Structure and Fluxional Behaviour of μ-Diphenylacetylene-*closo*-tetrakis(tricarbonylruthenium)(4 *Ru–Ru*)

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The *X*-ray structure determination of $[Ru_4(CO)_{12}(C_2Ph_2)]$ confirms the previously proposed *closo*-Ru_4C_2 unit with the alkyne capping a butterfly arrangement of the four ruthenium atoms. Crystals are monoclinic, space group $P2_1/c$, $Z = 4$, $a = 9.69(1)$, $b = 16.88(2)$, $c = 17.13(2)$ Å, $\beta = 90.67(5)°$; R 0.056 for 2 929 independent reflections. Variable-temperature ^{13}C n.m.r. spectroscopy has enabled the activation energy and entropy to be measured for the mutual exchange of three carbonyl groups attached to one ruthenium, and also indicates that no exchange of carbonyls between different rutheniums occurs at <373 K.

REACTION of diphenylacetylene with $[Ru_3(CO)_{12}]$ leads to formation of $[Ru_4(CO)_{12}(C_2Ph_2)]$.[1] The solid-state structure of this compound has now been determined by *X*-ray diffraction and this confirms the presence of a *closo*-Ru_4C_2 unit. The solution structure and fluxionality has also been investigated by ^{13}C n.m.r. spectroscopy and the enthalpy and entropy barriers to the exchange of carbonyls in one $Ru(CO)_3$ unit have been measured.

TABLE 1

Atomic co-ordinates ($\times 10^4$) and isotropic temperature factors (Å$^2 \times 10^3$)

	x/*a*	*y*/*b*	*z*/*c*	*U*
Ru(1)	3 103(1)	5 799(1)	1 931(1)	
Ru(2)	2 534(1)	4 160(1)	1 680(1)	
Ru(3)	4 562(1)	4 626(1)	2 681(1)	
Ru(4)	651(1)	5 160(1)	2 346(1)	
C(1)	2 602(14)	6 817(8)	2 292(8)	47(3)
O(1)	2 235(11)	7 425(7)	2 504(6)	74(3)
C(2)	4 970(16)	6 092(9)	1 790(9)	57(4)
O(2)	6 067(12)	6 317(7)	1 693(6)	75(3)
C(3)	2 695(17)	6 025(10)	867(10)	64(4)
O(3)	2 369(14)	6 187(8)	236(8)	97(4)
C(4)	3 258(14)	3 127(8)	1 767(8)	45(3)
O(4)	3 677(11)	2 483(7)	1 825(6)	68(3)
C(5)	807(14)	3 770(8)	1 313(8)	42(3)
O(5)	−178(11)	3 479(6)	1 081(6)	65(3)
C(6)	3 284(15)	4 280(9)	666(8)	55(4)
O(6)	3 800(12)	4 355(7)	74(7)	77(3)
C(7)	5 059(13)	3 663(8)	3 153(7)	40(3)
O(7)	5 332(10)	3 062(6)	3 442(5)	58(3)
C(8)	5 790(15)	4 442(8)	1 870(8)	49(4)
O(8)	6 559(12)	4 310(7)	1 369(7)	76(3)
C(9)	5 855(15)	5 153(8)	3 347(8)	48(4)
O(9)	6 671(12)	5 471(7)	3 724(6)	72(3)
C(10)	−820(13)	4 499(7)	2 701(7)	40(3)
O(10)	−1 667(10)	4 105(6)	2 940(5)	56(3)
C(11)	−170(14)	6 059(8)	2 812(7)	43(3)
O(11)	−645(11)	6 619(6)	3 068(6)	64(3)
C(12)	−170(15)	5 394(9)	1 372(9)	55(4)
O(12)	−673(11)	5 505(6)	777(6)	68(3)
C(13)	2 317(11)	4 421(6)	2 909(6)	26(3)
C(14)	2 641(11)	5 256(7)	3 042(6)	27(3)
C(15)	2 546(12)	5 721(7)	3 804(6)	31(3)
C(16)	1 462(12)	5 602(7)	4 302(7)	32(3)
C(17)	1 344(15)	6 052(8)	4 995(8)	50(4)
C(18)	2 316(15)	6 612(9)	5 159(9)	60(4)
C(19)	3 384(16)	6 738(9)	4 666(9)	61(4)
C(20)	3 515(14)	6 301(8)	3 976(8)	45(3)
C(21)	2 022(12)	3 812(7)	3 536(7)	32(3)
C(22)	2 616(13)	3 857(7)	4 278(7)	37(3)
C(23)	2 377(14)	3 248(8)	4 812(8)	49(4)
C(24)	1 573(15)	2 624(9)	4 634(9)	59(4)
C(25)	974(14)	2 577(9)	3 906(8)	50(4)
C(26)	1 176(12)	3 170(7)	3 357(7)	32(3)

