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THE REACTIONS OF [$Fe_2(\eta$-DIENYL$)_2(CO)_4$] (DIENYL = C_5H_5 or MeC_5H_4) WITH SbF_3, AsF_3, AND ORGANOHALO-ARSINES

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Summary

In refluxing dry butanol or xylene [$Fe_2(\eta$-dienyl$)_2(CO)_4$] (dienyl = C_5H_5 or MeC_5H_4) and SbF_3 react to give [{(η-dienyl)Fe$(CO)_2$}$_3$SbF]$^+$ or, more normally, [{(η-dienyl)Fe$(CO)_2$}$_3$Sb—O—Sb {Fe$(CO)_2$(η-dienyl)}$_3$]$^{2+}$ cations as their $[SbF_4]^-$, $[Sb_2F_7]^-$ or $[Sb_5F_{17}]^{2-}$ salts. Anion exchange with $[BF_4]^-$, $[BPh_4]^-$ or $[PF_6]^-$ is straightforward, whilst an aqueous solution of iodine in hydriodic acid cleaves the oxygen-bridged cations to give [{(η-dienyl)Fe$(CO)_2$}$_3$SbI][I_3]. Neat AsF_3 at 50°C converts [$Fe_2(\eta$-dienyl$)_2(CO)_4$] to [{(η-dienyl)Fe$(CO)_2$}$_2$AsF_2][AsF_4] which are very readily hydrolysed to [{(η-dienyl)Fe$(CO)_2$}$_2$As$(OH)_2$][AsF_4], alcoholised by methanolic $NaBPh_4$ to [{(η-dienyl)Fe$(CO)_2$}$_2$As$(OMe)_2$][BPh_4] and by ethanolic $NaBPh_4$ to [{(η-dienyl)Fe$(CO)_2$}$_2$As(F)(OEt)][BPh_4] and [{(η-dienyl)Fe$(CO)_2$}$_2$As$(OEt)_2$][BPh_4] in turn. When refluxed in benzene or UV irradiated in dichloromethane, [$Fe_2(\eta$-$C_5H_5)_2(CO)_4$] reacts with various $RAsX_2$ to give [{(η-C_5H_5)Fe$(CO)_2$}$_2$As(R)X]$^+$ salts, and with R_2AsX to give [{(η-C_5H_5)Fe$(CO)_2$}$_2$AsR_2]$^+$ salts. Spectroscopic data suggest that in all of the products there is pseudo-octahedral coordination about the iron atoms, distorted tetrahedral coordination about the As or Sb atoms, and two Fe—As or three Fe—Sb covalent bonds.

A reaction which has received considerable attention in these and other laboratories is the oxidative addition of transition metal carbonyl complexes to tin(II) halides. The products usually contain tin(IV)—transition metal bonds (ref. 1, and references therein). Similar reactions have been observed with germanium(II) halides [2], and with the monohalides of the Group III elements indium and thallium [3]. Therefore it seemed probable that the trihalides of arsenic and antimony would undergo related oxidative-addition reactions to give derivatives of As^V or Sb^V rather than acting as monodentate ligands (cf. $Ni(CO)_3(SbCl_3)$ [4]).

During the course of our work, it was reported that MX_3 (M = As, Sb, or Bi;

X = Cl, Br or I) react with metal carbonyl anions or metal carbonyls containing metal—metal bonds to give covalent and/or ionic derivatives of M^{III} or M^{V} containing transition metal to M bonds [5,6,7]. Consequently we describe herein only the reactions of $[Fe_2(\eta\text{-dienyl})_2(CO)_4]$ (dienyl = C_5H_5 or MeC_5H_4) with AsF_3, SbF_3, and organohaloarsines. Campana, Sinclair and Dahl have shown that in refluxing xylene $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ and AsF_3 give $[Fe_3(\eta\text{-}C_5H_5)_3(CO)_5As_4O_5][BF_4]$ as a minor product [8], but we have not observed it under our reaction conditions.

