Ruthenium Complexes containing Group 5B Donor Ligands. Part 5.[1] Synthesis and Crystal and Molecular Structure of Acetone(carbonyl)-chloro(trichlorostannio)bis(triphenylphosphine)ruthenium(II)–Acetone (1/1)

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The lemon-yellow crystals (1) obtained by reaction of the red ' carbonyl-containing' ruthenium solution with $SnCl_2$ and PPh_3 in acetone have been shown to be $[RuCl(SnCl_3)(CO)(PPh_3)_2(OCMe_2)]\cdot Me_2CO$ and not $[Ru_2Cl_3(SnCl_3)(CO)_2(PPh_3)_3(OCMe_2)_2]$ (3) as previously suggested. The crystals are monoclinic, space group $P2_1/c$ with $a = 11.950(3)$, $b = 14.988(3)$, $c = 24.916(2)$ Å, and $\beta = 92.51(1)°$. The structure has been solved with 3 601 diffractometer data and refined to R 0.037. It is, however, possible to obtain (3) by warming (1) in benzene, but it readily loses $SnCl_2$ to give some $[(Ph_3P)(OC)ClRuCl_3Ru(CO)(PPh_3)_2]$.

OVER 10 years ago one of us[2] reported that the reaction of the well known ' carbonyl-containing ' red solution (*i.e.* ' $RuCl_3\cdot xH_2O$ ' in ethanol treated with CO for 5 h) with a mixture of anhydrous tin(II) chloride and triphenylphosphine in the presence of acetone gave a small yield of lemon-yellow crystals (1). On the basis of full elemental analyses (C, H, Cl, O, and Sn) and i.r. studies [ν(CO) at 1 957 cm^{-1} (Nujol); 1 701 and 1 661 cm^{-1} (acetone)] this complex was tentatively formulated as $[Ru_2Cl_3(SnCl_3)(CO)_2(PPh_3)_3(OCMe_2)_2]$. In the absence of acetone only a mixture of products was formed and attempts to separate these by recrystallisation resulted in loss of $SnCl_2$ and the formation of *cis*-$[RuCl_2(CO)_2(PPh_3)_2]$.

Recently, we have been studying the preparation and detailed mechanism of formation of various dimeric ruthenium(II) complexes containing both $RuCl_2Ru$ and $RuCl_3Ru$ bridging units. Some examples of those

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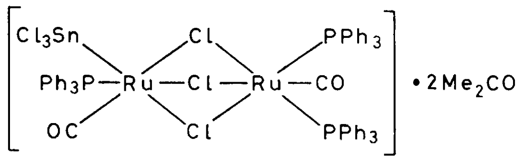
[1] Part 4, R. O. Gould, C. L. Jones, W. J. Sime, and T. A. Stephenson, *J.C.S. Dalton*, 1977, 669.

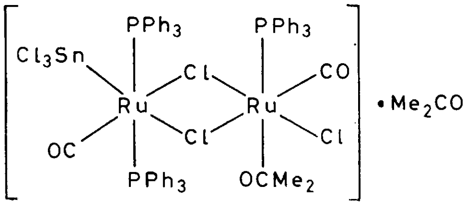
[2] T. A. Stephenson and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1966, **28**, 945.

synthesised in our laboratory are $[\{RuCl_2Y(PPh_3)_2\}_2]$, $[(Ph_3P)_2ClRuCl_3RuY(PPh_3)_2]\cdot 2Me_2CO$, $[(Ph_3P)(Y)ClRuCl_3RuY(PPh_3)_2]$, and $[(Ph_3P)_2YRuCl_3RuY(PPh_3)_2][BPh_4]$ (Y = CO or CS).[3,4,*]

In the light of these studies it was considered that two possible structures for (1) might be either the triple chloride-bridged (A) or the double chloride-bridged one



(A)



(B)

(B) (or isomers of these complexes). However, the proton noise-decoupled ^{31}P n.m.r. spectrum of (1) in C_6D_6 at 303 K showed only *one* PPh_3 resonance at 35.4 p.p.m. plus two broad weak signals arising from ^{117}Sn and ^{119}Sn satellites [*J*(PSn) 250 Hz] which is *not* compatible with either structure (A) or (B). Therefore an *X*-ray structural determination of (1) was undertaken both to establish its formulation and to ascertain its detailed geometry.