EXPERIMENTAL

Intensities from a crystal with dimensions *ca.* 0.20 × 0.08 × 0.08 mm were collected on a Syntex $P2_1$ four-circle diffractometer with graphite-monochromated Mo-K_α radiation for $0 < 2\theta < 50°$. Lorentz, polarization, and absorption corrections were applied. Of the 4 351 independent reflections recorded only the 2 929 with $|F_o| > 4\sigma(F_o)$ were employed for structure refinement.

TABLE 2

Anisotropic temperature factors (Å$^2 \times 10^3$) *

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru(1)	41(1)	29(1)	33(1)	4(1)	8(1)	−3(1)
Ru(2)	34(1)	30(1)	25(1)	−5(1)	1(1)	1(1)
Ru(3)	26(1)	32(1)	33(1)	−5(1)	3(1)	0(1)
Ru(4)	28(1)	29(1)	32(1)	−1(1)	−1(1)	4(1)

* The temperature factor exponent takes the form: $-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^*)$.

Crystal Data.—$C_{26}H_{10}O_{12}Ru_4$, $M = 918.63$, Monoclinic, space group $P2_1/c$, $a = 9.69(1)$, $b = 16.88(2)$, $c = 17.13(2)$ Å, $\beta = 90.67(5)°$, $U = 2\,802$ Å^3, $Z = 4$, $D_c = 2.18$ g cm^{-3}, μ(Mo-K_α) = 19.7 cm^{-1}, λ(Mo-K_α) = 0.710 69 Å.

Structure Solution and Refinement.—The four ruthenium atoms were located by multisolution sigma-2 expansion, and the other non-hydrogen atoms from difference electron-density syntheses. The structure was refined by a novel blocked-cascade least-squares algorithm, with anisotropic temperature factors for ruthenium and isotropic for the light atoms. Hydrogen atoms were constrained to be on the external bisectors of the C–C–C angles with C–H fixed at 1.08 Å and isotropic temperature factors 0.02 Å^2 higher than the carbon atoms to which they were attached. The refinement converged to $R' = \Sigma w^{\frac{1}{2}}(|F_o| - |F_c|)/\Sigma w^{\frac{1}{2}}|F_o| = 0.054$, with a corresponding unweighted R of 0.056. The final weighting

TABLE 3

Hydrogen-atom co-ordinates ($\times 10^4$) and isotropic temperature factors (Å$^2 \times 10^3$)

	x/*a*	*y*/*b*	*z*/*c*	*U*
H(16)	692	5 160	4 163	52(3)
H(17)	497	5 952	5 387	70(4)
H(18)	2 239	6 959	5 687	80(4)
H(19)	4 144	7 185	4 809	81(4)
H(20)	4 357	6 414	3 584	65(3)
H(22)	3 254	4 357	4 439	57(3)
H(23)	2 853	3 281	5 385	69(4)
H(24)	1 400	2 164	5 060	79(4)
H(25)	337	2 072	3 759	70(4)
H(26)	676	3 133	2 792	52(3)

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[1] B. F. G. Johnson, J. Lewis, and K. T. Schorpp, *J. Organometallic Chem.*, 1975, **91**, C13.

scheme was $w = 1/[\sigma^2(F_o) + 0.001|F_o|^2]$. Complex neutral-atom scattering factors[2] were employed. Atom co-ordinates and temperature factors are given in Tables 1—3. A final difference synthesis displayed no features higher than 1.0 $e\text{Å}^{-3}$. A list of observed and calculated structure factors is available as Supplementary Publication No. SUP 22049 (19 pp.).*