Experimental

Published methods were used to prepare $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ [9], $[Fe_2(\eta\text{-}C_5H_4Me)_2(CO)_4]$ [9], AsF_3 [10], $MeAsCl_2$ [11], $PhAsCl_2$ [12], Me_2AsCl [13], Me_2AsBr [13], Me_2AsI [13], Et_2AsBr [13], Ph_2AsCl [13], phenarsazine hydrochloride [14], and chlorophenoxarsine [15]. Other chemicals were purchased. Solvents were purified by refluxing over magnesium (n-butanol), calcium oxide (methanol and ethanol), calcium chloride (acetone), or calcium hydride (others) under an atmosphere of nitrogen. They were distilled before use. Unless it is stated otherwise, all reactions were carried out in purified solvents under an atmosphere of nitrogen.

Infrared spectra in the $\nu(CO)$ region were recorded on a Perkin Elmer 337 IR spectrometer fitted with a readout recorder in acetonitrile solution unless it is stated otherwise. They were calibrated using DCl and H_2O vapour [16], and are quoted as peak positions in cm^{-1} with relative peak heights in parentheses. ^1H NMR spectra were measured on a Perkin Elmer R12 spectrometer. They are reported as δ values with the Me_4Si internal standard as $\delta = 0$. In parentheses s = singlet, t = triplet, q = quartet, and m = multiplet whilst the numbers give the relative integrations.

Reactions of $[Fe_2(\eta\text{-dienyl})_2(CO)_4]$ with SbF_3

(1) A solution of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ (1 g) and SbF_3 (1 g) in n-butanol (50 ml) was refluxed for 1 h. The hot reaction mixture was filtered, the solvent removed at reduced pressure, and the residue recrystallized from acetone to give brown crystals of $[\{(\eta\text{-}C_5H_5)Fe(CO)_2\}_3SbF][Sb_2F_7]$ (Yield 19%) [$\nu(CO)$ = 1978 (5.8), 2008(sh), 2014(10), 2037(5.4); ^1H NMR = 5.41 (s)].

(2) (a) As for (1) but with a reaction time of 2 h to give brown crystals of $[\{(\eta\text{-}C_5H_5)Fe(CO)_2\}_6Sb_2O][Sb_2F_7]_2$ (Yield 20%) after recrystallization from acetone-methanol [$\nu(CO)$ = 1983(8.3), 2019(10), 2041(7.5); ^1H NMR = 5.54 (s)].

(b) If the $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$: SbF_3 mole ratios are varied the $[Sb_2F_7]^-$ anion in the product may be replaced by $[SbF_4]^-$ or $[Sb_5F_{17}]^{2-}$. Alternatively, the addition of excess $NaBF_4$, NH_4PF_6, or $NaBPh_4$ to the n-butanol solution after 2 h followed by heating for a further 1 h allows the isolation of the $[\{(\eta\text{-}C_5H_5)Fe(CO)_2\}_6Sb_2O]^{2+}$ cation as its $[BF_4]^-$, $[PF_6]^-$ or $[BPh_4]^-$ salts.

(3) (a) $[\{(\eta\text{-}MeC_5H_4)Fe(CO)_2\}_6Sb_2O]^{2+}[X]_2^-$ salts were obtained in the same way as their (η-C_5H_5) counterparts [see (2) above]. [X = SbF_4, $\nu(CO)$ = 1981(8.4), 2009(sh), 2016(10), 2036(7.5); ^1H NMR = 2.11 (s, 3), 5.41 (s, 4)].

(4) A 0.1 *M* solution of iodine in 55% aqueous hydriodic acid (50 ml) and

an aqueous suspension of [$\{(\eta$-$C_5H_5)Fe(CO)_2\}_6Sb_2O$][BF_4]$_2$ (1 g in 50 ml) was stirred for 2 h. The oily precipitate was filtered off and recrystallized from chloroform-methanol mixtures to give red-brown crystals of [$\{(\eta$-$C_5H_5)Fe(CO)_2\}_3SbI$][I_3] (yield 23%) [ν(CO) = 1987(10), 2018(sh), 2025(9.3), 2041(9.1); ^{1}H NMR = 5.52 (s)].

(5) [$\{(\eta$-$MeC_5H_4)Fe(CO)_2\}_2SbI$][I_3] was prepared in the same way as its (η-C_5H_5) counterpart in (4) [ν(CO) = 1983(7.8), 2011(sh), 2018(10), 2038(8.3); ^{1}H NMR = 2.18 (s), 5.42 (s)].