RESULTS AND DISCUSSION

The most important distances and angles in (1) are given in Tables 2 and 3, based on the parameters in Table 1. A view of the molecule is given in the Figure. The molecule deviates only very slightly from $C_s(m)$ symmetry; the maximum deviation of the atoms Ru, Sn, Cl(1), Cl(2), O(1), C(1), O(2), C(39), C(40), and C(41) from their best plane is 0.02 Å. Within this plane the short Ru–C(1) bond is reflected in the large Sn–Ru–C(1) and Cl(1)–Ru–C(1) angles. Conversely, both PPh_3 groups are substantially tilted away from the bulky $[SnCl_3]^-$ group. Within the latter the in-plane Sn–Cl(2) bond is significantly shorter than the two out-of-plane bonds, and the distortion from $C_{3v}(3m)$ local symmetry is marked in the angles.

The phenyl rings are staggered in three ways. The mean angles between the plane of a ring and the plane defined by the Ru–P and P–C bonds are 39° for the rings beginning with C(3) and C(27), 4° for those at C(15) and C(33), and 82° for those at C(9) and C(21). These last rings lie in planes above and below the co-ordinated acetone molecule, and probably interact with it, since, for example, C(26) comes to within 3.15 Å of O(2). The other rings make larger Ru–P–C angles, and the only other outstandingly close contacts not involving hydrogen atoms are Cl(1) · · · C(16) and Cl(1) · · · C(34) (3.30 Å).

TABLE 1

Fractional co-ordinates for (1) with standard deviations in parentheses

Atom	10^5x	10^5y	10^5z
Ru	36 497(5)	17 621(4)	24 522(2)
Sn	20 603(4)	6 393(3)	22 018(2)
Cl(1)	47 852(16)	30 639(12)	26 252(8)
Cl(2)	22 054(20)	−9 291(13)	22 442(11)
Cl(3)	12 058(18)	7 731(16)	13 226(9)
Cl(4)	3 375(17)	8 026(16)	26 356(10)
P(1)	43 501(15)	18 492(13)	15 687(8)
P(2)	32 330(16)	18 470(13)	33 821(8)
O(1)	52 275(50)	2 986(40)	27 274(24)
O(2)	22 243(41)	26 199(32)	22 162(20)
O(3)	−3 506(129)	22 951(106)	49 852(61)
C(1)	46 240(63)	8 823(50)	26 200(30)
C(3)	40 562(61)	9 149(48)	11 052(30)
C(4)	41 543(66)	559(53)	13 168(32)
C(5)	39 868(73)	−6 897(61)	9 790(35)
C(6)	37 446(80)	−5 586(67)	4 507(39)
C(7)	36 492(85)	2 813(68)	2 312(41)
C(8)	37 969(70)	10 255(56)	5 580(34)
C(9)	38 656(60)	28 485(48)	12 166(29)
C(10)	27 930(67)	28 705(54)	9 676(32)
C(11)	24 076(78)	36 394(63)	7 145(38)
C(12)	30 871(78)	43 806(65)	6 964(37)
C(13)	41 233(73)	43 736(61)	9 545(35)
C(14)	45 178(67)	36 118(55)	12 140(33)
C(15)	58 801(62)	18 921(50)	15 219(30)
C(16)	66 181(68)	18 784(55)	19 673(33)
C(17)	77 842(77)	18 661(63)	18 970(38)
C(18)	81 764(75)	18 802(61)	13 963(36)
C(19)	74 654(72)	19 143(58)	9 539(35)
C(20)	63 198(70)	19 150(56)	10 094(34)
C(21)	24 884(62)	28 736(50)	35 157(30)
C(22)	30 686(65)	36 288(53)	36 965(31)
C(23)	25 291(71)	44 405(58)	37 326(34)
C(24)	14 128(77)	45 074(61)	35 892(36)
C(25)	8 275(76)	37 692(62)	34 129(37)
C(26)	13 547(66)	29 536(53)	33 672(32)
C(27)	24 345(65)	9 478(51)	36 872(31)
C(28)	16 007(81)	10 941(64)	40 363(38)
C(29)	10 817(91)	3 857(74)	42 896(44)
C(30)	13 965(93)	−4 780(74)	41 684(44)
C(31)	22 224(85)	−6 332(71)	38 207(41)
C(32)	27 329(73)	806(58)	35 720(35)
C(33)	44 632(62)	18 586(50)	38 557(30)
C(34)	55 439(68)	18 701(55)	36 881(33)
C(35)	64 516(75)	18 277(62)	40 619(37)
C(36)	62 476(81)	17 827(67)	46 035(39)
C(37)	51 982(88)	17 793(70)	47 650(42)
C(38)	42 798(77)	18 218(62)	43 999(37)
C(39)	17 814(67)	33 543(54)	21 254(32)
C(40)	23 893(73)	42 023(61)	22 113(36)
C(41)	5 852(81)	33 773(65)	19 304(39)
C(42)	−1 561(142)	30 234(109)	48 517(63)
C(43)	9 807(152)	33 428(119)	49 142(70)
C(44)	−9 932(239)	34 939(192)	45 631(111)

