DALTON

Iron-substituted arsine, $[Fe(AsPh_2)(dppe)(\eta\text{-}C_5H_5)]\cdot 2thf$ (dppe = $Ph_2PCH_2CH_2PPh_2$, thf = tetrahydrofuran)

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The reaction of $K(AsPh_2)\cdot 2C_4H_8O_2$-1,4 with $[FeI(dppe)(\eta\text{-}C_5H_5)]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) afforded a good yield of the new metalloarsine $[Fe(AsPh_2)(dppe)(\eta\text{-}C_5H_5)]\cdot 2thf$ (thf = tetrahydrofuran) which has been structurally characterised.

As part of a study of the structural chemistry of the heavier alkali-metal phosphides and arsenides we have examined the salt metathesis reaction of $K(AsPh_2)\cdot 2C_4H_8O_2$-1,4. Salts of this type have general utility as transfer agents for the arsenido group but are seldom studied. Little is known about their actual constitution in solution and the solid state, the common thesis being that they closely follow the chemistry of the lithium analogues. This might not always be true for the heavier alkali metals because they have higher co-ordinative demands, with the metal centre rather than the anionic ligand largely determining the structure.[1] Transition-metal phosphido and arsenido complexes are also of interest. They are potential precursors to thin films of phosphides and arsenides by chemical vapour deposition.[2] The arsenide group is able to bond in both a terminal and bridging manner (Scheme 1); the latter is common for secondary arsenides and phosphides. Previous synthetic procedures for the preparation of monomeric transition-metal arsenides have used a number of methods. These include the metathesis reaction of a transition-metal anion with a halogenoarsine[3a,b] [Equation (1)], metathesis with a lithium

$$\begin{aligned}&Na[Fe(CO)_2(\eta\text{-}C_5H_5)] + AsMe_2Cl \longrightarrow \\ &\qquad [Fe(AsMe_2)(CO)_2(\eta\text{-}C_5H_5)] + Me_2AsAsMe_2 + \\ &\qquad\qquad [\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2(\mu\text{-}AsMe_2)]Cl \qquad (1)\end{aligned}$$

arsenide[3c] [Equation (2)] (thf = tetrahydrofuran) or the reaction

$$\begin{aligned}&[FeBr(CO)_2(\eta\text{-}C_5Me_5)] + LiAs(SiMe_3)_2\cdot 3.5thf \longrightarrow \\ &\qquad\qquad [Fe\{As(SiMe_3)_2\}(CO)_2(\eta\text{-}C_5Me_5)] \qquad (2)\end{aligned}$$

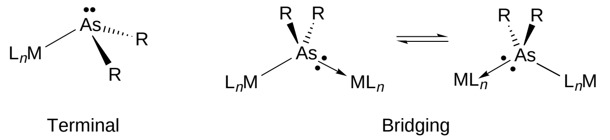
between a diarsine and a metal–metal bond[4] [Equation (3)].

$$\begin{aligned}&[\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2] + (CF_3)_2As\text{–}As(CF_3)_2 \longrightarrow \\ &\qquad\qquad 2[Fe\{As(CF_3)_2\}(CO)_2(\eta\text{-}C_5H_5)] \qquad (3)\end{aligned}$$

Results and Discussion

Addition of a slight excess of $K(AsPh_2)\cdot 2C_4H_8O_2$-1,4 to a solution of $[FeI(dppe)(\eta\text{-}C_5H_5)]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) in thf gave a deep red solution. Work-up removed KI and crystallisation from thf–hexane gave X-ray-quality crystals of $[Fe(AsPh_2)(dppe)(\eta\text{-}C_5H_5)]\cdot 2thf$ **1**.

The results of the room-temperature single-crystal analysis are consistent with the stoichiometry and connectivity as expressed in compound **1** above and Fig. 1. Table 1 gives selected bond lengths and angles. The Fe–As bond length is closely approximated by the sum of the arsenic and iron covalent radii and lies in the range found for other Fe–As compounds, *e.g.* terminal $[\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2(\mu,\eta^1\text{-}As_2Ph_2)]$,[5a] 2.450(2) Å, $[Fe\{As{=}C(OSiMe_3)Bu^t\}(CO)_2(\eta\text{-}C_5H_5)]$,[5b] 2.407(1) Å, $[Fe\{As{=}C(NMe_2)_2\}(CO)_2(\eta\text{-}C_5Me_5)]$,[3c] 2.443(2) Å and bridging arsenide, $[\{Fe(CO)_4\}_2(\mu\text{-}AsMe_2)]$,[6] 2.395(1) Å. The iron atom co-ordination sphere is best described as pseudo-octahedral. The arsenic atom has a pyramidal geometry, presumably because of the steric effect of the lone pair of electrons localised in one sp^3 orbital. The repulsion of the lone pair causes a contraction in the bond angles at the arsenic from the ideal tetrahedral values of 109.5°. The Fe–As–C(321, 311) [110.4(2), 106.0(2)°] angles of **1** are significantly larger than the C_{ipso}–As–C_{ipso} [100.6(2)°] angle found in the structure of Ph_3As[7] while the analogous angle in **1** [94.2(2)°] is significantly smaller; presumably this results from the steric interaction of the large $Fe(dppe)(\eta\text{-}C_5H_5)$ moiety. The Fe–P distances [2.208(1), 2.177(1) Å] are as expected for this type of neutral $Fe(dppe)(\eta\text{-}C_5H_5)$ complex. The P–Fe–P angle is contracted with respect to both the P–Fe–As angles as expected from the tethered nature of the chelate. The two thf solvent molecules of crystallisation occupy voids in the lattice.



