Formation of a cobaltacyclopentene complex by the reaction of 2-ethynylpyridine with [Co(η^5-C$_5$H$_5$)(PPh$_3$)$_2$]

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Abstract

The reaction of 2-ethynylpyridine with [Co(η^5-C$_5$H$_5$)(PPh$_3$)$_2$] in addition to the expected two isomeric cobaltacyclopentadienes, gives a new complex formulated as [Co(η^5-C$_5$H$_5$)(NC$_5$H$_4$C$_2$H)$_3$]. An X-ray diffraction study proved this to be a cobaltacyclopentene complex which presumably results from a pyridyl group-assisted Diels–Alder addition of 2-ethynylpyridine to the intermediate 2,4-pyridylcobaltacyclopentadiene, followed by hydrogen migration.

Introduction

The cobaltacyclopentadiene complex, a versatile intermediate for stoichiometric and catalytic production of various organic cyclic compounds [1], can be readily formed from two molecules of acetylene and [CoCp(PPh$_3$)$_2$] (**1**, Cp = η^5-C$_5$H$_5$) [2]. When an unsymmetrically substituted acetylene is employed, the reaction usually gives two regioisomers (**a** and **b**). It has been established that in the cobalt metallacycle of type **a**, bulkier substituents prefer α-positions while less bulky substituents occupy β-positions of the metallacycle [3].
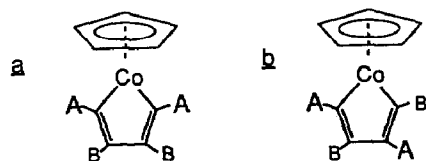

Further reaction of the metallacyclodiene with acetylene is believed to proceed by prior coordination of the acetylene to the metal and insertion into one of the metal–C bonds giving a metallacycloheptatriene intermediate, which then releases a polysubstituted benzene. When dimethyl acetylenedicarboxylate is employed, however, kinetic evidence indicates that direct attack of the acetylene on the metallacy-

clodiene, i.e. Diels–Alder addition to give a [2,2,1]-metallabicyclic intermediate, takes place [4].

We have found that the reaction of 1 with 2-ethynylpyridine gives a cobalta-cyclopentene complex which we believe is formed by yet another type of Diels–Alder addition taking place in the coordination sphere of the metal.

Results and discussion

The reaction of 1 and 2-ethynylpyridine in a 1 : 2 molar ratio at room temperature and subsequent work up on column chromatography gave four products.

$$C_p : \eta^5-C_5H_5, \quad Py:$$
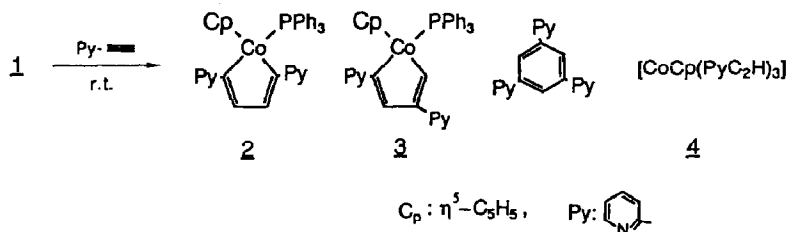
Complexes 2 and 3 were the expected metallacycles: 2 was crystalline (brown crystals, melting with decomposition at 129–132°C, yield 11%) while 3 was a brown oil (yield ca. 18%). The ^1H NMR spectrum of 2 reveals the presence of two equivalent pyridyl groups and two equivalent metallacycle ring-protons (6.47 ppm). The rather large J(PH) value of the latter, 6.8 Hz, is in accord with our previous observation that in analogous cobaltacyclopentadiene complexes the long-range ^1H–^{31}P coupling occurs with the methyl group attached to β-carbons of the metallacycle [2]. The two pyridyl rings in 3 were found to be non-equivalent. The β-proton of the metalloring was observed as a double-doublet at the expected position (6.81 ppm, J(PH) 6.8 Hz, J(HH) 3.2 Hz) in accord with the assigned structure, although the resonance of the α-proton was overlapped by those of the phenyl protons.

The only organic product obtained from this reaction was 1,3,5-tris(2-pyridyl)benzene (colorless crystals, mp. 224°C, 18% yield based on 2-ethynylpyridine used). Interestingly, no 1,2,4-isomer could be detected despite careful chromatography.

The third complex (4) had the composition [CoCp(PyC$_2$H)$_3$] (Py = 2-pyridyl) which was isolated as air-stable dark-purple crystals (mp. 188°, 11% yield) and whose structure was determined by X-ray diffraction.