With the exception of the tin analysis figure, the

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[*] For detailed references to other ruthenium complexes of this type see ref. 3.

[3] T. A. Stephenson, E. S. Switkes, and P. W. Armit, *J.C.S. Dalton*, 1974, 1134.

[4] P. W. Armit, W. J. Sime, and T. A. Stephenson, *J.C.S. Dalton*, 1976, 2121.

structure found for (1) is consistent with the ^{31}P n.m.r. spectrum and all the experimental data published previously.[2] Also the ν(CO) and ^{31}P n.m.r. values of (1) are similar to those of the related $[RuCl_2(CO)(HOMe)(PPh_3)_2]$ (2) [1 940 cm^{-1} (CH_2Cl_2) and 37.0 p.p.m. ($CDCl_3$ at 303 K) respectively].[4] The two i.r. bands at 1 661 and 1 701 cm^{-1} correspond to the carbonyl-stretching frequencies of co-ordinated and solvate acetone respectively {*cf.* $[RuCl_3(PPh_3)_2(OCMe_2)]$, ν(CO) at 1 656 cm^{-1}}.[2] There is also a strong band at 300 cm^{-1} assigned to a ν(SnCl) vibration.[5]

TABLE 2

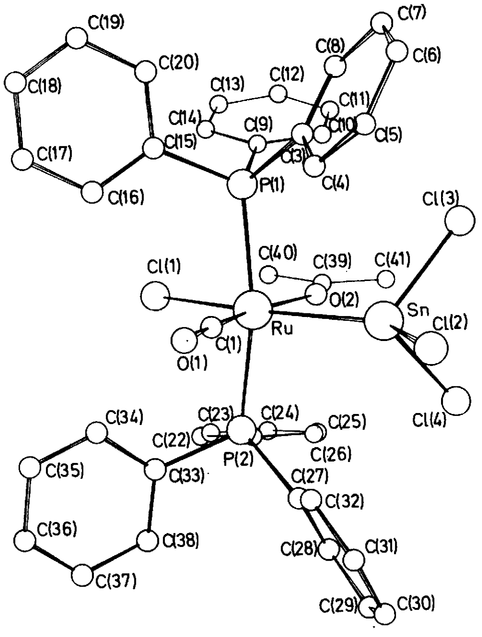
Bond lengths (Å) for (1). Quantities related by the pseudo-symmetry are printed on the same line

	Ru–Sn	2.5935(9)	
	Ru–Cl(1)	2.405(2)	
	Ru–C(1)	1.796(8)	
	Ru–O(2)	2.194(8)	
Ru–P(1)	2.393(2)	Ru–P(2)	2.395(2)
	Sn–Cl(2)	2.359(2)	
Sn–Cl(3)	2.385(2)	Sn–Cl(4)	2.379(2)
P(1)–C(3)	1.839(8)	P(2)–C(27)	1.835(2)
P(1)–C(9)	1.818(7)	P(2)–C(21)	1.816(8)
P(1)–C(15)	1.838(8)	P(2)–C(33)	1.844(8)
	C(1)–O(1)	1.156(9)	
	O(2)–C(39)	1.238(9)	
	C(39)–C(40)	1.475(12)	
	C(39)–C(41)	1.490(12)	
	O(3)–C(42)	1.17(2)	
	C(42)–C(43)	1.44(2)	
	C(42)–C(44)	1.44(3)	
	C–C(phenyl)	1.334 (min.)	
		1.412 (max.)	
		1.382 (mean)	

