Journal of Organometallic Chemistry, 73 (1974) C53–C55

Preliminary communication

NOVEL CLEAVAGE PRODUCTS FROM THE REACTION OF A DITERTIARY ARSINE WITH $M_2(CO)_{10}$ (M = Mn OR Re)

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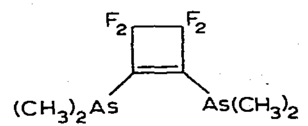
(Received April 2nd, 1974)

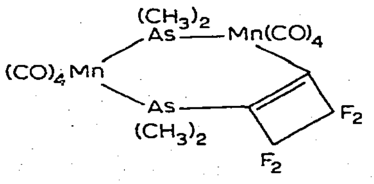
Summary

The ditertiary arsine *cis*-$(CH_3)_2AsC(CF_3)$=$C(CF_3)As(CH_3)_2$ reacts with $M_2(CO)_{10}$ to give compounds of formulae $C_{16}H_{18}As_3F_5O_6Mn_2$ and $C_{11}H_8AsF_6O_5Re$. The former contains a fluorinated π-allyl group bonded to one Mn atom and the latter a CH_2O fragment σ-bonded to rhenium.

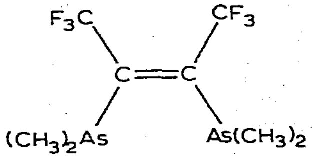
We have recently reported [1] that the reaction of the fluoroalicyclic ligand I with $Mn_2(CO)_{10}$ leads to two products; one in which the intact ligand is bridging the two metal atoms [2] and the other, an isomer, in which both a C—As and the Mn—Mn bonds have been cleaved so that the two metal atoms are bridged as shown in II [3]. The closely related ligand III [4] has a chemistry which is similar to I although some important differences do occur [5]. Thus it was of interest to study its reactions with $M_2(CO)_{10}$ (M = Mn or Re).



(I)



(II)



(III)

The manganese carbonyl and III when heated at 110° (4h, sealed tube) afford a yellow air stable product IV of formula $C_{16}H_{18}As_3F_5O_6Mn_2$ (23%) as determined by microanalysis and mass spectrometry, $\nu(CO)(C_6H_{12})$: 2036 m, 2009 vs, 1977 m, 1949 s, 1941 w, 1933 m cm^{-1}. The ^1H NMR spectrum shows six inequivalent As—CH_3 resonances. The ^{19}F NMR spectrum consists of a C—CF_3 doublet (42.5 ppm, $J(CF_3, F)$ 26 Hz) a broad C—F doublet (60.86 ppm, $J(F, F)$ 121 Hz) and another C—F doublet of quartets (67.78 ppm, $J(F, F)$ 121 Hz, $J(CF_3, F)$ 26 Hz)*. These data indicated the presence of a novel fluorine substituted π-allyl fragment in the molecule. This has been subsequently confirmed by an X-ray structural determination.

Crystals of IV are triclinic, space group $P\bar{1}$, a 9.580(4), b 15.279(6), c 9.292(3) Å, α 93.07(2), β 119.26(2), γ 82.80(2)°, U 1180.2 Å^3, $Z = 2$, D_m 2.05, D_c 2.02 g cm^{-3}. Independent intensity data were collected on a Picker 4-circle diffractometer by the θ—2θ scan technique, using Mo-K_α radiation (niobium filter). The structure was solved by conventional Patterson and Fourier methods on the basis of 2234 intensities having $\sigma(I)/I \leqslant 0.43$. Full-matrix least-squares refinement with all atoms anisotropic excepting the non-carbonyl carbon atoms gave R = 8.0%. The hydrogen atoms have not yet been included.

A view of the molecule showing all atoms except the CH_3 groups is given in Fig. 1. The coordination around Mn(1) is closely octahedral with the three As atoms *cis* to each other. The coordination around Mn(2) is distorted octahedral with the π-allyl system formed by C(11), C(12), and C(16) occupying two adjacent positions. Table 1 gives some important distances and angles.