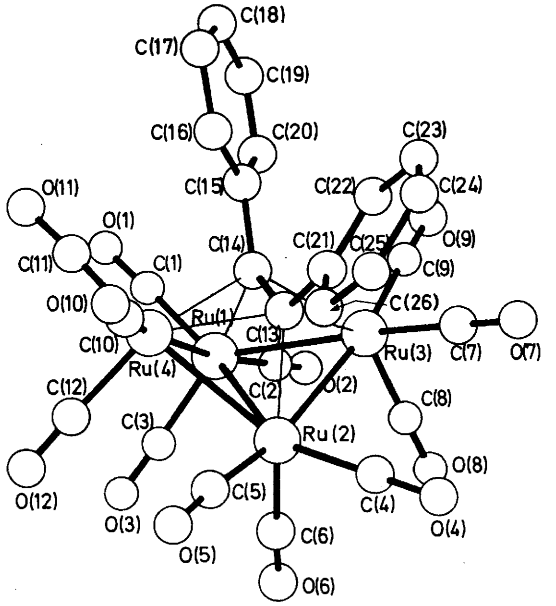

FIGURE 1 The molecule of *closo*-$[Ru_4(CO)_{12}(C_2Ph_2)]$ showing the labelling scheme

Carbon-13 *N.M.R. Spectra*.—These were obtained at 25.2 MHz with a Varian XL-100 spectrometer operating in the Fourier-transform mode, using toluene, CH_2Cl_2, or $CHFCl_2$ solutions of ^{13}C-enriched samples in 12-mm tubes, and noise decoupling of protons. Tris(pentane-2,4-dionato)chromium(III) was added to the solutions to reduce T_1 for ^{13}C. Chemical shifts were measured relative to the solvent, and subsequently converted into p.p.m. downfield from $SiMe_4$. Data constants for the exchange process were obtained by least-squares fitting of experimental and calculated line shapes at various temperatures.[3]

TABLE 4

Selected bond lengths (Å)

Ru(1)–Ru(2)	2.85(1)	Ru(2)–C(6)	1.90(2)
Ru(1)–Ru(3)	2.74(1)	Ru(3)–C(7)	1.88(1)
Ru(1)–Ru(4)	2.71(1)	Ru(3)–C(8)	1.87(2)
Ru(2)–Ru(3)	2.71(1)	Ru(3)–C(9)	1.91(2)
Ru(2)–Ru(4)	2.74(1)	Ru(4)–C(10)	1.91(1)
C(13)–Ru(2)	2.16(1)	Ru(4)–C(11)	1.89(1)
C(13)–Ru(3)	2.24(1)	Ru(4)–C(12)	1.88(2)
C(13)–Ru(4)	2.25(1)	C(1)–O(1)	1.15(2)
C(14)–Ru(1)	2.16(1)	C(2)–O(2)	1.14(2)
C(14)–Ru(3)	2.24(1)	C(3)–O(3)	1.16(2)
C(14)–Ru(4)	2.26(1)	C(4)–O(4)	1.16(2)
C(13)–C(14)	1.46(2)	C(5)–O(5)	1.14(2)
C(14)–C(15)	1.53(2)	C(6)–O(6)	1.14(2)
C(13)–C(21)	1.52(2)	C(7)–O(7)	1.16(2)
Ru(1)–C(1)	1.89(2)	C(8)–O(8)	1.16(2)
Ru(1)–C(2)	1.89(2)	C(9)–O(9)	1.15(2)
Ru(1)–C(3)	1.90(2)	C(10)–O(10)	1.14(2)
Ru(2)–C(4)	1.88(2)	C(11)–O(11)	1.14(2)
Ru(2)–C(5)	1.90(2)	C(12)–O(12)	1.14(2)

DISCUSSION

Crystal Structure.—The structure of the $[Ru_4(CO)_{12}(C_2Ph_2)]$ molecule is shown in Figure 1. More important bond lengths and angles are given in Tables 4 and 5.