Scheme 1 Bonding modes of the arsenide moiety

Table 1 Selected bond distances (Å) and angles (°) for compound **1**

Fe–As(3)	2.443(1)	C(1)–C(2)	1.514(7)
Fe–P(1)	2.208(1)	C(2)–P(2)	1.832(5)
Fe–P(2)	2.177(1)	P(2)–C(211)	1.844(5)
P(1)–C(111)	1.852(5)	P(2)–C(221)	1.822(5)
P(1)–C(121)	1.838(6)	As(3)–C(311)	1.972(4)
P(1)–C(1)	1.860(4)	As(3)–C(321)	1.979(4)
P(1)–Fe–P(2)	85.45(6)	Fe–P(2)–C(211)	116.1(2)
P(1)–Fe–As(3)	91.32(5)	Fe–P(2)–C(221)	121.7(1)
P(2)–Fe–As(3)	90.65(6)	Fe–As(3)–C(311)	106.0(2)
Fe–P(1)–C(111)	121.5(2)	Fe–As(3)–C(321)	110.4(2)
Fe–P(1)–C(121)	120.6(1)	C(311)–As(3)–C(321)	94.2(2)
Fe–P(1)–C(1)	109.4(2)	As(3)–C(311)–C(312)	117.5(3)
P(1)–C(1)–C(2)	110.5(3)	As(3)–C(311)–C(316)	124.8(4)
C(1)–C(2)–P(2)	106.6(3)	As(3)–C(321)–C(322)	116.1(4)
Fe–P(2)–C(2)	108.9(1)	As(3)–C(321)–C(326)	126.5(4)

Compound **1** is stable to air over several weeks as a solid, although it decomposes rapidly in solution. The FAB mass spectrum contained a molecular ion peak of low intensity but also a peak corresponding to $[M + O]^+$. Presumably this ion is due to the trivalent arsenic centre being oxidised in the

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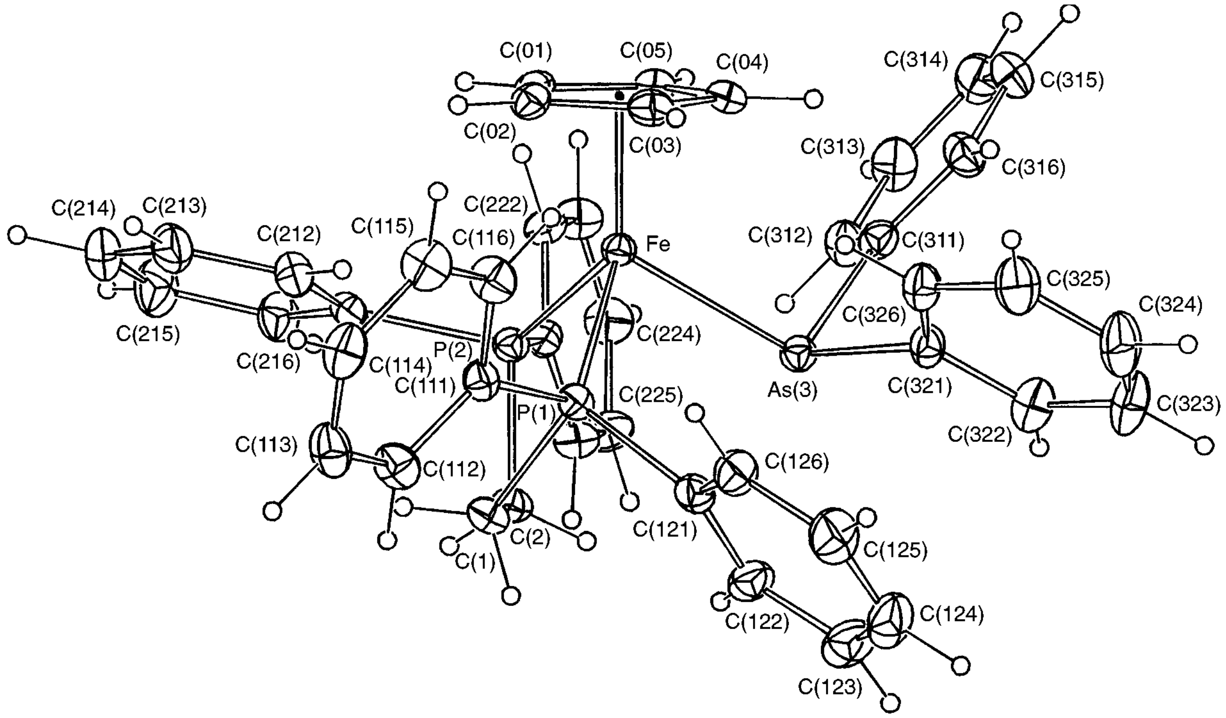