Reactions of [$Fe_2(\eta$-dienyl$)_2(CO)_4$] with AsF_3

(6) A solution of [$Fe_2(\eta$-$C_5H_5)_2(CO)_4$] (1 g) in AsF_3 (3 ml) was stirred at 50°C for 6 h. Removal of the excess AsF_3 at reduced pressure gave an oily residue. The addition of dry acetone (10 ml) gave yellow crystals of [$\{(\eta$-$C_5H_5)Fe(CO)_2\}_2AsF_2$][AsF_4]Me_2CO (yield 18%) which were quickly filtered off, washed with pentane, and dried [ν(CO) = 1995(9.9), 2029(10), 2045(9.8)].

(7) As for (6), but recrystallization of the residue from wet acetone gave yellow crystals of [$\{(\eta$-$C_5H_5)Fe(CO)_2\}_2As(OH)_2$][$AsF_4$] (yield 35%) [$\nu$(CO) = 1995(10), 2034(9.9), 2044(9.1)]. This compound was also obtained by allowing [$\{(\eta$-$C_5H_5)Fe(CO)_2\}_2AsF_2$][AsF_4] to stand in air for 2 days.

(8) A solution of [$Fe_2(\eta$-$MeC_5H_4)_2(CO)_4$] (1 g) in AsF_3 (3 ml) was stirred at 50° for 3 h. The excess AsF_3 was removed at reduced pressure and the residue quickly recrystallized from dry acetone to give very impure [$\{(\eta$-$MeC_5H_4)Fe(CO)_2\}_2AsF_2$][$AsF_4$] as yellow crystals (yield 10%).

(9) As for (8) but the residue left after removal of the excess AsF_3 was dissolved in hot methanol (50 ml). To this solution was added one of $NaBPh_4$ (2 g) in methanol (50 ml). The precipitate was recrystallized from acetone-methanol to give yellow crystals of [$\{(\eta$-$MeC_5H_4)Fe(CO)_2\}_2As(OMe)_2$][$BPh_4$] (Yield 18%) [$\nu$(CO) = 1997(10), 2036(10), 2047(sh); ^{1}H NMR = 1.94 (s), 3.28 (s), 5.40 (s), ~7.0 (m)]. Replacement of $NaBPh_4$ by NH_4PF_6 (2 g) allowed the isolation of [$\{\eta$-$MeC_5H_4)Fe(CO)_2\}_2As(OMe)_2$][$PF_6$].

(10) As for (8) but the reaction product left after removal of the AsF_3 was dissolved in ethanol (20 ml). Addition of a solution of $NaBPh_4$ (2 g) in ethanol (50 ml) followed immediately by cooling and filtration gave yellow crystals of [$\{(\eta$-$MeC_5H_4)Fe(CO)_2\}_2As(F)(OEt)$][$BPh_4$] (Yield 11%) [$\nu$(CO) = 1993(sh), 2001(9.9), 2022(sh), 2033(10)], but if the cooled solution was allowed to stand for 1 week at —20°C, the product was [$\{(\eta$-$MeC_5H_4)Fe(CO)_2\}_2As(OEt)_2$]-[$BPh_4$] (Yield 3%) [$\nu$(CO) = 1980(10), 2029(9.8); ^{1}H NMR = 1.11 (t, 3) 1.98 (s, 3), 3.80 (q, 2), 5.32 (s, 4), ~7.0 (m, 10)].

Reactions of [$Fe_2(\eta$-$C_5H_5)_2(CO)_4$] with organohaloarsines

(11) (a) A solution of [$Fe_2(\eta$-$C_5H_5)_2(CO)_4$] (2 g) and $PhAsCl_2$ (1 ml) in benzene (80 ml) was refluxed for 2 h. The precipitated orange solid was filtrated from the hot solution, and recrystallized from dichloromethane to give orange crystals of [$\{(\eta$-$C_5H_5)Fe(CO)_2\}_2As(Ph)Cl$][$AsCl_4$] (Yield 18%). [$\nu$(CO) in CH_2Cl_2 = 2001(sh), 2016(9.8), 2026(sh), 2043(9.3)].

The same product was obtained in ca. 16% yield when the above reaction mixture in dichloromethane (80 ml) was UV irradiated (Philips HPR 125 W lamp) at 25°C for 2 h.

