Table I. Bond Distances and Angles in the $[HFe(CO)_4]^-$ Anion

| | | | |
|---|---|---|---|
| | Bond Distances (in Ångströms) | | |
| Fe–$C_1$ | 1.72 (2) | $C_1$–$O_1$ | 1.18 (2) |
| Fe–$C_2$ | 1.76 (2) | $C_2$–$O_2$ | 1.14 (2) |
| Fe–$C_3$ | 1.78 (2) | $C_3$–$O_3$ | 1.15 (3) |
| Fe–$C_4$ | 1.71 (2) | $C_4$–$O_4$ | 1.15 (3) |
| Fe–H | 1.57 (12) | | |
| | Bond Angles (in degrees) | | |
| Fe–$C_1$–$O_1$ | 177.2 (14) | H–Fe–$C_1$ | 175 (5) |
| Fe–$C_2$–$O_2$ | 177.4 (16) | H–Fe–$C_2$ | 84 (5) |
| Fe–$C_3$–$O_3$ | 177.1 (14) | H–Fe–$C_3$ | 82 (5) |
| Fe–$C_4$–$O_4$ | 179.2 (18) | H–Fe–$C_4$ | 78 (5) |
| $C_1$–Fe–$C_2$ | 98.4 (7) | $C_2$–Fe–$C_3$ | 115.3 (8) |
| $C_1$–Fe–$C_3$ | 101.9 (7) | $C_3$–Fe–$C_4$ | 115.1 (8) |
| $C_1$–Fe–$C_4$ | 96.9 (8) | $C_4$–Fe–$C_2$ | 122.4 (9) |

diffractometer, corrected for absorption effects,[4] and merged to give 1573 independent nonzero reflections. The Fe and P positions were located using direct methods and the rest of the atoms located through a series of difference Fourier maps. All the hydrogen atoms in the molecule were found without any difficulty. Least-squares refinement of all the atoms resulted in a final *R* factor of 7.6%. The fact that a fairly large number of low-angle reflections were available probably contributed to the successful refinement of the metal-bound hydrogen atom.

The geometry of the $[HFe(CO)_4]^-$ anion is shown in Figure 1. Bond lengths and angles of the anion are given in Table I. Bond lengths and angles associated with the $[(Ph_3P)_2N]^+$ cation (Table II) and a complete listing of positional and thermal parameters of all the atoms in the molecule (Table III) are available elsewhere.[5] The configuration of the anion is that of a distorted trigonal bipyramid, with the hydrogen in an axial position. The Fe–H distance of 1.57 (12) Å compares favorably with other M–H bond lengths, such as 1.51 (4) Å found in $H_2Fe[PPh(OEt)_2]_4$,[6] 1.601 (16) Å in $HMn(CO)_5$,[7] and 1.60 (12) Å in $HRh(CO)(PPh_3)_3$.[8] As in $HMn(CO)_5$, the equatorial carbonyl groups are bent toward the hydrogen atom, the average C(ax)–Fe–C(eq) angle being 99.1° (the corresponding angle in $HMn(CO)_5$ is 97.1°). The $Fe(CO)_4$ part of the anion may thus be described as half-way between tetrahedral and trigonal bipyramidal. The Fe atom is displaced 0.27 Å from the plane of the three equatorial carbons.

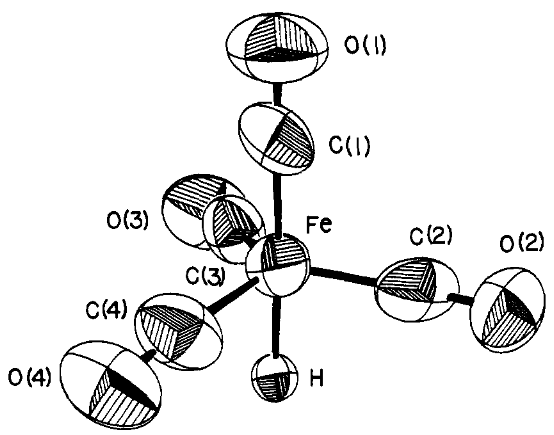

Figure 1. The geometry of the $[HFe(CO)_4]^-$ anion.