Fig. 1 Molecular structure of compound **1**: 20% probability ellipsoids are shown for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å

spectrometer, or during sample preparation. The major fragmentation involves loss of the arsenide moiety.

Given the apparent facile oxidation of compound **1** we attempted selective oxidation using S_8 or dimethyldioxirane but failed to isolate a tractable product. The selective oxidation of transition-metal co-ordinated phosphides has been successful using the latter reagent.[3b]

Experimental

Manipulation of oxygen- and moisture-sensitive compounds was performed under an atmosphere of high-purity argon using standard Schlenk techniques or in a dry-box (Miller Howe).

Infrared spectra were recorded using a Bio-Rad FTS 45 or 40 FTIR spectrometer as Nujol mulls (NaCl discs), ^1H and ^{13}C NMR spectra using Varian Gemini 200 or Bruker ARX 500 spectrometers and ^{31}P NMR spectra using a Bruker ARX 500 spectrometer. The ^1H and ^{13}C NMR spectra were referenced with respect to incompletely deuteriated solvent signals, ^{31}P NMR spectra relative to external H_3PO_4 (0.0 ppm) and proton decoupled. Mass spectra were obtained on a VG AutoSpec spectrometer employing a fast atom bombardment (FAB) ionisation source in all samples unless otherwise specified.

Elemental analyses were performed by Chemical and Micro Analytical Services Pty. Ltd., Melbourne, Australia. Tetrahydrofuran was dried over sodium metal and distilled from potassium–benzophenone under an atmosphere of argon, *n*-hexane and toluene were dried over sodium metal and distilled from sodium–benzophenone under an atmosphere of argon. The compound $K(AsPh_2)\cdot 2C_4H_8O_2$-1,4 was prepared by a known procedure.[8]

Crystallography

A unique room-temperature diffractometer data set was measured (2θ–θ scan mode, $2\theta_{max}$ 50°; monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å; $T \approx 295$ K), yielding 7790 independent reflections, 5170 of which with $I > 3\sigma(I)$ were considered 'observed' and used in the full-matrix least-squares refinement after gaussian absorption correction. Anisotropic thermal parameter forms were refined for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ being constrained at estimated values. The geometry of the thf molecules of solvation were restrained to ideal values, the occupancy of both solvent molecules refining to 1.0 population. Conventional residuals R, R' on $|F|$ were 0.045 and 0.047 at convergence, statistical weights being derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$. Neutral atom complex scattering factors were employed. Computation used the XTAL 3.4 program system implemented by S. R. Hall.[9] Diffraction data are summarised in Table 2.

Table 2 Summary of diffraction data for $[Fe(AsPh_2)(dppe)(\eta\text{-}C_5H_5)]\cdot 2thf$ **1**

Formula	$C_{43}H_{39}AsFeP_2\cdot 2C_4H_8O$
M_r	892.72
Crystal system	Monoclinic
Space group	$P2_1/c$ (no. 14)
a/Å	12.442(4)
b/Å	31.488(16)
c/Å	12.290(6)
β/°	113.02(3)
U/Å^3	4432(4)
D_c/g cm^{-3}	1.33_8
Z	4
F(000)	1864
μ_{Mo}/cm^{-1}	11.9
Specimen size/mm	0.42 × 0.58 × 0.65
A^*_{min}, A^*_{max}	1.67, 1.78

CCDC reference number 186/667.

