

Stereochemistry of the MX_4Y System (M = Metal; X = Unidentate, Y = Bidentate Ligand): Crystal Structure of Tetrachloro-[1,2-bis(dimethylarsino)-3,3,4,4-tetrafluorocyclobut-1-ene]rhenium(IV)

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The title compound has been prepared and its crystal structure determined by the heavy-atom method from diffractometer data; it was refined by full-matrix least-squares to R 0.045 (949 independent observed reflections). Crystals are monoclinic, space group $P2_1$, $a = 8.834(2)$, $b = 16.090(4)$, $c = 6.596(1)$ Å, $\beta = 109.78(1)^\circ$, $Z = 2$.

Mean distances are: $Re^{IV}-As$ 2.560(4), $Re^{IV}-Cl$ 2.32(1) Å. The geometry is considerably distorted from octahedral; this is generally true for $[M(\text{bidentate})(\text{monodentate})_4]^{2\pm}$ compounds and a repulsion model has been developed to account for this.

THE ligand 1,2-bis(dimethylarsino)-3,3,4,4-tetrafluorocyclobut-1-ene, $(CF_2)_2C_2(AsMe_2)_2$, has a relatively large $As \cdots As$ distance or 'bite', and in all complexes so far structurally characterized behaves as a bridging bidentate ligand. Isolation and characterization of the title compound suggested the possibility of its existence as a monomer with a bidentate ligand and, as part of our studies in the stereochemical conse-

quences of bidentate ligands of large and small bites, the structure was determined in anticipation of an extreme example. An electron pair repulsion model has been developed for the MX_4Y system and is presented here.

CRYSTALLOGRAPHY

A single compact polyhedral crystal, approximated to a sphere of diameter 0.15 mm for absorption-correction

purposes, was used for data collection. Unit-cell dimensions were obtained by a least-squares fit of 15 reflections (2θ ca. 20–30°) centred in the counter aperture of a Syntex

Publication No. SUP 21055 (4 pp., 1 microfiche).^{*} Positional parameters are shown in Table 1, and bond lengths and angles in Table 2.

TABLE 1

Atomic fractional co-ordinates (a decimal point precedes x , y , and z) and thermal parameters ($\times 10^3$), with least-squares estimated standard deviations in parentheses

| Atom | x | y | z | U_{11} | U_{22} | U_{33} | U_{12} | U_{13} | U_{23} |
|-------|---------|---------|-----------|----------|----------|----------|----------|----------|----------|
| Re | 5839(2) | 5000(—) | 8010(2) | 28.2(9) | 26.7(9) | 33.8(9) | 1.4(11) | −0.4(7) | 2(3)·11 |
| Cl(1) | 330(1) | 486(1) | 547(2) | 41(6) | 93(14) | 60(7) | −5(9) | −14(5) | −1(9) |
| Cl(2) | 661(2) | 6294(7) | 713(2) | 87(9) | 17(6) | 82(9) | −2(6) | 14(7) | 13(6) |
| Cl(3) | 702(1) | 4292(8) | 582(2) | 62(7) | 46(6) | 53(7) | −9(6) | 19(6) | −9(6) |
| Cl(4) | 488(1) | 5526(8) | 059(2) * | 62(8) | 52(8) | 67(8) | 14(6) | 24(6) | 0(7) |
| As(1) | 8647(4) | 4950(4) | 0881(6) * | 27(2) | 37(3) | 35(2) | −4(3) | 2(2) | 0(3) |
| As(2) | 5463(5) | 3541(3) | 9310(7) | 29(3) | 31(3) | 37(3) | −1(2) | 4(2) | 1(2) |