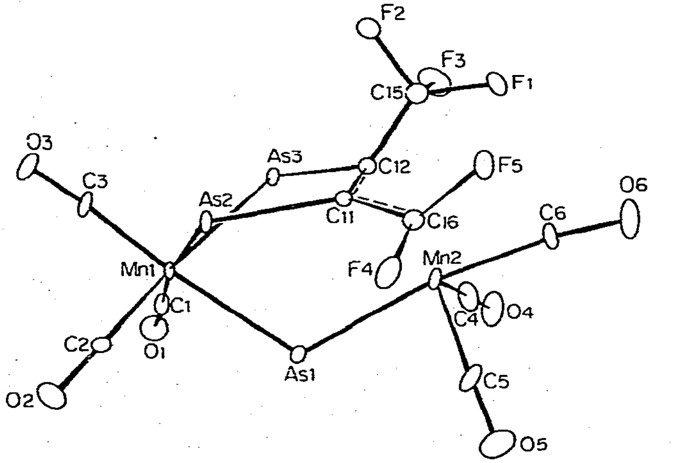


Fig. 1. The structure of IV. All atoms except the two CH_3 groups on each arsenic are shown.

TABLE 1

C(16)—C(11)	1.38(4) Å	C(12)—C(11)—C(16)	122(2)°
C(11)—C(12)	1.40(4)	As(2)—C(11)—C(16)	122(1)
C(12)—C(15)	1.45(4)	As(2)—C(11)—C(12)	116(1)
Mn(2)—C(11)	2.07(3)	C(15)—C(12)—C(11)	121(2)
Mn(2)—C(12)	2.13(3)	As(3)—C(12)—C(11)	113(1)
Mn(2)—C(16)	2.09(3)	As(3)—C(12)—C(15)	113(1)
Mn(2)—C(12)—C(11)	68(1)°	F(4)—C(16)—F(5)	101(2)
Mn(2)—C(11)—C(12)	73(1)	C(11)—C(16)—F(5)	126(2)
Mn(2)—C(11)—C(16)	72(1)	C(11)—C(16)—F(4)	119(2)
Mn(2)—C(16)—C(11)	70(1)		

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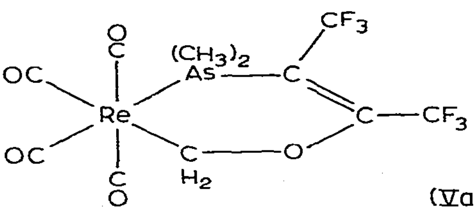
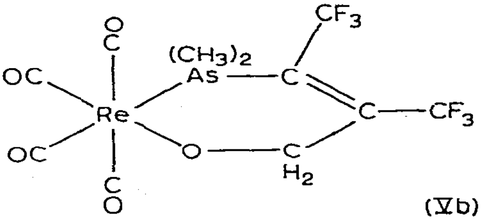
* ^1H chemical shifts are downfield from TMS, ^{19}F are upfield from $CFCl_3$.

The π-allyl group is somewhat distorted from ideal geometry. This is seen particularly in the angles about C(12) and C(16).

Reaction of III with $Re_2(CO)_{10}$ on ultraviolet irradiation (C_6H_6 solution) affords a different type of product. It is an orange solid V of formula $C_{11}H_8AsF_6O_5Re$ (22%) as determined by microanalysis and mass spectrometry. The infrared spectrum, $\nu(CO)(C_6H_{12})$: 2100 m, 2021 s, 1995 s(br), 1981 vs cm^{-1}, indicates a $Re(CO)_4$ fragment together with a C=C group (1608 cm^{-1}). The NMR spectra are as follows: ^{19}F (CH_2Cl_2), two quartets (53.2 and 59.1 ppm, $J(CF_3, CF_3)$ 12.4 Hz); ^1H ($CDCl_3$), singlet at 2.13 ppm with a shoulder on the low field side at 100 MHz. These data best fit the structures Va or Vb. Addition of the shift reagent $Eu(FOD)_3$* to a solution of V separated the CH_2 resonance from the $As(CH_3)_2$ signal confirming its presence. This also confirmed the presence of the oxygen atom since it is our experience that terminal carbonyl groups do not interact with shift reagents. Under high resolution the low field ^{19}F quartet is split further because of coupling to the $As(CH_3)_2$ group [6] but the high field quartet shows no triplet structure expected for Vb. Thus we prefer Va.



(Va)



(Vb)

These structures provide further examples of unusual ligand reactions which are not confined to fluorocarbon bridged donors [7]. The origin of the CH_2 group in V is unknown but it does not come from the solvent as the identical product was produced using benzene-d_6.

Acknowledgments

We are grateful to the National Research Council of Canada for financial support of this work in the form of operating grants to W.R.C. and F.W.B.E. and scholarships to L.M.

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*FOD = heptafluorodimethyloctanedionate.