TABLE 3

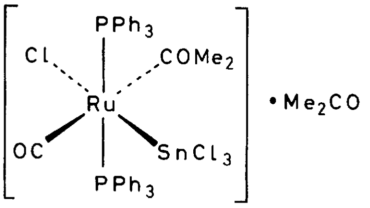
Angles (°) for (1). Quantities related by the pseudo-symmetry are printed on the same line

	Sn–Ru–Cl(1)	166.23(8)	
	Sn–Ru–C(1)	92.3(2)	
	Sn–Ru–O(2)	76.3(2)	
Sn–Ru–P(1)	95.51(6)	Sn–Ru–P(2)	94.94(5)
	Cl(1)–Ru–C(1)	101.5(2)	
	Cl(1)–Ru–O(2)	89.9(1)	
Cl(1)–Ru–P(1)	84.45(7)	Cl(1)–Ru–P(2)	85.58(7)
	C(1)–Ru–O(2)	168.6(2)	
C(1)–Ru–P(1)	90.3(2)	C(1)–Ru–P(2)	88.5(2)
O(2)–Ru–P(1)	91.2(2)	O(2)–Ru–P(2)	92.1(2)
	P(1)–Ru–P(2)	169.52(8)	
	Ru–Sn–Cl(2)	125.75(7)	
Ru–Sn–Cl(3)	98.78(9)	Ru–Sn–Cl(4)	98.37(8)
	Cl(3)–Sn–Cl(4)	93.69(8)	
	Ru–C(1)–O(1)	178.1(7)	
	Ru–O(2)–C(39)	153.0(5)	
	O(2)–C(39)–C(40)	122.4(7)	
	O(2)–C(39)–C(41)	118.5(7)	
	C(40)–C(39)–C(41)	119.1(7)	
Ru–P(1)–C(3)	118.1(2)	Ru–P(2)–C(27)	119.7(3)
Ru–P(1)–C(9)	111.8(2)	Ru–P(2)–C(21)	110.3(3)
Ru–P(1)–C(15)	116.7(3)	Ru–P(2)–C(33)	115.2(3)
C(3)–P(1)–C(9)	106.0(3)	C(27)–P(2)–C(21)	106.1(4)
C(3)–P(1)–C(15)	98.6(3)	C(27)–P(2)–C(33)	99.0(3)
C(9)–P(1)–C(15)	103.7(3)	C(21)–P(2)–C(33)	105.0(3)
	O(3)–C(42)–C(43)	119(2)	
	O(3)–C(42)–C(44)	118(2)	
	C(43)–C(42)–C(44)	123(2)	
	P–C–C(phenyl)	117.1 (min.)	
		123.5 (max.)	
		120.4 (mean)	
	C–C–C(phenyl)	118.6 (min.)	
		122.1 (max.)	
		120.0 (mean)	

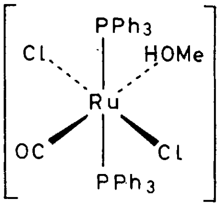


View of the molecule (1)

Although (1) is not a dimer, the complex $[(Ph_3P)(OC)(Cl_3Sn)RuCl_3Ru(CO)(PPh_3)_2]$ (3) can be synthesised by gently warming (1) in benzene for several hours and precipitating the product as a pale yellow powder with light petroleum (b.p. 60—80 °C) {*cf.* the formation of $[(Ph_3P)(OC)ClRuCl_3Ru(CO)(PPh_3)_2]$ by heating $[RuCl_2(CO)(HOMe)(PPh_3)_2]$ in dichloromethane–light petroleum (b.p. 60—80 °C)[4]}. A closely related complex to (3), $[(OC)_2(Cl_3Sn)RuCl_3Ru(CO)_3]$, was obtained by reaction of $[Ru_3(CO)_{12}]$ with $SnCl_4$.[6]