| Atom | x | y | z | U | Atom | x | y | z | U |
|------|----------|--------|----------|----------|------|----------|--------|----------|--------|
| C(1) | 045(5) * | 501(5) | 986(6) | 57(11) † | C(7) | 844(5) | 262(3) | 282(7) * | 43(11) |
| C(2) | 919(6) | 575(3) | 330(8) * | 58(13) | C(8) | 750(5) | 330(3) | 139(6) * | 38(10) |
| C(3) | 396(5) | 336(3) | 074(6) * | 39(10) | F(1) | 121(3) * | 302(2) | 290(4) * | 60(7) |
| C(4) | 490(5) | 263(3) | 717(7) | 45(11) | F(2) | 045(3) * | 336(2) | 559(4) * | 67(8) |
| C(5) | 875(4) | 388(2) | 211(6) * | 29(9) | F(3) | 802(4) | 229(2) | 428(5) * | 86(9) |
| C(6) | 991(5) | 323(2) | 357(6) * | 33(10) | F(4) | 871(3) | 197(2) | 159(5) * | 75(8) |

* Add 1. † Isotropic thermal parameters.

$P\bar{1}$ diffractometer. A unique data set in the range $2\theta < 100^\circ$ was collected by a conventional 2θ — θ scan; 957 reflections were obtained of which 949, having $I > \sigma(I)$, were considered observed and used with unit weights in the structure solution and refinement. All data processing and computation was done by use of a local version of the 'X-Ray '72' programme system on the CDC 6200 computer at this University.¹

Crystal Data.— $C_8H_{12}As_2Cl_4F_4Re$, $M = 662.0$, Monoclinic, $a = 8.834(2)$, $b = 16.090(4)$, $c = 6.596(1)$ Å, $\beta = 109.78(1)^\circ$, $U = 882.2(3)$ Å³, $D_m = 2.47$ (floatation), $Z = 2$, $D_c = 2.49$, $F(000) = 610$, Cu- $K\alpha$ radiation, nickel filtered, $\lambda = 1.5418$ Å; $\mu(\text{Cu-}K\alpha) = 235$ cm^{−1}. Space group $P2_1$ (No. 4, C_2^2).

Intensity statistics suggested the space group to be $P2_1$ rather than the alternative $P2_1/m$ (No. 11, C_2^2h) with equivalent systematic absences: $\{0k0\}$ $k = 2n + 1$. Successful solution of the structure (by the heavy-atom method) confirmed this choice. Final refinement stages were by full-matrix least-squares, with anisotropic thermal parameters for rhenium, arsenic, and chlorine of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}k^2b^*c^*)]$. Neutral atom scattering factors were used,² those for rhenium, arsenic, and chlorine being corrected for the effects of anomalous dispersion ($\Delta f'$, $\Delta f''$).³ Data were corrected for effects of absorption but not extinction. In the final cycle of refinement, no parameter shift was $> 0.02\sigma$ and a difference map showed no significant features. The final R was 0.045, $R' \{ = [\Sigma(|F_o| - |F_c|)^2 / \Sigma|F_o|^2]^{1/2} \}$ being 0.070 for the preferred hand.

Structure factor tables are given in Supplementary

* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

¹ 'X-Ray '72' program system, Technical Report TR 192, Computer Science Centre, University of Maryland, U.S.A., June 1972.

TABLE 2

Bond lengths (Å) and angles ($^\circ$), with least-squares estimated standard deviations in parentheses

| (a) Rhenium environment | | | |
|-------------------------|----------|----------------|----------|
| Re—Cl(1) | 2.31(1) | Cl(1)—Re—Cl(2) | 101.4(6) |
| Re—Cl(2) | 2.32(1) | Cl(1)—Re—Cl(3) | 91.9(5) |
| Re—Cl(3) | 2.35(1) | Cl(1)—Re—Cl(4) | 93.5(5) |
| Re—Cl(4) | 2.30(1) | Cl(1)—Re—As(1) | 172.7(5) |
| Re—As(1) | 2.562(4) | Cl(1)—Re—As(2) | 87.2(5) |
| Re—As(2) | 2.559(5) | Cl(2)—Re—Cl(3) | 93.0(5) |
| | | Cl(2)—Re—Cl(4) | 93.8(5) |
| | | Cl(2)—Re—As(1) | 85.5(3) |
| Cl(3)—Re—Cl(4) | 170.3(4) | Cl(2)—Re—As(2) | 171.0(3) |
| Cl(3)—Re—As(1) | 85.3(3) | Cl(4)—Re—As(1) | 88.4(3) |
| Cl(3)—Re—As(2) | 84.1(3) | Cl(4)—Re—As(2) | 88.1(3) |
| As(1)—Re—As(2) | 85.8(2) | | |

