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Preliminary communication

Iron carbonyl complexes of fluorocarbon-bridged di(tertiary arsines)

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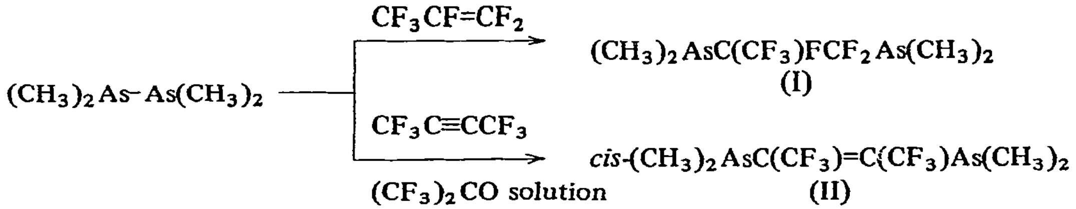
A few examples of the addition of olefins and acetylenes to the arsenic–arsenic bond of tetramethyldiarsine to give di(tertiary arsines) have been described[1]



(I)

(II)

This reaction has now been extended to a number of olefins to provide a range of potentially bidentate ligands including the compounds $(CH_3)_2AsCH_2CF_2As(CH_3)_2$ (III), and $(CH_3)_2AsCHFCF_2As(CH_3)_2$ (IV). This communication describes some of the reactions of these products with iron carbonyls.

The ligand II which is closely related to the versatile ffars, $(CH_3)_2As\overline{C{=}CAs(CH_3)_2CF_2C}F_2$, forms both $Fe(CO)_3$ and $Fe_2(CO)_6$ derivatives, whereas ffars forms ffars$Fe_2(CO)_6$, ffars$Fe(CO)_4$, ffars$Fe_2(CO)_8$, and ffars$Fe_3(CO)_{10}$ in which the ligand remains intact[2-4]. The chelate $Fe(CO)_3$ complex of II has no ffars analogue. In fact ffars shows a surprising reluctance to form chelate complexes with iron and ruthenium carbonyls without also utilizing the double bond of the bridging fluorocarbon group as in the complexes ffars$M_2(CO)_6$ (M = Ru, Fe)[3,5,6].

The $Fe_2(CO)_6$ complex of II has very similar spectroscopic properties to the ffars compounds indicating that the double bond of II is also participating in the bonding in spite of its not being present in a strained ring. This tendency of II to act as both a bidentate and tridentate ligand is unexpected in view of our experience with the related di(tertiary phosphines) $(C_6H_5)_2P\overline{C{=}CP(C_6H_5)_2(CF_2)_nC}F_2$ ($n = 1 - 3$) which indicates that the chelating tendency to form $Fe(CO)_3$ complexes increases as n increases (and ring strain decreases) and the tendency to form $Fe_2(CO)_6$ complexes decreases as n increases. In fact when $n = 3$ no $Fe_2(CO)_6$ derivative can be obtained [3,4,7]

The difference in properties between II and ffars is also seen in their reaction with $Fe(CO)_2(NO)_2$. A chelate $Fe(NO)_2$ derivative is formed by II yet ffars is only monodentate, giving ffars$Fe(CO)(NO)_2$.

Unlike ffars, II does not form a $Fe_3(CO)_{10}$ derivative, however the ligands I, III and IV do. The compound ffars$Fe_3(CO)_{10}$ has the ligand bridging the two equivalent iron atoms of the $Fe_3(CO)_{12}$ skeleton[2,8] having displaced two equatorial carbonyl groups. The Mössbauer spectrum of the ffars complex is only slightly different from that of the parent iron carbonyl[2,8], but the spectrum of the $Fe_3(CO)_{10}$ derivative of I is considerably different. It consists of four lines at -0.36, -0.05, +0.53, +1.07 mm•sec^{-1} at 80°K (with respect to sodium nitroprusside) of approximate relative area 1/2/1/2. This spectrum can best be interpreted in terms of the ligand displacing two carbonyl groups from one of the equivalent iron atoms of the $Fe_3(CO)_{12}$ skeleton. The Mössbauer parameters are listed in Table 1.

TABELE 1

ISOMER SHIFT (δ) AND QUADRUPOLE SPLITTING (Δ) DATA FOR DERIVATIVES OF $Fe_3(CO)_{12}$[a]

	δ(Δ)Fe^a	δ(Δ)Fe^b	δ(Δ)Fe^c
$(CO)_4\overline{Fe^{b}(CO)_3Fe^{a}(CO^{x})_2Fe}^{c}(CO)_3$	0.37(1.14)	0.30(0.12)	0.37(1.14)
$(CO)_4\overline{Fe^{b}(CO)_2Fe^{a}(CO^{x})_2Fe}^{c}(CO)_2$ffars	0.42(1.52)	0.28(0.14)	0.42(1.52)
$(CO)_4\overline{Fe^{b}(CO)_3Fe^{a}(CO^{x})_2Fe}^{c}(CO)(CH_3)_2AsCF(CF_3)CF_2As(CH_3)_2$	0.36(1.43)	0.24(0.58)	0.51(1.12)

[a] Values in mm•sec^{-1} at 80°K relative to sodium nitroprusside.
In the formulae $(CO^{x})_2$ indicates two bridging CO groups.

The Mössbauer data for the $Fe_3(CO)_{10}$ complexes of III and IV indicate that the former may be chelated like the complex of I and the latter may be bridged like ffars$Fe_3(CO)_{10}$. The infrared spectra of all the $Fe_3(CO)_{10}$ complexes show weak bands in the bridging CO region and the mass spectra show a parent ion with successive loss of ten carbonyl groups.

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