(1)



(2)

Unfortunately, (3) is not very stable in solution, readily eliminating a molecule of $SnCl_2$ to give some $[(Ph_3P)(OC)ClRuCl_3Ru(CO)(PPh_3)_2]$ (^{31}P n.m.r. evidence). Originally,[2] the pale yellow solid obtained either by *heating* (1) in benzene or refluxing a mixture of the 'red solution', PPh_3, and $SnCl_2$ was assigned the formulation $[Ru_2Cl_3(SnCl_3)(CO)_2(PPh_3)_4]$ on the basis of

[5] For detailed references see D. M. Adams, 'Metal Ligand and Related Vibrations,' Edward Arnold, London, 1967, ch. 2.

[6] R. K. Pomeroy, M. Elder, D. Hall, and W. A. G. Graham, *Chem. Comm.*, 1969, 381; M. Elder and D. Hall, *J. Chem. Soc.* (*A*), 1970, 245.

elemental analyses. However, a much better explanation is that the product generated under these conditions in 1966 was a mixture of [$(Ph_3P)(OC)(Cl_3Sn)RuCl_3Ru(CO)(PPh_3)_2$] and [$(Ph_3P)(OC)ClRuCl_3Ru(CO)(PPh_3)_2$]. In fact, a 48 : 52 mixture of these two complexes gives excellent agreement with *all* the earlier analytical data (see Experimental section).

EXPERIMENTAL

Microanalyses were by the University of Edinburgh Chemistry Department (or taken from ref. 2) and the molecular weight was measured in $CHCl_3$ on a Mechrolab model 301A vapour-pressure osmometer (calibrated with benzil). Infrared spectra were recorded in the 250—4 000 cm^{-1} region on a Perkin-Elmer 457 grating spectrometer using Nujol and hexachlorobutadiene mulls on caesium iodide plates. Phosphorus-31 n.m.r. spectra were obtained on a Varian Associates XL100 spectrometer operating in the pulse and Fourier-transform mode at 40.5 MHz. Chemical shifts are reported in p.p.m. to high frequency of 85% H_3PO_4.

Acetone(carbonyl)chloro(trichlorostannio)bis(triphenylphosphine)ruthenium(II)*-Acetone* (1/1) (1).—This was prepared as described in ref. 2 (Found: C, 49.9; H, 4.1; Cl, 14.7; O, 4.6; Sn, 7.9. Calc. for $C_{43}H_{42}Cl_4O_3P_2RuSn$: C, 50.1; H, 4.1; Cl, 13.8; O, 4.7; Sn, 11.6%). Complex (1) was also obtained by the following modification of the method in ref. 2.

The ' red solution ' (made from 0.50 g of ' $RuCl_3 \cdot xH_2O$ ') (15 cm^3) was treated with anhydrous $SnCl_2$ (1.50 g) in ethanol (5 cm^3) followed by PPh_3 (1.00 g) in acetone (20 cm^3). To the resulting yellow-brown solution was added acetone (20 cm^3) and the solution was allowed to stand overnight to deposit lemon-yellow *crystals* which were washed with acetone and diethyl ether, and dried in air {ν(CO) (Nujol) at 1 957 cm^{-1}, 1 701 and 1 661 cm^{-1} (acetone); ν(SnCl) at 300 cm^{-1}; ^{31}P n.m.r. in C_6D_6 at 303 K, 35.4 p.p.m. (t) [$^2J(PSn)$ 250 Hz]}.

ag-*Dicarbonyl-tri-μ-chloro-*b*-trichlorostanniotris(triphenylphosphine)diruthenium*(II) (3).—Complex (1) was dissolved in warm benzene. After 2 h the solution was reduced in volume and a pale yellow *powder* precipitated with light petroleum (b.p. 60—80 °C) [Found: C, 47.2; H, 3.3%; *M* ($CHCl_3$) 1 090. Calc. for $C_{56}H_{45}Cl_6O_2P_3Ru_2Sn$: C, 48.8; H, 3.3%; *M* 1 376 [ν(CO) at 1 975br cm^{-1}; ν(SnCl) at 320 cm^{-1}]. Phosphorus-31 n.m.r. spectrum in $CDCl_3$ at 303 K: main resonances 53.2 (s) * and 41.4 (q) p.p.m. (J_{AB} 25.9, δ_{AB} 66.1 Hz) corresponding to [$(Ph_3P)(OC)ClRuCl_3Ru(CO)(PPh_3)_2$] (see ref. 4) but weaker resonances at 49.9(t) [$^2J(PSn)$ 270 Hz] and 40.7 (q) p.p.m. (J_{AB} 25.5, δ_{AB} 183.1 Hz) assigned to [$(Ph_3P)(OC)(Cl_3Sn)RuCl_3Ru(CO)(PPh_3)_2$].

