]; Fe–P, 2.253(4) [2.264(4)]; Fe–C(1), 1.79(1) [1.78(1)]; Fe–C(2), 1.77(1) [1.75(1)]; Fe–C(3), 2.11(1) [2.12(1)]; Selected bond angles (deg) for molecule A [molecule B]: As(1)–Fe–As(2), 85.7(0) [85.9(0)]; As(1)–Fe–P, 177.4(0) [172.2(0)]; As(1)–Fe–C(1), 91.9(4) [94.6(4)]; As(1)–Fe–C(2), 88.9(3) [87.1(4)]; As(1)–Fe–C(3), 86.8(3) [85.9(3)]; As(2)–Fe–P, 95.7(0) [98.1(0)]; As(2)–Fe–C(1), 93.0(4) [90.8(4)]; As(2)–Fe–C(2), 170.4(3) [171.3(4)]; As(2)–Fe–C(3), 85.7(3) [85.3(3)]; P–Fe–C(1), 90.3(4) [92.1(4)]; P–Fe–C(2), 89.4(3) [88.3(4)]; P–Fe–C(3), 91.1(3) [87.7(3)]; C(1)–Fe–C(2), 95.1(5) [94.9(6)]; C(1)–Fe–C(3), 178.2(5) [176.1(5)]; C(2)–Fe–C(3), 86.1(5) [89.0(5)].

Crystal data for C<sub>16</sub>H<sub>28</sub>As<sub>2</sub>BF<sub>4</sub>FeO<sub>2</sub>P: triclinic<sup>§</sup>, spacegroup *P* $\bar{1}$  with  $a = 13.075(2)$ ,  $b = 14.696(2)$ ,  $c = 16.112(2)$  Å;  $\alpha = 117.36(1)$ ,  $\beta = 89.96(1)$ ,  $\gamma = 116.34(1)$  deg;  $V = 2382.5(5)$  Å<sup>3</sup>;  $Z = 4$ ;  $\rho_{\text{calc'd}} = 1.605$ ,  $\rho_{\text{measured}} = 1.60$  g cm<sup>-3</sup>;  $F(000) = 1152$  electrons;  $(\text{MoK}\alpha) = 36.66$  cm<sup>-1</sup>. Intensity data were col-

<sup>§</sup> Careful examination of photographs revealed the absence of a 2-fold axis and thus confirmed the assignment as triclinic with two independent molecules per unit cell.

lected on a crystal of dimensions 0.15 × 0.16 × 0.20 mm using  $\theta$ – $2\theta$  scans ( $3.2 < 2\theta < 42$  deg) with a variable scan speed of 2.0–29.3 deg min<sup>-1</sup> and a scan width of 0.8 deg below  $K\alpha_1$  to 0.8 deg above  $K\alpha_2$  on a Syntex *P*2<sub>1</sub> diffractometer. From a total of 5115 measured reflections, 3372 with  $I > 3\sigma(I)$  were considered observed and used in the structure solution and refinement. Two standard reflections (131 and 334) monitored after every 100 reflections showed no change in the intensity over the course of data collection. Data were corrected for Lorentz and polarisation effects but not for absorption.

Transmission factors varied between 0.45 and 0.66. The arsenic and iron atoms of both independent molecules in the unit cell were located from a Patterson synthesis and light atoms via a subsequent Fourier map. Refinement of all non-hydrogen atoms with isotropic thermal parameters gave an  $R$  value ( $R = \sum |F_o| - |F_c| / \sum |F_o|$ ) of 0.081. Refinement with anisotropic thermal parameters to convergence gave an  $R$  of 0.040 with an  $R_w$  ( $R_w = [\sum w(|F_o| - |F_c|)^2] / \sum w(|F_o|)^2$ )<sup>1/2</sup> of 0.048 ( $w^{-1} = 2.58 - 0.018|F_o| + 0.00023|F_o|^2$ ). A final difference Fourier map revealed the presence of all hydrogen atoms but these were not included in the refinement. Maximum residuals of ca. 0.6 eÅ<sup>-3</sup> were located in the vicinity of the BF<sub>4</sub><sup>-</sup> groups.

Scattering factors were taken from the compilation of the International Tables [19]. Both real and imaginary components of the anomalous dispersion were applied to corrections for the iron and arsenic atoms. Computer programmes have been described elsewhere [20].

The structure of the title compound 3 (L = PMe<sub>3</sub>, X<sup>-</sup> = BF<sub>4</sub><sup>-</sup>, cf. Fig. 1) describes a slightly distorted octahedron with the Fe–Me group *cis* to both arsenic atoms. Steric requirements of the PMe<sub>3</sub> group (cone angle 118° [16]) are accommodated principally via a significant opening of the P–Fe–As(2) angle (95.7° for molecule A, 98.1° for molecule B) as well as a closing of the C(3)–Fe–As(1) and C(3)–Fe–As(2) angles (86.8° and 85.7°; 85.9° and 85.3° for molecules A; B respectively). The Fe–C(3) bond distance of 2.11 Å (Molecule A) and 2.12 Å (molecule B) conforms with the average value of 2.11 Å found for Fe–C(sp<sup>3</sup>) bonds [21].

Although we have yet to unequivocally demonstrate whether the all-*cis* alkyl of Fig. 1 is the kinetic product, it is mechanistically significant to note that: i) no other isomeric alkyls were detected (*viz.* <sup>1</sup>H NMR) on partially decarbonylated samples of 2, ii) the decarbonylation rate of 2a ≫ 2b, and iii) neither *cis*, *trans* 2a nor *cis*, *cis* 2b can decarbonylate directly to give the title alkyl 3 via a CO heterolysis/methyl migration involving a static square pyramidal MD<sub>5</sub> intermediate. These observations are consistent with a preliminary isomerization of 2a, 2b prior to CO dissociation.

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