| (b) Ligand | | | |
|----------------|---------|-----------------|-----------|
| As(1)—C(1) | 1.93(5) | C(1)—As(1)—C(2) | 104(2) |
| As(1)—C(2) | 1.98(5) | C(1)—As(1)—C(5) | 105(2) |
| As(1)—C(5) | 1.89(4) | C(1)—As(1)—Re | 116.5(11) |
| As(2)—C(3) | 1.89(5) | C(2)—As(1)—Re | 119(1) |
| As(2)—C(4) | 1.98(4) | C(2)—As(1)—C(5) | 106(2) |
| As(2)—C(8) | 1.90(4) | C(3)—As(2)—C(4) | 101(2) |
| C(5)—C(8) | 1.39(5) | C(3)—As(2)—C(8) | 105(2) |
| C(5)—C(6) | 1.54(5) | C(3)—As(2)—Re | 120(1) |
| C(6)—C(7) | 1.58(6) | C(4)—As(2)—Re | 118(1) |
| C(7)—C(8) | 1.51(6) | C(4)—As(2)—C(8) | 108(2) |
| C(6)—F(1) | 1.41(5) | C(5)—As(1)—Re | 104(1) |
| C(6)—F(2) | 1.27(5) | C(8)—As(2)—Re | 103(1) |
| C(7)—F(3) | 1.26(6) | As(1)—C(5)—C(8) | 122(2) |
| C(7)—F(4) | 1.39(6) | As(2)—C(8)—C(5) | 124(3) |
| C(5)—C(6)—F(1) | 114(3) | As(1)—C(5)—C(6) | 144(3) |
| C(5)—C(6)—F(2) | 119(3) | As(2)—C(8)—C(7) | 142(3) |
| C(7)—C(6)—F(1) | 115(3) | C(6)—C(5)—C(8) | 93(3) |
| C(7)—C(6)—F(2) | 114(8) | C(7)—C(8)—C(5) | 94(3) |
| C(6)—C(7)—F(3) | 117(3) | C(5)—C(6)—C(7) | 86(3) |
| C(6)—C(7)—F(4) | 112(4) | C(8)—C(7)—C(6) | 87(3) |
| C(8)—C(7)—F(3) | 123(4) | F(1)—C(6)—F(2) | 108(3) |
| C(8)—C(7)—F(4) | 110(3) | F(3)—C(7)—F(4) | 107(4) |

² D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

³ D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

DISCUSSION

The unit cell (Figure 1) comprises discrete molecules of the complex, the molecular symmetry being a good approximation to C_{2v} . Chemical evidence⁴ indicates