When (1) was heated in benzene, or the ' red solution ', $SnCl_2$, and PPh_3 in acetone were heated under reflux, a pale yellow solid was deposited (see ref. 2) {Found: C, 53.2; H, 3.4; Cl, 13.7. Calc. for a mixture of 48% [$(Ph_3P)(OC)(Cl_3Sn)RuCl_3Ru(CO)(PPh_3)_2$] and 52% [$(Ph_3P)(OC)ClRuCl_3Ru(CO)(PPh_3)_2$]: C, 52.9; H, 3.5; Cl, 13.7%}.

Crystal Data for (1).—$C_{43}H_{42}Cl_4O_3P_2RuSn$, $M = 1\,030$, yellow monoclinic prisms, $a = 11.950(3)$, $b = 14.988(3)$, $c = 24.916(2)$ Å, $\beta = 92.51(1)°$, $U = 4\,458$ Å^3, $D_m = 1.528$, $Z = 4$, $D_c = 1.534$ g cm^{-3}, space group $P2_1/c$ (no. 14), Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 11.8$ cm^{-1}.

Structure Determination.—All the data were collected using a Nonius CAD-4 goniometer. Cell dimensions were obtained by refinement of 22 reflections with θ *ca.* 15° (Mo-K_α). Two asymmetric units of data were collected with $2 \leqslant \theta \leqslant 22°$, using a crystal with a mean radius of 0.1 mm. No absorption corrections were applied. Symmetry-equivalent data were merged to give 5 671 independent data of which 3 601 with $I > 3\sigma(I)$ were used to solve the structure. The Ru and Sn atoms were found by a Patterson synthesis, the P and Cl atoms in a difference-Fourier phased by these, and all the non-hydrogen atoms in the complex in a further cycle. The structure was partly refined before the unexpected second acetone molecule was found. Refinement was carried out using large-block least squares. In the last few cycles the Sn, Ru, Cl, and P atoms were given anisotropic thermal parameters, and fixed hydrogen atoms were entered in calculated positions (C–H bonds 1.0 Å, methyl hydrogens staggered with respect to the C=O bond in acetone, temperature factors equal to those of the atoms to which they are attached). Unit least-squares weights were used except for $|F_o| > 120$, where $w = 120/|F_o|$. In the last cycle no shift was greater than 0.3σ and $w\Delta F$ was uniformly spread over ranges of sinθ and $|F_o|$. At convergence, $R = 0.037$. Positional parameters are given in Table 1, and structure factors and thermal parameters are in Supplementary Publication No. SUP 22154 (22 pp.).† The ' *X*-ray '72 ' computer programs of Stewart *et al.*[7] implemented at the University of Nijmegen Computer Centre were used for all the crystallographic calculations.

We thank Johnson, Matthey Ltd. for loans of ruthenium(III) trichloride, the S.R.C. for the award of a research studentship (to W. J. S.), Dr. A. S. F. Boyd for obtaining the ^{31}P n.m.r. spectra, the University of Glasgow Chemistry Department for the use of their Mechrolab osmometer, and Dr. J. H. Noordik and Mr. J. Smits for help with the *X*-ray data collection.

[7/1160 *Received*, 4*th July*, 1977]

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* In ref. 4, Table 1, a singlet at 54.7 and a quartet at 40.8 p.p.m. were assigned to isomer (5a) but this shows that, in fact, the singlet at 53.2 p.p.m. [originally assigned to isomer (5b) or (5c)] arises from (5a).

† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[7] ' *X*-Ray ' program system, Technical Report TR 192, Computer Science Center, University of Maryland, version of June 1972.