(b) $NaBPh_4$ (2 g) in acetone (40 ml) was added to a solution of $[\{(\eta\text{-}C_5H_5)Fe(CO)_2\}_2As(Ph)Cl][AsCl_4]$ (0.5 g) in acetone (40 ml). The reaction mixture was filtered and the solvent removed at reduced pressure. The residue was recrystallized from methanol to give $[\{(\eta\text{-}C_5H_5)Fe(CO)_2\}_2As(Ph)Cl][BPh_4] \cdot 2\,MeOH$ as a yellow powder.

(12) $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ (1 g) and $MeAsCl_2$ (3 ml) were dissolved in dichloromethane (20 ml) and the whole irradiated at 25° C for 6 h using a Philips HPR 125 W lamp. The reaction mixture was filtered, cooled, and the deep yellow crystals filtered off. These analysed as $[\{(\eta\text{-}C_5H_5)Fe(CO)_2\}_2As(Me)Cl][MeAsCl_4]$ (Yield 25%) [ν(CO) 1989(9.8), 2018(10)].

(13) (a) In refluxing benzene (80 ml), $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ (2 g) and Me_2AsCl (1 ml) gave a yellow precipitate. After 4.5 h this was filtered off and recrystallized from dichloromethane to give yellow crystals of $[\{(\eta\text{-}C_5H_5)Fe(CO)_2\}_2AsMe_2]_2[AsCl_5]$ (Yield = 27%) [ν(CO) in CH_2Cl_2 = 1989(10), 2027(10), 2040(9.0); ^1H NMR = 0.96 (s), 4.60 (s)].

(b) The procedure described in (11b) was used to convert $[\{(\eta\text{-}C_5H_5)Fe(CO)_2\}_2AsMe_2]_2[AsCl_5]$ to $[\{(\eta\text{-}C_5H_5)Fe(CO)_2\}_2AsMe_2][BPh_4]$ as yellow crystals (Yield 71%).

(14) As for (13a) but with Me_2AsBr replacing Me_2AsCl and a reaction time of 3.5 h. Yellow crystals of $[\{(\eta\text{-}C_5H_5)Fe(CO)_2\}_2AsMe_2][Br_3]$ were obtained in 23% yield. [ν(CO) in CH_2Cl_2 = 1988(9.7), 2028(10), 2037(8.0); ^1H NMR = 1.24 (s, 5), 4.98 (s, 3)].

(15) As for (13a) but with Me_2AsI replacing Me_2AsCl. Yellow crystals of $[\{(\eta\text{-}C_5H_5)Fe(CO)_2\}_2AsMe_2][I] \cdot \frac{1}{2}\,CH_2Cl_2$ were obtained in 33% yield. [ν(CO) in CH_2Cl_2 = 1991(9.1), 2030(10), 2043(6.7); ^1H NMR in $CDCl_3$ = 1.90 (s, 3), 5.43 (s, 5)].

(16) As for (13a) but with Et_2AsBr (1.5 ml) replacing Me_2AsCl (1 ml). Yellow crystals of $[\{(\eta\text{-}C_5H_5)Fe(CO)_2\}_2AsEt_2][Br_3] \cdot \frac{1}{2}\,CH_2Cl_2$ were obtained in 13% yield. [ν(CO) in CH_2Cl_2 = 1986(9.4), 2026(10), 2039(6.4)].

(17) (a) A solution of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ (1 g) and chlorophenarsazine $[HN(C_6H_4)_2AsCl]$ (0.8 g) in xylene (50 ml) were refluxed for 5 min. A high yield of a crystalline solid was precipitated. Consistent analyses could not be obtained, but spectroscopic data indicated that it was $[\{(\eta\text{-}C_5H_5)Fe(CO)_2\}_2As(C_6H_4)_2NH][X]$ where X^- = $[AsCl_4]^-$ or $[As_2Cl_7]^-$ etc.

(b) The product from (7a) (0.35 g) was dissolved in methanol (25 ml) and a solution of $NaBPh_4$ (0.6 g) in methanol (25 ml) added. Orange crystals of $[\{(\eta\text{-}C_5H_5)Fe(CO)_2\}_2As(C_6H_4)_2NH][BPh_4]$ were obtained (Yield 45%). [ν(CO) = 1984(9.8), 2023(8.5), 2041(10)].