Molecular structure of 4

Dark-purple, air stable, single crystals were grown by the diffusion of hexane into a dichloromethane solution of 4 at room temperature. The unit cell contains two crystallographically distinct monomers, molecules A and B, which are approximately related by a pseudo center of symmetry but differ slightly in the rotations of the substituents and the cyclopentadienyl ring. Figure 1 shows the perspective view and numbering scheme for the resulting molecular configuration. The atomic coordinates are listed in Table 1 and important bond lengths and angles are given in Table 2. The cobalt atom is incorporated in a cyclopentene ring which is fused to a six-membered ring. The 2-pyridyl group attached to the latter ring coordinates to cobalt in a highly chelated and rigid piano stool geometry.
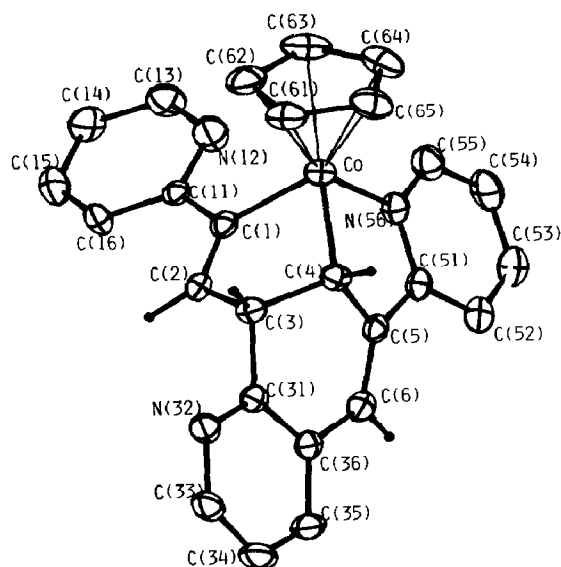
Fig. 1. The molecular structure of complex **4** with atomic numbering scheme. Only one of the two independent molecules (molecule A) is shown for clarity.

Table 1

Atomic parameters ($\times 10^4$) for non-hydrogen atoms

Atom	x	y	z	Atom	x	y	z
Co(A)	7078(1)	1162(1)	3139(1)	Co(B)	1806(1)	4687(1)	8360(1)
C(1A)	5553(3)	1815(3)	2675(3)	C(1B)	333(3)	4572(3)	7846(3)
C(2A)	4883(3)	1233(3)	2650(3)	C(2B)	−410(3)	5491(3)	7704(3)
C(3A)	5416(3)	147(3)	2898(3)	C(3B)	16(4)	6421(3)	7823(3)
C(4A)	6597(3)	−116(3)	2595(3)	C(4B)	1231(3)	5910(3)	7611(3)
C(5A)	6643(3)	−396(3)	1334(3)	C(5B)	1355(3)	5469(3)	6389(3)
C(6A)	5955(4)	−866(3)	676(3)	C(6B)	656(3)	5910(3)	5597(3)
C(11A)	5135(3)	2918(3)	2501(3)	C(11B)	−6(3)	3606(3)	7683(3)
N(12A)	5886(3)	3405(3)	2453(4)	N(12B)	−1040(3)	3665(3)	7249(3)
C(13A)	5525(4)	4431(4)	2366(4)	C(13B)	−1364(4)	2807(4)	7095(4)
C(14A)	4433(4)	5000(4)	2325(4)	C(14B)	−729(4)	1859(4)	7340(4)
C(15A)	3683(4)	4483(4)	2334(4)	C(15B)	328(4)	1790(4)	7760(4)
C(16A)	4033(3)	3456(3)	2434(4)	C(16B)	687(4)	2676(4)	7941(4)
C(31A)	4878(3)	−674(3)	2251(4)	C(31B)	−588(3)	7132(3)	7015(4)
N(32A)	4175(3)	−909(3)	2763(3)	N(32B)	−1415(3)	7980(3)	7376(3)
C(33A)	3696(4)	−1636(4)	2183(4)	C(33B)	−1974(4)	8575(4)	6626(5)
C(34A)	3895(4)	−2131(4)	1093(5)	C(34B)	−1737(4)	8336(4)	5534(4)
C(35A)	4611(4)	−1889(4)	550(4)	C(35B)	−877(4)	7465(4)	5159(4)
C(36A)	5149(3)	−1155(3)	1137(4)	C(36B)	−269(4)	6840(3)	5910(3)
C(51A)	7377(3)	26(3)	925(3)	C(51B)	2236(3)	4483(3)	6133(3)
C(52A)	7813(4)	−331(4)	−125(4)	C(52B)	2769(4)	4097(4)	5146(4)
C(53A)	8464(4)	175(4)	−411(4)	C(53B)	3590(4)	3148(4)	5027(4)
C(54A)	8676(4)	1030(4)	335(4)	C(54B)	3853(4)	2593(4)	5882(4)
C(55A)	8240(4)	1340(4)	1365(4)	C(55B)	3304(4)	3011(3)	6837(4)
N(56A)	7613(3)	849(3)	1677(3)	N(56B)	2504(3)	3953(3)	6980(3)
C(61A)	7168(4)	1149(4)	4818(4)	C(61B)	2646(4)	3792(4)	9604(4)
C(62A)	6872(4)	2205(4)	4670(4)	C(62B)	3274(4)	4415(4)	9430(4)
C(63A)	7733(5)	2325(4)	4201(4)	C(63B)	2656(4)	5473(4)	9676(4)
C(64A)	8563(4)	1358(4)	4063(4)	C(64B)	1628(4)	5521(4)	9978(4)
C(65A)	8228(4)	635(4)	4452(4)	C(65B)	1627(4)	4482(4)	9940(4)

Table 2

Selected bond distances (Å) and angles (°).