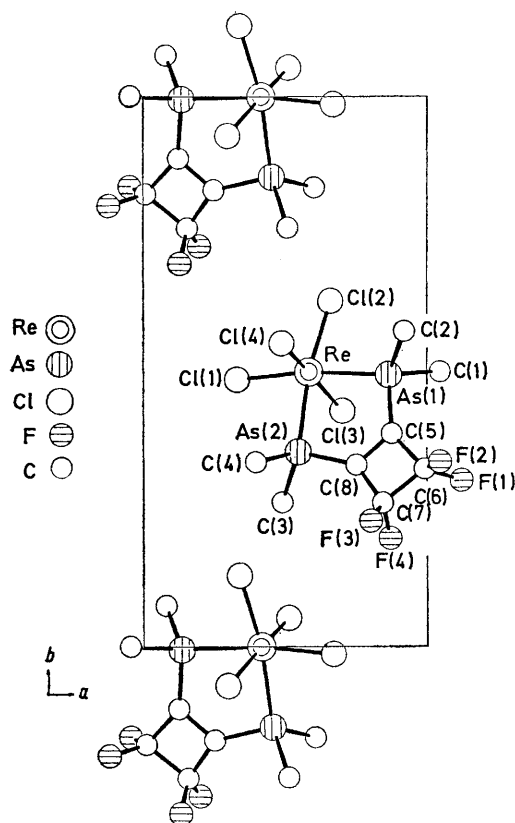


FIGURE 1 Unit-cell contents, projected down c^*

that $C_4F_4(AsMe_2)_2$ can function as a uni- or a bi-dentate ligand, or, by utilising the C=C double bond, a terdentate ligand.⁵ Its large 'bite', arising from the large As-C(ring) distances and the large exocyclic angles, results in the ligand bridging two metal atoms in all cases in which bidentate co-ordination has been structurally characterised.⁶⁻¹³ The present complex is the first whose structure has been characterised in which the ligand acts as a bidentate chelate.

The $Re^{IV}-As$ distance (mean 2.560 Å) appears to be the first $Re-As$ distance established crystallographically. The $Re-Cl$ distances do not differ significantly and the mean $Re^{IV}-Cl$ distance [2.32(1) Å] is similar to or slightly shorter than that found in the $ReCl_6^{2-}$ anion

⁴ W. R. Cullen, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 323.

⁵ F. W. B. Einstein and J. Trotter, *J. Chem. Soc. (A)*, 1967, 824.

⁶ P. J. Roberts, B. R. Penfold, and J. Trotter, *Inorg. Chem.*, 1970, **9**, 2137.

⁷ P. J. Roberts and J. Trotter, *J. Chem. Soc. (A)*, 1970, 3246.

⁸ J. P. Crow, W. R. Cullen, F. L. Hou, L. Y. Y. Chan, and F. W. B. Einstein, *Chem. Comm.*, 1971, 1229.

⁹ P. J. Roberts and J. Trotter, *J. Chem. Soc. (A)*, 1971, 1479.

[2.35(2) Å].¹⁴ The opposed pair of $Re-Cl$ bonds are tilted backwards, slightly towards the ligand [$Cl(3)-Re-Cl(4)$ 170.3(4)°], and the angle between the pair of equatorial chlorines is opened up to 101.4(6)°. The equation of the least-squares plane, calculated in the frame $X = ax + cz \cos \beta$, $Y = by$, $Z = cz \sin \beta$ takes the form $-0.6297X + 0.3967Y + 0.6679Z = 4.389$, for the $ReAs_2$ system; deviations (Å) are: $Cl(1)$ -0.086, $Cl(2)$ -0.089, $C(5)$ -0.06, $C(8)$ -0.13, $C(6)$ -0.30, and $C(7)$ -0.30, indicating dihedrals between the $Re, Cl(1), Cl(2)$ plane, the $ReAs_2$, and the As_2C_4 ligand planes.

The stereochemical effect of introducing a bidentate ligand into the co-ordination sphere of a metal complex can be predicted by summing the repulsion energy between individual donor atoms (or alternatively between the valence-shell electron pairs), but omitting that between the two donor atoms of the bidentate ligand, which is assumed to form a rigid chelate ring. The procedure is the same as that used for previous calculations.¹⁵

The stereochemistry of the system is shown in Figure 2. The bidentate ligand AB and the four unidentate ligands C, D, E, and F lie on the surface of a sphere of unit radius, their positions being given by the spherical co-ordinates ϕ_i and θ_i . The axes are defined by placing the bidentate ligand AB symmetrically across the 'North pole' at ϕ 0, with the 'longitudes' given by θ_A 0°, θ_B 180°. The angle ϕ_i is defined as the