(18) (a) As for (17a) but with chlorophenarsazine replaced by chlorophenoxarsine $[O(C_6H_4)_2AsCl]$ and a reaction time of 1 h. The precipitated product analysed as $[\{(\eta\text{-}C_5H_5)Fe(CO)_2\}_2As(C_6H_4)_2O][AsCl_4]$ (Yield 8%) [ν(CO) = 1985(sh), 1998(10), 2027(10), 2048(9.8)].

(b) As for (17b) but with $[\{(\eta\text{-}C_5H_5)Fe(CO)_2\}_2As(C_6H_4)_2NH][X]$ replaced by $[\{(\eta\text{-}C_5H_5)Fe(CO)_2\}_2As(C_6H_4)_2O][AsCl_4]$. Yellow crystals of $[\{(\eta\text{-}C_5H_5)Fe(CO)_2\}_2As(C_6H_4)_2O][BPh_4]$ were obtained (Yield 2%) [ν(CO) = 1980(8.4), 1998(7.1), 2028(6.0), 2048(10)].

The products obtained are listed in Table 1 together with their analyses. Elemental analyses were determined in the Microanalytical Laboratory of the Chemistry Department, University College, Dublin.

TABLE 1

MELTING POINTS AND ANALYSES OF COMPOUNDS DESCRIBED IN THE TEXT

Compound [a]	M.p. [b]	Analyses [c] found (calcd.) (%)		
		C	H	F
$[\mathrm{M_3SbF}][\mathrm{Sb_2F_7}]$	160	24.0 (24.0)	1.7 (1.4)	14.0 (14.5)
$[\mathrm{M'_3SbF}][\mathrm{BF_4}]$	119—120	35.2 (36.0)	2.6 (2.7)	11.7 (11.9)
$[\{\mathrm{M_3Sb}\}_2\mathrm{O}][\mathrm{Sb_2F_7}]_2$	120 (d)	24.4 (24.1)	2.1 (1.6)	12.2 (12.7)
$[\{\mathrm{M'_3Sb}\}_2\mathrm{O}][\mathrm{SbF_4}]_2$	171 (d)	32.6 (32.2)	2.6 (2.3)	8.8 (8.5)
$[\{\mathrm{M_3Sb}\}_2\mathrm{O}][\mathrm{BPh_4}]_2$	224 (d)	55.1 (55.1)	3.6 (3.8)	0.0 (0.0)
$[\mathrm{M_3SbI}][\mathrm{I_3}]$	137—140	21.7 (21.9)	1.1 (1.3)	42.8 (43.8) [d]
$[\mathrm{M'_3SbI}][\mathrm{I_3}]$	134—136	23.6 (24.0)	1.6 (1.8)	42.3 (42.3) [d]
$[\mathrm{M_2AsF_2}][\mathrm{AsF_4}]\cdot\mathrm{Me_2CO}$	170 (d)	30.6 (30.2)	2.4 (2.3)	17.6 (16.9)
$[\mathrm{M_2As(OH)_2}][\mathrm{AsF_4}]$	150 (d)	27.6 (27.4)	2.0 (2.0)	12.3 (12.4)
$[\mathrm{M'_2As(OMe)_2}][\mathrm{BPh_4}]$	149—151	60.0 (60.1)	4.8 (4.7)	0.0 (0.0)
$[\mathrm{M'_2As(F)(OEt)}][\mathrm{BPh_4}]$	134—136	59.9 (60.0)	4.8 (4.6)	2.1 (2.3)
$[\mathrm{M'_2As(OEt)_2}][\mathrm{BPh_4}]$	153 (d)	60.3 (61.0)	4.9 (5.1	0.0 (0.0)
$[\mathrm{M_2As(Me)Cl}][\mathrm{MeAsCl_3}]$	156—159	28.4 (28.4)	2.4 (2.3)	20.7 (21.0) [e]
$[\mathrm{M_2As(Ph)Cl}][\mathrm{AsCl_4}]$	184—186	31.4 (31.5)	1.9 (2.0)	23.4 (23.3) [e]
$[\mathrm{M_2As(Ph)Cl}][\mathrm{BPh_4}]\cdot 2\,\mathrm{MeOH}$	150 (d)	59.9 (59.8)	4.7 (4.1)	
$[\mathrm{M_2AsMe_2}]_2[\mathrm{AsCl_5}]$	160 (d)	32.8 (32.5)	2.7 (2.7)	14.4 (15.2) [e]
$[\mathrm{M_2AsMe_2}][\mathrm{BPh_4}]$	132—134	62.1 (61.8)	4.7 (4.6)	
$[\mathrm{M_2AsMe_2}][\mathrm{Br_3}]$	135 (d)	27.5 (27.5)	2.2 (2.3)	33.4 (34.4) [f]
$[\mathrm{M_2AsMe_2}][\mathrm{I}]\cdot\frac{1}{2}\,\mathrm{CH_2Cl}$	180 (d)	31.5 (31.5)	2.6 (2.7)	20.1 (20.2) [d]
$[\mathrm{M_2AsEt_2}][\mathrm{Br_3}]\cdot\frac{1}{2}\,\mathrm{CH_2Cl_2}$	110 (d)	28.9 (28.9)	3.1 (2.7)	30.4 (31.2) [f]
$[\mathrm{M_2As(C_6H_4)_2NH}][\mathrm{BPh_4}]$	215 (d)	65.6 (65.5)	4.4 (4.3)	1.7 (1.5) [g]
$[\mathrm{M_2As(C_6H_4)_2O}][\mathrm{AsCl_4}]$	156 (d)	39.5 (38.3)	2.8 (2.2)	16.7 (17.4) [e]
$[\mathrm{M_2As(C_6H_4)_2O}][\mathrm{BPh_4}]$	205—208 (d)	65.3 (65.5)	4.1 (4.2)	0.0 (0.0) [e]