Because of the close similarities between the vibrational spectra[9] of $HCo(CO)_4$ and $[HFe(CO)_4]^-$, our result strongly implies that the geometry of $HCo(CO)_4$ is very similar to the one described here. The finding that the H atom in $[HFe(CO)_4]^-$ occupies a discrete coordination position is gratifying. Although the question of "sterically active" *vs.* "sterically inactive" hydride ligands seemed to have been settled in favor of the former some years ago, recent structure determinations have shown that there are cases (mainly involving pentacoordinated species such as $HRh(PPh_3)_4$,[10] $HRh(AsPh_3)(PPh_3)_3$,[11] and $HCo(PF_3)_4$[12]) in which the hydride ligand appears to exert very little influence on the geometry of the rest of the molecule. The difference between the geometries of $[HFe(CO)_4]^-$ and $HCo(PF_3)_4$ (which can also be considered isoelectronic with $HCo(CO)_4$) might be attributed to the difference in steric bulk between the CO and $PF_3$ ligands.

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[4] Programs used in this work: absorption correction, GONO9 (by W. C. Hamilton); direct methods, REL (by R. E. Long); Fourier maps, CRYSIS (by G. N. Reeke); least-squares refinements, CRYM (by R. E. Marsh); molecular diagram, ORTEP (by C. K. Johnson).

[5] Listings of the bond lengths and angles of the $[(Ph_3P)_2N]^+$ cation (Table II) and the final atomic parameters of the molecule (Table III) will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth Street, N.W., Washington, D. C. 20036, by referring to code number JACS-73-2388. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

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## Synthesis and Reactions of Anionic Phosphide and Arsenide Complexes Derived from Disodium Tetracarbonylferrate(−II)

*Sir:*

We have shown $Na_2Fe(CO)_4$ to be an inexpensive reagent for selective organic syntheses.[1–4] Here we report its use in the preparation of isolable anionic

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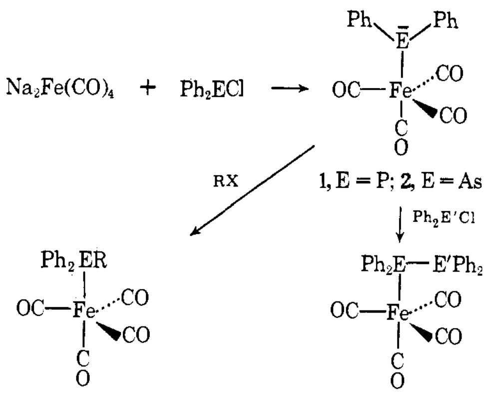
phosphide and arsenide complexes **1** and **2** and their facile *in situ* transformation into neutral phosphine and arsine complexes (Scheme I). These simple synthetic schemes have yielded some unusual derivatives.

**Scheme I**



**3a**, E = P; R = $CH_3$
**b**, E = P; R = $CH_2C(CH_3){=}CH_2$
**4a**, E = As; R = $CH_2Ph$
**b**, E = As; R = $CH_2C(CH_3){=}CH_2$
**c**, E = As; R = $CH_2CO_2C_2H_5$
**d**, E = As; R = $CH_2C{\equiv}CH$
**e**, E = As; R = $GePh_3$
**f**, E = As; R = $\pi\text{-}C_5H_5Fe(CO)_2$
**5a**, E = E′ = P
**b**, E = E′ = As
**c**, E = P; E′ = As
**d**, E = As; E′ = P

Reaction of $Na_2Fe(CO)_4$ with $Ph_2PCl$ or $Ph_2AsCl$ (1 equiv each in THF) affords **1** or **2** which have been isolated and fully characterized (elemental analyses and ir and pmr spectra) as yellow crystalline $[(Ph_3P)_2N]^+$ salts. The $\nu_{CO}$ patterns for **1** and **2** (2004, 1910, and 1893 cm$^{-1}$ in acetone for **1** and 1999, 1910, and 1890 for **2**) are consistent with the expected trigonal-bipyramidal coordination in which the $Ph_2E$ group occupies an axial position. X-Ray crystallographic studies are planned.