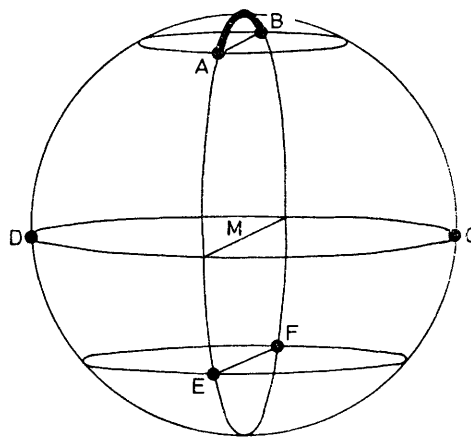


FIGURE 2 General stereochemistry of $[MX_4Y]^\pm$ ($X =$ unidentate, $Y =$ bidentate)

angle between the $M-i$ bond and the axis passing through the metal atom and the mid-point of AB. The 'longitude' θ_i is defined as the angle between the

¹⁰ W. Harrison and J. Trotter, *J. Chem. Soc. (A)*, 1971, 1607.

¹¹ F. W. B. Einstein and R. D. G. Jones, *J. Chem. Soc. (A)*, 1971, 3359.

¹² F. W. B. Einstein and R. D. G. Jones, *Inorg. Chem.*, 1972, **11**, 395.

¹³ L. Y. Y. Chan and F. W. B. Einstein, *J.C.S. Dalton*, 1973, 111.

¹⁴ E. Adam and T. N. Margulis, *Inorg. Chem.*, 1967, **6**, 210.

¹⁵ D. L. Kepert, *J.C.S. Dalton*, 1974, 617.

M,A,B plane and the plane incorporating M, *i*, and the mid-point of AB.

The 'normalised bite' of the bidentate ligand is defined by $b = AB/MA = AB/MB$.

Although the calculations were carried out with all angular co-ordinates able to vary independently, for this particular stoichiometry it was found that the stereochemistry corresponding to the single minimum on the potential-energy surface always contained the two mirror planes shown in Figure 2, *i.e.* $\phi_C = \phi_D$, $\phi_E = \phi_F$, $\theta_C = 90^\circ$, $\theta_D = 270^\circ$, $\theta_E = 0^\circ$, and $\theta_F = 180^\circ$.

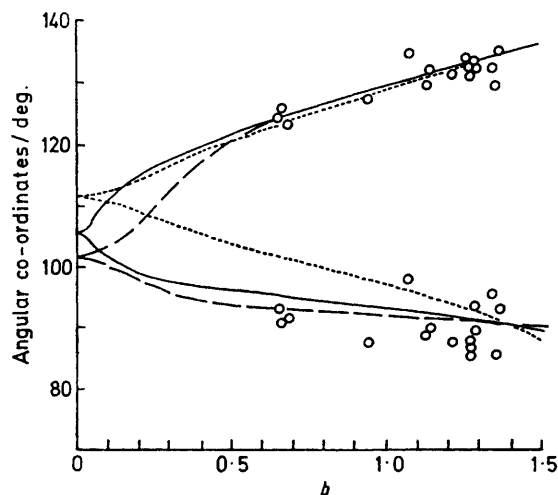


FIGURE 3 Angular co-ordinates for MX_4Y as a function of normalised bite, b : dotted line, $n = 1$, full line $n = 6$, broken line $n = 12$. Open circles denote the co-ordinates of the compounds listed in Table 3

The variation of the two remaining variables ϕ_C and ϕ_E with normalised bite b is shown in Figure 3. The three sets of curves correspond to values for the exponent n in the repulsion energy term of $n = 1, 6$, and 12 , respectively. These curves cross at $b = 2^{1/2}$, $\phi_C = 90^\circ$, $\phi_E = 135^\circ$, corresponding to a regular octahedron. The potential-energy minima are relatively insensitive to the variation of ϕ_C with n . As the bite approaches zero, ϕ_C approaches ϕ_E with the formation of a five-coordinate square pyramid, with the bidentate ligand AB at the apex.