[a] M = $\{\mathrm{Fe}(\eta\text{-C}_5\mathrm{H}_5)(\mathrm{CO})_2\}$; M′ = $\{\mathrm{Fe}(\eta\text{-MeC}_5\mathrm{H}_4)(\mathrm{CO})_2\}$. [b] °C. Determined in sealed tubes. (d) = decomposition. [c] Found values with those calculated in parentheses. [d] I; [e] Cl; [f] Br; [g] N.

Results and discussion

All products from the reactions of SbF$_3$, AsF$_3$, RAsX$_2$ and R$_2$AsX (R = Me, Et, or Ph; X = Cl, Br, or I) with [Fe$_2$(η-dienyl)$_2$(CO)$_4$] (dienyl = C$_5$H$_5$ or MeC$_5$H$_4$) were air-stable crystalline solids with the exception of [{(η-dienyl)Fe(CO)$_2$}$_2$AsF$_2$][AsF$_4$] which hydrolysed rapidly. All were salts; their solutions in nitromethane conducted electricity. Typical values for Λ_M were 100.4 ohm^{-1} mol^{-1} cm^2 (solution concentration 0.43 × 10^{-3} *M*) for [{(η-C$_5$H$_5$)Fe(CO)$_2$}$_6$Sb$_2$O][Sb$_2$F$_7$]$_2$, 57.9 (0.462 × 10^{-3} *M*) for [{(η-MeC$_5$H$_4$)Fe(CO)$_2$}$_2$As(OMe)$_2$][BPh$_4$], and 80.2 (1.0 × 10^{-3} *M*) for [{(η-C$_5$H$_5$)Fe(CO)$_2$}$_2$As(Ph)Cl][AsCl$_4$].

The reaction of [Fe$_2$(η-dienyl)$_2$(CO)$_4$] with SbF$_3$ in refluxing butanol or xylene proceeded via an intermediate which was detectable by IR spectroscopy [ν(CO) = 2030 and 2070 cm^{-1}]. It was always present in small quantities only, and could not be isolated. The final products from these reactions were always salts which contained the [{(η-dienyl)Fe(CO)$_2$}$_3$SbX]$^+$ cations. Occasionally what appeared to be [{(η-dienyl)Fe(CO)$_2$}$_3$SbF]$^+$[Y]$^-$ derivatives were obtained but could only be distinguished by a fluorine analysis from the more usual products, the previously unreported [{(η-dienyl)Fe(CO)$_2$}$_3$Sb—O—Sb{Fe(η-dienyl)(CO)$_2$}$_3$]$^{2+}$[Y]$_2^-$. The infrared and proton NMR spectra of the two were similar.