Complexes **1** and **2** are potentially ambient nucleophiles (at Fe or P–As) but *in situ* alkylation occurs exclusively at P or As affording monomeric phosphine or arsine complexes **3** and **4** (Scheme I) in respectable (53–72%) yields.[5]

In a typical preparation of **3** or **4**, 1 mmol of chlorodiphenylarsine was added dropwise to a stirred suspension of $Na_2Fe(CO)_4$ in 15 ml of THF at 25° under nitrogen. After 15 min, 1.2 mmol of 3-chloro-2-methylpropene was added to the yellow solution and stirring was continued for an additional 15 min. The THF was removed *in vacuo* and the residue was recrystallized from methanol or methanol–water giving 301 mg (67%) of the diphenylmethallylarsine complex, **4b**, mp 121–123°; ir ($CHCl_3$): 2053, 1971, 1940 (terminal CO on iron), and (KBr) 1640 cm$^{-1}$ ($\nu_{C=C}$); nmr ($CDCl_3$): $\delta$ 1.52 (s, 3 H), 3.28 (s, 2 H), 4.95 (d, 2 H, $J$ = 4.5 cps), 7.5 (m, 10 H). This method is a simpler version of the two-step sequence recently reported by Treichel requiring the prior isolation of the diphenylphosphine complex (eq 1).[6,7] The versatility of our method is illustrated by the wide range of phosphine and arsine complexes prepared in this way (Scheme I). Of special interest is the use of this method to introduce into **3** and **4** R groups having functionality capable of serving as a ligand, *e.g.*, $CH_2{=}C(CH_3)CH_2$, **3b** and **4b** and $HC{\equiv}CCH_2$, **4d**. The spectral properties of these complexes indicate no interaction between the saturated metal and these neighboring latent ligands. The preparation of novel heterometallic bridging arsenide complexes **4e** ($\nu_{CO}$ = 2045, 1965, and 1940 cm$^{-1}$) and **4f**[8] ($\nu_{CO}$ = 2040, 2025, 1988, 1948, and 1927 cm$^{-1}$) further illustrates the versatility of this method.

$$Fe(CO)_4PPh_2H \xrightarrow{n\text{-BuLi}} [Fe(CO)_4PPh_2]Li \xrightarrow{CH_3I} Fe(CO)_4PPh_2CH_3 \quad (1)$$

Reaction of **1** or **2** with an additional equivalent of $Ph_2PCl$ or $Ph_2AsCl$ affords a general synthesis of diphosphine, diarsine, or mixed phosphine–arsine complexes **5a–d** which have been isolated and fully characterized (Scheme I). A few diarsine and diphosphine complexes have been previously isolated[9–11] and characterized, but mixed phosphine–arsine complexes have not been described. The $\nu_{CO}$ patterns for **5a–d** closely resemble those of the simple phosphine and arsine derivatives **3** and **4** suggesting a similar coordination geometry and no direct interaction between the saturated iron and the terminal P or As. The presence of two $^{31}P$ doublets ($\delta$ 61.5 and 2.98,[12] $J_{P-P}$ = 322.5 Hz) in the diphosphine complex **5a** is consistent with this idea and shows that the iron does not migrate from one phosphorus to the other on the nmr time scale. The mixed phosphine–arsine complexes exhibit distinctive $^{31}P$ spectra (singlets at $\delta$ 57.8 and 10.7 for **5c** and **5d**, respectively) demonstrating their separate identities and confirming our expectation that the individual isomers do not interconvert under ambient conditions over prolonged periods.

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## Photolysis of 4-Substituted 1,2,3-Benzotriazine 3-*N*-Oxides

*Sir:*

Although the photolysis of many aromatic *N*-oxides has been extensively studied in recent years,[1] the 1,2,3-benzotriazine 3-*N*-oxides[2] have been overlooked. We report here the surprising results of their photolysis.

[1] G. G. Spence, E. C. Taylor, and O. Buchardt, *Chem. Rev.*, 70, 231 (1970), and references cited therein.

[2] The ir, uv, nmr, and mass spectra of the 1,2,3-benzotriazine 3-*N*-oxides studied are only in agreement with the 1,2,3-benzotriazine 3-*N*-oxide structure.