Structural parameters for compounds of the type $[MX_4Y]^{z\pm}$ ($M = \text{metal}$; $X = \text{unidentate}$, $Y = \text{bidentate ligand}$), restricted for simplicity to the case of those with four identical unidentate ligands, are listed in Table 3, and are also shown in Figure 3. The agreement is satisfactory, considering the different natures of the donor atoms of the bi- and of the uni-dentate ligands.

EXPERIMENTAL

Preparation of Tetrachloro-[1,2-bis(dimethylarsino)-3,3,4,4-tetrafluorocyclobut-1-ene]rhenium(IV).—*Method* (1). Commercial grade rhenium pentachloride (1 g) dissolved in

deoxygenated dry carbon tetrachloride under nitrogen was added with stirring to the ligand (0.6 g) in carbon tetrachloride. The yellow-brown solution turned green, and after stirring for 1 h the complex was deposited as a light

TABLE 3

Stereochemical parameters for $[MX_4Y]^{z\pm}$

| | b | ϕ_C | ϕ_E |
|---|--------|----------|----------|
| $[Mn(Me_2As-CF_2-CHCl-CF_2-AsMe_2)(CO)_4]^a$ | 1.37 | 92.7 | 135.1 |
| $[Re\{C_4F_4(AsMe_2)_2\}Cl_4]^b$ | 1.36 | 85.2 | 129.3 |
| $[Cr\{C_4Me_4H_2(AsMe_2)_2\}(CO)_4]^c$ | 1.35 | 95.4 | 132.4 |
| $[Fe\{C_6H_4(NH)_2\}(CN)_4]^d$ | 1.29 | 93.2 | 133.2 |
| $[Mn(C_6H_4-CH_2-NMe_2)(CO)_4]^e$ | 1.29 | 89.2 | 133.5 |
| $[Mn(C_6H_4-CH-NPh)(CO)_4]^f$ | 1.28 | 87.5 | 134.1 |
| $[Si(bipy)F_4]^g$ | 1.28 | 85.3 | 131.3 |
| $[Ge(bipy)F_4], MeNO_2^g$ | 1.28 | 86.8 | 132.1 |
| $[Sn(bipy)F_4], MeNO_2^g$ | 1.22 | 87.2 | 131.4 |
| $[Co(CO)_3(NH_3)_4]Br^h$ | 1.15 | 89.4 | 132.0 |
| $[Co(CO)_3(C_2H_5N)_4]ClO_4 \cdot H_2O^i$ | 1.14 | 88.8 | 129.5 |
| $[W\{N_4P_4(NMe_2)_8\}(CO)_4]^j$ | 1.08 | 97.7 | 134.7 |
| $[Co(NO)_3(C_4H_8N_2)_4](NO)_3 \cdot \frac{1}{2}EtOH^k$ | 0.95 | 87.1 | 127.2 |
| $[Fe(C_2F_4)(CO)_4]^l$ | (0.77) | (91) | (128) |
| $[Fe(C_2H_4)(CO)_4]^m$ | (0.69) | | (127) |
| <i>vac</i> - $[Fe(HO_2C-CH:CH-CO_2H)(CO)_4]^n$ | 0.69 | 90.9 | 123.2 |
| $[Fe(CH_2:CH-CN)(CO)_4]^o$ | 0.67 | 90.5 | 125.9 |
| (-)- $[Fe(HO_2C-CH:CH-CO_2H)(CO)_4]^p$ | 0.66 | 92.8 | 124.5 |

^a I. W. Nowell and J. Trotter, *J.C.S. Perkin II*, 1972, 2378.