Preparations

$[FeI(dppe)(\eta\text{-}C_5H_5)]$. The compound $[FeI(dppe)(\eta\text{-}C_5H_5)]$ was prepared by a modified literature method.[10] Iron powder (1.25 g, 22.4 mmol), iodine (6.34 g, 25.0 mmol) and thf (100 cm^3) were refluxed for 6 h, and the black solution cooled to room temperature. A solution of dppe (8.76 g, 22.0 mmol) in thf (100 cm^3) was added dropwise with stirring over an hour. The solution was refluxed (1 h) and allowed to cool. The compound $Tl(C_5H_5)$ (22 mmol) was added portionwise to the green slurry over 1 h, and the mixture stirred (12 h). The resulting black solution was filtered, and the yellow precipitate (TlI) washed several times with thf until the extracts were colourless. Solvent was removed from the combined filtrate and extracts using a rotary evaporator, and the resulting black solid was chromatographed on silica (BDH, 43–60 μm). Elution of the column with hexane and evaporation of the orange band yielded ferrocene (0.75 g, 4 mmol). Elution with CH_2Cl_2–hexane (1 : 1) gave a black band, which when evaporated gave a black solid. Recrystallisation from CH_2Cl_2–hexane at −20 °C gave black crystals of [FeI(dppe)(η-C_5H_5)] (7.32 g, 11.4 mmol, 51%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 2.5 (s, 4 H, dppe CH_2CH_2), 4.2 (s, 5 H, C_5H_5), 7.2, 7.4 and 8.0 (m, 20 H, dppe Ph). ^{31}P NMR ($CDCl_3$, 202 MHz): δ 33.4 [s, Fe(dppe)].

[Fe(AsPh$_2$)(dppe)(η-C_5H_5)] 1. A red solution of K($AsPh_2$)·$2C_4H_8O_2$-1,4 (0.66 g, 1.5 mmol) in thf (20 cm^3) was added to a black solution of [FeI(dppe)(η-C_5H_5)] (0.84 g, 1.3 mmol) in thf (20 cm^3) and stirred overnight. The resulting burgundy solution was evaporated *in vacuo*, and the residue extracted with toluene. The solvent was removed *in vacuo*, and the solid recrystallised from thf–hexane at −20 °C, to yield red crystals suitable for X-ray diffraction of [Fe($AsPh_2$)(dppe) (η-C_5H_5)]·2thf (0.89 g, 0.99 mmol, 76%), m.p. >120 °C (decomp.) [Found: C, 68.73; H, 5.31. $C_{43}H_{39}AsFeP_2$ (unsolvated) requires C, 69.00; H, 5.25%]. ^{1}H NMR (C_6D_6, 500 MHz): δ 1.42 (m, 4 H, dppe CH_2CH_2), 4.25 (s, 5 H, C_5H_5), 6.83, 6.97, 7.34 and 7.39 (m, 30 H, Ph). ^{13}C NMR (C_6D_6, 125 MHz): δ 30.17 (dppe), 78.28 (C_5H_5), 124.88, 127.05, 127.91, 128.29, 129.01, 131.33, 132.76 and 135.58 (Ph). ^{31}P NMR (C_6D_6, 202 MHz): δ 90.29 (s, dppe). IR (Nujol): $\tilde{\nu}$ 1463vs, 1433vs, 1378s, 1187w, 1091m, 1066s, 1022m, 912w, 876m, 855m, 828m, 811m, 733s, 699vs, 673w and 650w cm^{-1}. FAB mass spectrum: *m/z* 765 ([M + O]$^+$, 22), 749 (M^+, 0.2) and 519 ([M − $AsPh_2$]$^+$, 100%).

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References

1 K. Gregory, P. v. Rague Schleyer and R. Snaith, *Adv. Inorg. Chem.*, 1991, **37**, 47.
2 T. S. Lewkebandara and C. H. Winter, *Chem. Vap. Dep.*, 1996, **2**, 75.
3 (*a*) W. Malisch, H. Blau, H. Rößner and G. Jäth, *Chem. Ber.*, 1980, **113**, 1180; (*b*) W. Malisch, K. Hindahl, K. Grün, W. Adam, F. Prechtl and W. S. Sheldrick, *J. Organomet. Chem.*, 1996, **509**, 209; (*c*) L. Weber, O. Kaminski, H.-G. Stammler and B. Neumann, *Chem. Ber.*, 1996, **129**, 223.
4 W. R. Cullen and R. G. Hayter, *J. Am. Chem. Soc.*, 1964, **86**, 1030.
5 (*a*) A. L. Rheingold, M. J. Foley and P. J. Sullivan, *Organometallics*, 1982, **1**, 1429; (*b*) L. Weber, G. Meine and D. Bungardt, *Z. Anorg. Allg. Chem.*, 1987, **549**, 73.
6 W. Deck and H. Vahrenkamp, *Z. Anorg. Allg. Chem.*, 1991, **598**, 83.
7 A. N. Sobolev, V. K. Belsky, N. Y. Chernikova and F. Y. Akhmadulina, *J. Organomet. Chem.*, 1983, **244**, 129.
8 A. Tzschach and W. Lange, *Chem. Ber.*, 1962, **95**, 1360.
9 *XTAL 3.4 User's Manual*, eds. S. R. Hall, G. S. D. King and J. M. Stewart, University of Western Australia, Perth, 1995.
10 M. J. Mays and P. L. Sears, *J. Chem. Soc., Dalton Trans.*, 1973, 1873.

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