The counteranions in the "normal" product could be $[SbF_4]^-$, $[Sb_2F_7]^-$ or $[Sb_5F_{17}]^{2-}$ depending on the amount of SbF_3 used and the (η-dienyl) ligand. These anions may be replaced readily by others such as $[BPh_4]^-$, $[BF_4]^-$ or $[PF_6]^-$.

The formulation of $[\{(\eta\text{-dienyl})Fe(CO)_2\}_3Sb{-}O{-}Sb\{Fe(\eta\text{-dienyl})(CO)_2\}_3]^{2+}$ as such rather than $[\{(\eta\text{-dienyl})Fe(CO)_2\}_3SbOH]^+$ rests on the absence of (a) IR absorption bands due to ν(OH) vibrations and (b) proton NMR resonances due to hydroxyl protons in the spectra of the salts. The alternative possibility of $[\{(\eta\text{-dienyl})Fe(CO)_2\}_3SbF]^+$ may be excluded by the absence of fluorine in those compounds where the counteranion is $[BPh_4]^-$ whereas the IR spectra in the ν(CO) region are virtually independent of anion. It seems reasonable to suggest that the fluoro-cations are the initial products of these reactions, but are hydrolysed during their further course. The source of the water may have been the solvent although we took care to dry this; it may have arisen from SbF_3-catalysed dehydration of n-butanol although we were not able to detect the by-products by GLC and in any event the reaction proceeds equally well in xylene; or it may have come from the pyrex glass flasks used for the reaction. This last is the most likely explanation (cf. ref. 8).

Although water hydrolysed the Sb—F bond to a Sb—O—Sb system, alcoholysis was not observed. Some acids reversed the hydrolysis so that aqueous HI converted $[\{(\eta\text{-dienyl})Fe(CO)_2\}_6Sb_2O]^{2+}$ to $[\{(\eta\text{-dienyl})Fe(CO)_2\}_3SbI]^+$ [7b]. A similar reaction took place with HBr, although a pure product could not be isolated, but not with aqueous hydrochloric acid or hydrofluoric acid. This behaviour is what one would expect from the relative susceptibilities of antimony trihalides to hydrolysis.

The products from the reactions of $[Fe_2(\eta\text{-dienyl})_2(CO)_4]$ with AsF_3 were all of the type $[\{(\eta\text{-dienyl})Fe(CO)_2\}_2AsX_2]^+[Y]^-$. The anion $[Y]^-$ was usually $[AsF_4]^-$ but it may be replaced readily by $[PF_6]^-$, $[BF_4]^-$, or $[BPh_4]^-$. The initial reaction products had X = F, but the As—F bonds were very susceptible to hydrolysis or alcoholysis so that it was only when dry acetone was used as the recrystallization solvent that $[\{(\eta\text{-}C_5H_5)Fe(CO)_2\}_2AsF_2][AsF_4] \cdot Me_2CO$ could be isolated and even this hydrolysed on standing in air. Product purification in wet acetone gave $[\{(\eta\text{-}C_5H_5)Fe(CO)_2\}_2As(OH)_2][AsF_4]$. Although we formulate the compound as such the only absorption band in its IR spectrum which could be assigned to ν(OH) is very weak and has a frequency of 3520 cm^{-1}. Consequently it is possible that this compound is of the type $[\{(\eta\text{-}C_5H_5)_2Fe_2(CO)_4AsO\}_n]^{n+}[AsF_4]_n^-$ with n = 2 or more and with As—O—As bridges. However IR and NMR spectra show that it is not previously reported $[(\eta\text{-}C_5H_5)_3Fe_3(CO)_5As_4O_5]^+[Y]^-$ [8].

If the crude product from the $[Fe_2(\eta\text{-}MeC_5H_4)_2(CO)_4]/AsF_3$ reaction is recrystallized from methanol in the presence of $NaBPh_4$, $[\{(\eta\text{-}MeC_5H_4)Fe(CO)_2\}_2As(OMe)_2][BPh_4]$ is obtained. If methanol is replaced by ethanol, alcoholysis is slower and $[\{(\eta\text{-}MeC_5H_4)Fe(CO)_2\}_2As(F)(OEt)][BPh_4]$ and $[\{(\eta\text{-}MeC_5H_4)Fe(CO)_2\}_2As(OEt)_2][BPh_4]$ are formed in turn.