^b This work. ^c F. W. B. Einstein and R. D. G. Jones, *Inorg. Chem.*, 1973, **12**, 1148. ^d G. G. Christoph and V. L. Goedken, *J. Amer. Chem. Soc.*, 1973, **95**, 3869. ^e R. G. Little and R. J. Doedens, *Inorg. Chem.*, 1973, **12**, 844. ^f R. G. Little and R. J. Doedens, *ibid.*, 1973, **12**, 840. ^g A. D. Adley, P. H. Bird, A. R. Fraser, and M. Onyszczuk, *ibid.*, 1972, **11**, 1402. ^h M. R. Snow, *Austral. J. Chem.*, 1972, **25**, 1307; B. A. Barclay and B. F. Hoskins, *J. Chem. Soc.*, 1962, 586. ⁱ K. Kaas and A. B. Sørensen, *Acta Cryst.*, 1973, **B29**, 113. ^j H. P. Calhoun, N. L. Paddock, and J. Trotter, *J.C.S. Dalton*, 1973, 2708. ^k F. Akhtar, F. Huq, and A. C. Skapski, *ibid.*, 1972, 1353. ^l Gas-phase electron-diffraction study: B. Beagley, D. G. Schmidling, and D. W. J. Cruickshank, *Acta Cryst.*, 1973, **B29**, 1499. ^m Gas-phase electron-diffraction study: M. I. Davis and C. S. Speed, *J. Organometallic Chem.*, 1970, **21**, 401. ⁿ C. Pedone and A. Sirigu, *Acta Cryst.*, 1967, **23**, 759. ^o A. R. Luxmoore and M. R. Truter, *ibid.*, 1962, **15**, 1117. ^p Three independent molecules in the unit cell; C. Pedone and A. Sirigu, *Inorg. Chem.*, 1968, **7**, 2614.

green gelatinous solid, and was washed with carbon tetrachloride, and dried *in vacuo* (Found: C, 14.6; H, 2.0; Cl, 21.7; F, 11.3. $C_8H_{12}As_2Cl_4F_4Re$ requires C, 14.5; H, 1.80; Cl, 21.4; F, 11.5%).

Method (2). Potassium perrhenate (1 g), hydrochloric acid (3 g), and hypophosphorous acid (50%, 1 g) were added to ethanol (50 ml) and water (15 ml), and the perrhenate dissolved with heating. The ligand (2.34 g) was then added and the solution heated under reflux for 8 h. Addition of perchloric acid to the filtered brown solution yielded a brown solid, which was dried and recrystallised from nitromethane. Small yellow crystals of $[ReCl_2\{C_4F_4(AsMe_2)_2\}_2]ClO_4$ (Found: C, 19.0; H, 2.5; As, 28.3; Cl, 9.1; F, 13.7. $C_{16}H_{24}As_2Cl_3F_8O_4Re$ requires C, 18.8; H, 2.3; As, 29.2; Cl, 10.3; F, 14.8%) were mechanically separated from the green crystalline product (Found: C, 14.8; H, 1.8; As, 22.2; Cl, 20.6; F, 11.6. $C_8H_{12}As_2Cl_4F_4Re$ requires C, 14.5; H, 1.8; As, 22.6; Cl, 21.4; F, 11.5%).

The conductivity of a 10^{-3} M-solution in acetonitrile was $17 \text{ cm}^2 \text{ ohm}^{-1} \text{ mol}^{-1}$, corresponding to a nonelectrolyte.¹⁶ The visible spectrum in acetonitrile showed bands ($\epsilon \times 10^3$ in parentheses) at 29,900 (2.0), 26,100 (6.2), and 43,000 cm^{-1} (6.4); μ_{eff} (room temperature) 2.97 B.M.

This work is partly supported by the Australian Research Grants Committee.

[4/649 Received, 1st April, 1974]

¹⁶ W. J. Geary, *Co-ordination Chem. Rev.*, 1971, **7**, 81.