TABLE 5

Selected bond angles (°)

Ru(2)–Ru(1)–Ru(3)	57.9(1)	Ru(3)–Ru(2)–C(4)	87.2(4)
Ru(2)–Ru(1)–Ru(4)	59.0(1)	Ru(4)–Ru(2)–C(4)	141.7(4)
Ru(3)–Ru(1)–Ru(4)	92.2(1)	Ru(1)–Ru(2)–C(5)	123.7(4)
Ru(2)–Ru(1)–C(14)	71.4(3)	Ru(3)–Ru(2)–C(5)	160.1(4)
Ru(3)–Ru(1)–C(14)	52.7(3)	Ru(4)–Ru(2)–C(5)	76.3(4)
Ru(4)–Ru(1)–C(14)	53.9(3)	C(4)–Ru(2)–C(5)	91.8(6)
Ru(1)–Ru(2)–Ru(3)	59.0(1)	Ru(1)–Ru(2)–C(6)	87.7(4)
Ru(1)–Ru(2)–Ru(4)	58.0(1)	Ru(3)–Ru(2)–C(6)	105.3(4)
Ru(3)–Ru(2)–Ru(4)	92.3(1)	Ru(4)–Ru(2)–C(6)	125.3(4)
Ru(1)–Ru(2)–C(13)	71.1(3)	C(4)–Ru(2)–C(6)	91.4(6)
Ru(3)–Ru(2)–C(13)	53.4(3)	C(5)–Ru(2)–C(6)	94.6(6)
Ru(4)–Ru(2)–C(13)	53.0(3)	C(4)–Ru(2)–C(13)	98.7(5)
Ru(1)–Ru(3)–Ru(2)	63.1(1)	C(5)–Ru(2)–C(13)	107.3(5)
Ru(1)–Ru(3)–C(13)	72.4(3)	C(6)–Ru(2)–C(13)	155.4(5)
Ru(2)–Ru(3)–C(13)	50.8(3)	Ru(1)–Ru(3)–C(7)	162.8(4)
Ru(1)–Ru(3)–C(14)	50.3(3)	Ru(2)–Ru(3)–C(7)	101.7(4)
Ru(2)–Ru(3)–C(14)	73.3(3)	Ru(1)–Ru(3)–C(8)	95.8(4)
C(13)–Ru(3)–C(14)	38.1(4)	Ru(2)–Ru(3)–C(8)	86.9(4)
Ru(1)–Ru(4)–Ru(2)	63.0(1)	C(7)–Ru(3)–C(8)	90.8(6)
Ru(1)–Ru(4)–C(13)	72.9(3)	Ru(1)–Ru(3)–C(9)	106.0(4)
Ru(2)–Ru(4)–C(13)	50.2(3)	Ru(2)–Ru(3)–C(9)	169.0(4)
Ru(1)–Ru(4)–C(14)	50.6(3)	C(7)–Ru(3)–C(9)	89.0(6)
Ru(2)–Ru(4)–C(14)	72.3(3)	C(8)–Ru(3)–C(9)	95.9(6)
C(13)–Ru(4)–C(14)	37.8(4)	C(7)–Ru(3)–C(13)	92.1(5)
Ru(2)–C(13)–Ru(3)	75.9(3)	C(8)–Ru(3)–C(13)	137.2(5)
Ru(2)–C(13)–Ru(4)	76.9(3)	C(9)–Ru(3)–C(13)	126.9(5)