Reactions of $RAsX_2$ and R_2AsX (R = Me, or Ph; R_2 = Me_2, Et_2, Ph_2, $HN(C_6H_4)_2$ or $O(C_6H_4)_2$; X = Cl, Br or I) with $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ gave salts containing the $[\{(\eta\text{-}C_5H_5)Fe(CO)_2\}_2As(R)(X)]^+$ and $[\{(\eta\text{-}C_5H_5)Fe(CO)_2\}_2AsR_2]^+$ cations. Compounds of a similar type have been obtained from the reaction of

$[Fe(\eta\text{-}C_5H_5)(CO)_2X]$ with diarsines, R_4As_2 [16]. Of particular interest with our products was the wide variety of counteranions which were formed in the reaction mixture. In some cases these were simple, e.g. $[I]^-$ from Me_2AsI, or even if they were more unusual were still explicable e.g. $[MeAsCl_3]^-$ arising from $[Cl]^-$ and $MeAsCl_2$. The others, $[AsCl_4]^-$, $[AsCl_5]^{2-}$ and $[Br_3]^-$, indicated that considerable rearrangement must have taken place in the reaction mixture despite the mild conditions. The IR and NMR spectra suggest considerable anion—cation interactions take place in solution for the $[\{(\eta\text{-}C_5H_5)Fe(CO)_2\}_2AsMe_2]$-$[X]$ derivatives as the $\nu(CO)$ frequencies vary markedly with the anion X^- in CH_2Cl_2 solution.

The compounds we report here have IR spectra in the $\nu(CO)$ region which are similar to those of related compounds of known structure such as $[\{(\eta\text{-}C_5H_5)Fe(CO)_2\}_3SbCl][FeCl_4]$ [5], $[\{(\eta\text{-}C_5H_5)Fe(CO)_2\}_2SbCl_2][Sb_2Cl_7]$ [16], and $[\{(\eta\text{-}C_5H_5)Fe(CO)_2\}_2SnCl_2]$ [17]. Consequently it is probable that in all of the cations there is pseudo-octahedral coordination about the iron atoms, distorted tetrahedral coordination about the antimony or arsenic atoms, and three Sb—Fe or two As—Fe covalent bonds. The proton NMR spectra are also consistent with such structures and are especially useful in the case of $[BPh_4]^-$ salts.

The formation of $[\{(\eta\text{-}C_5H_5)Fe(CO)_2\}_2AsF_2]^+$ may arise from the initial insertion of AsF_3 into the Fe—Fe bond of $[Fe_2(\eta\text{-dienyl})_2(CO)_4]$ followed by loss of F^-. However, the active species may be $[AsF_2]^+$ arising from the autoionization of AsF_3. The reaction is then directly comparable to that of SnF_2 with $[Fe_2(\eta\text{-dienyl})_2(CO)_4]$ [18]. A third alternative is scission of the Fe—Fe bond by AsF_3 to give $[(\eta\text{-dienyl})Fe(CO)_2AsF_2]$ and $[(\eta\text{-dienyl})Fe(CO)_2F]$ which then form $[\{(\eta\text{-dienyl})Fe(CO)_2\}_2AsF_2]^+[F]^-$. With pure AsF_3 as both reagent and solvent one of the first two possibilities is the more likely, but in the reactions involving R_2AsX or $RAsX_2$, the last is intrinsically more probable (cf. $SnCl_4$ and $[Fe_2(\eta\text{-dienyl})_2(CO)_4]$ [18]). The considerations which apply to the reactions of AsF_3 also apply to those of SbF_3, but here the more vigorous conditions required to bring about the insertion of SbF_3 or $[SbF_2]^+$ into the Fe—Fe bond may be sufficient to bring about the conversion of the bis-iron to the tris-iron derivative of antimony(V) (cf. the reaction of SnF_2 with $[Fe_2(\eta\text{-dienyl})_2(CO)_4]$ [18]).

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