Ru(3)–C(13)–Ru(4)	122.2(5)	C(7)–Ru(3)–C(14)	120.2(5)
Ru(2)–C(13)–C(14)	109.0(7)	C(8)–Ru(3)–C(14)	145.6(5)
Ru(3)–C(13)–C(14)	70.8(6)	C(9)–Ru(3)–C(14)	99.0(5)
Ru(4)–C(13)–C(14)	71.6(6)	Ru(1)–Ru(4)–C(10)	166.6(4)
Ru(1)–C(14)–Ru(3)	77.1(4)	Ru(2)–Ru(4)–C(10)	106.0(4)
Ru(1)–C(14)–Ru(4)	75.6(4)	Ru(1)–Ru(4)–C(11)	99.6(4)
Ru(3)–C(14)–Ru(4)	121.8(5)	Ru(2)–Ru(4)–C(11)	162.3(4)
Ru(1)–C(14)–C(13)	108.5(7)	C(10)–Ru(4)–C(11)	90.8(6)
Ru(3)–C(14)–C(13)	71.1(6)	Ru(1)–Ru(4)–C(12)	92.7(5)
Ru(4)–C(14)–C(13)	70.6(6)	Ru(2)–Ru(4)–C(12)	92.1(5)
Ru(2)–Ru(1)–C(1)	151.7(4)	C(10)–Ru(4)–C(12)	95.4(6)
Ru(3)–Ru(1)–C(1)	129.5(4)	C(11)–Ru(4)–C(12)	91.7(6)
Ru(4)–Ru(1)–C(1)	92.6(4)	C(10)–Ru(4)–C(13)	94.3(5)
Ru(2)–Ru(1)–C(2)	114.7(5)	C(11)–Ru(4)–C(13)	124.5(5)
Ru(3)–Ru(1)–C(2)	76.1(5)	C(12)–Ru(4)–C(13)	142.3(5)
Ru(4)–Ru(1)–C(2)	168.2(5)	C(10)–Ru(4)–C(14)	120.5(5)
C(1)–Ru(1)–C(2)	93.1(6)	C(11)–Ru(4)–C(14)	94.6(5)
Ru(2)–Ru(1)–C(3)	90.7(5)	C(12)–Ru(4)–C(14)	143.3(5)
Ru(3)–Ru(1)–C(3)	134.0(5)	Ru(2)–C(13)–C(21)	124.9(8)
Ru(4)–Ru(1)–C(3)	99.1(5)	Ru(3)–C(13)–C(21)	114.8(7)
C(1)–Ru(1)–C(3)	94.5(6)	Ru(4)–C(13)–C(21)	122.6(7)
C(2)–Ru(1)–C(3)	90.8(7)	C(14)–C(13)–C(21)	125.8(9)
C(1)–Ru(1)–C(14)	92.3(5)	Ru(1)–C(14)–C(15)	123.4(8)
C(2)–Ru(1)–C(14)	115.5(5)	Ru(3)–C(14)–C(15)	122.7(7)
C(3)–Ru(1)–C(14)	152.4(6)	Ru(4)–C(14)–C(15)	115.3(7)
Ru(1)–Ru(2)–C(4)	144.5(4)	C(13)–C(14)–C(15)	127.9(10)

The structure is perhaps best described as a butterfly arrangement of four ruthenium atoms capped by the alkyne. The rutheniums and acetylenic carbons describe a distorted octahedron, C(13) being almost equidistant from Ru(2), Ru(3), and Ru(4), and similarly C(14) from Ru(1), Ru(3), and Ru(4). The molecule possesses an approximate two-fold symmetry axis perpendicular to the C(13)–C(14) and Ru(1)–Ru(2) bonds. The angle

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

[2] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, pp. 99 and 149.

[3] M. Saunders, *Tetrahedron Letters*, 1963, 1699.

between the planes defined by Ru(1), Ru(2), Ru(3) and Ru(1), Ru(2), Ru(4) is 115.5°.

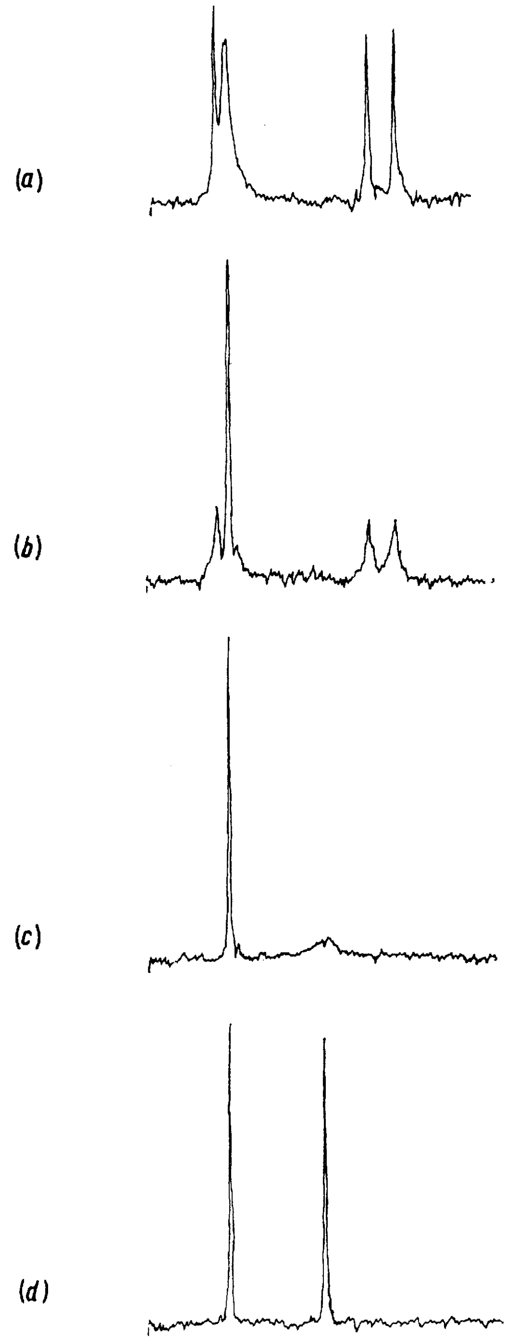

FIGURE 2 Carbon-13 n.m.r. spectra (carbonyl region) of *closo*-[$Ru(CO)_{12}(C_2Ph_2)$] in $CHFCl_2$ at (*a*) 161, (*b*) 173, (*c*) 203, and (*d*) 253 K

Carbon-13 *N.M.R. Spectra*.—At 233—373 K in CH_2Cl_2 and toluene two sharp singlets were observed at δ 197.4 and 190.4 p.p.m. (273 K, CH_2Cl_2) corresponding to the carbonyl groups on Ru(1), Ru(2), and Ru(3), Ru(4) or *vice versa*. Hence no exchange of carbonyls occurs between the pairs of ruthenium atoms. Below 233 K the higher-field peak broadened. In $CHFCl_2$ at the lowest temperature attained, *viz*. 161 K, this peak split into 3 sharp lines of equal intensity at δ 198.3, 187.1, and 185.1 p.p.m., the other peak at δ 197.6 p.p.m. being slightly broadened (Figure 2). At slightly higher temperatures, *viz*. 173 K, the peak at 197.6 p.p.m. became sharp and the other three broadened, these finally coalescing at *ca*. 200 K. It therefore appears that the three distinct carbonyls on one type of ruthenium [*i.e.* either Ru(1), Ru(2) or Ru(3), Ru(4)] can be observed at below *ca*. 170 K, but for the other ruthenium sites the exchange of the attached carbonyls is too rapid for the distinct positions to be seen at temperatures attained in this work. The broadening at 161 K does indicate slowing of the exchange and separation of the sites should be observed somewhat below this temperature.

Line-shape analysis of spectra from 173 to 213 K enabled thermodynamic functions for the exchange process to be deduced. The results are summarized in Table 6. The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were obtained by least-squares fitting of $\Delta G^{\ddagger}$(obs.) at]the various temperatures, and the $\Delta G^{\ddagger}$(calc.) values in the final column were calculated from these $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values at the appropriate temperature. As would be expected for an intermolecular process not involving dissociation, the $\Delta S^{\ddagger}$ value is very low.

TABLE 6

Temperature dependence of exchange rate and thermodynamic parameters

T/K	$k_{obs.}$/s^{-1}	$\Delta G^{\ddagger}$/kJ mol^{-1} obs.	$\Delta G^{\ddagger}$/kJ mol^{-1} calc.
173	29.8	36.74	36.58
183	210.3	35.97	36.18
193	910.1	35.67	35.78
203	3 102	35.53	35.38
213	11 760	35.00	34.98

$\Delta H^{\ddagger}$ = 43.50 kJ mol^{-1}
$\Delta S^{\ddagger}$ = 40.0 J K^{-1} mol^{-1}

Calculations were made on the Cambridge University IBM 370/165 computer with programs written by B. E. R. (n.m.r. line-shape analysis), G. M. S. (crystal-structure determination), and Dr. W. D. S. Motherwell (structural diagrams).

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