Bond lengths			
Co(A)–C(1A)	1.952(4)	Co(B)–C(1B)	1.964(4)
Co(A)–C(4A)	1.977(5)	Co(B)–C(4B)	1.986(5)
Co(A)–N(56A)	1.927(4)	Co(B)–N(56B)	1.940(3)
C(1A)–C(2A)	1.344(7)	C(1B)–C(2B)	1.347(6)
C(2A)–C(3A)	1.508(6)	C(2B)–C(3B)	1.508(7)
C(3A)–C(4A)	1.531(7)	C(3B)–C(4B)	1.533(6)
C(3A)–C(31A)	1.516(6)	C(3B)–C(31B)	1.519(6)
C(4A)–C(5A)	1.517(6)	C(4B)–C(5B)	1.496(6)
C(5A)–C(6A)	1.334(6)	C(5B)–C(6B)	1.349(6)
C(5A)–C(51A)	1.453(7)	C(5B)–C(51B)	1.458(5)
C(6A)–C(36A)	1.450(8)	C(6B)–C(36B)	1.455(5)
C(31A)–C(36A)	1.415(6)	C(31B)–C(36B)	1.408(6)
C(51A)–N(56A)	1.364(5)	C(51B)–N(56B)	1.356(6)
Bond angles			
C(1A)–Co(A)–C(4A)	80.4(2)	C(1B)–Co(B)–C(4B)	80.3(2)
C(1A)–Co(A)–N(56A)	95.6(2)	C(1B)–Co(B)–N(56B)	97.6(2)
C(4A)–Co(A)–N(56A)	85.3(2)	C(4B)–Co(B)–N(56B)	84.8(2)
Co(A)–C(1A)–C(2A)	114.6(3)	Co(B)–C(1B)–C(2B)	113.9(4)
C(1A)–C(2A)–C(3A)	116.3(4)	C(1B)–C(2B)–C(3B)	116.8(4)
C(2A)–C(3A)–C(4A)	103.3(4)	C(2B)–C(3B)–C(4B)	103.6(3)
C(4A)–C(3A)–C(31A)	111.8(3)	C(4B)–C(3B)–C(31B)	112.6(4)
Co(A)–C(4A)–C(3A)	108.4(3)	Co(B)–C(4B)–C(3B)	108.3(3)
Co(A)–C(4A)–C(5A)	107.0(3)	Co(B)–C(4B)–C(5B)	106.3(3)
C(3A)–C(4A)–C(5A)	109.8(3)	C(3B)–C(4B)–C(5B)	109.9(3)
C(4A)–C(5A)–C(6A)	121.4(5)	C(4B)–C(5B)–C(6B)	122.4(3)
C(4A)–C(5A)–C(51A)	114.0(4)	C(4B)–C(5B)–C(51B)	114.4(3)
C(5A)–C(6A)–C(36A)	121.4(4)	C(5B)–C(6B)–C(36B)	120.4(4)
C(3A)–C(31A)–C(36A)	118.6(4)	C(3B)–C(31B)–C(36B)	118.1(3)
C(6A)–C(36A)–C(31A)	118.7(4)	C(6B)–C(36B)–C(31B)	119.5(4)
C(5A)–C(51A)–N(56A)	112.9(4)	C(5B)–C(51B)–N(56B)	112.5(4)
Co(A)–N(56A)–C(51A)	116.5(4)	Co(B)–N(56B)–C(51B)	116.1(2)

Bond lengths and angles within the Cp ring and between the cobalt atom and Cp carbons are normal. The geometry of the cobaltacyclopentene moiety can be compare with those of Cp(PPh$_3$)CoC(Ph)=C(Z)CH(Z)CH(Z) (5, Z = CO$_2$CH$_3$) [5] and [2,2,1]-metallabicyclic cobaltacyclopentene (6) derived from 5 [6]. The conformation of the cobaltacyclopentene ring was found to be similar to that of 5; Co–C(1)–C(2)–C(3) forms a good plane and C(4) is displaced by 0.71 Å, (cf. 0.583 Å in 5), from that plane away from the Cp ring. The Co–C(1) bond lengths of 1.952(4) (molecule A) and 1.964(4) Å (molecule B) are not significantly different from the corresponding Co–C(sp^2) bond lengths of 1.947(11) Å in 5 and 1.954(6) Å in 6. In contrast, the Co–C(4) bond lengths of 1.977(5) Å (molecule A) and 1.985(5) Å (molecule B) in 4 are significantly shorter than the Co–C(sp^3) distance of 2.002 Å in 6 and distinctly shorter than the length of 2.097(12) Å found in 5. The average of the Co–C(sp^3) bond lengths in 4 is thus only 0.02 Å longer than the average of the Co–C(sp^2) distances. It is probably the compact puckering of the chelate ligand in 4 that has resulted in such short Co–C(sp^3) bond lengths. The fused six-membered ring (C(3)C(4)C(5)C(6)C(36)C(31)) is almost planar and the approximate dihedral angle between the cobaltacyclopentene is 77°.
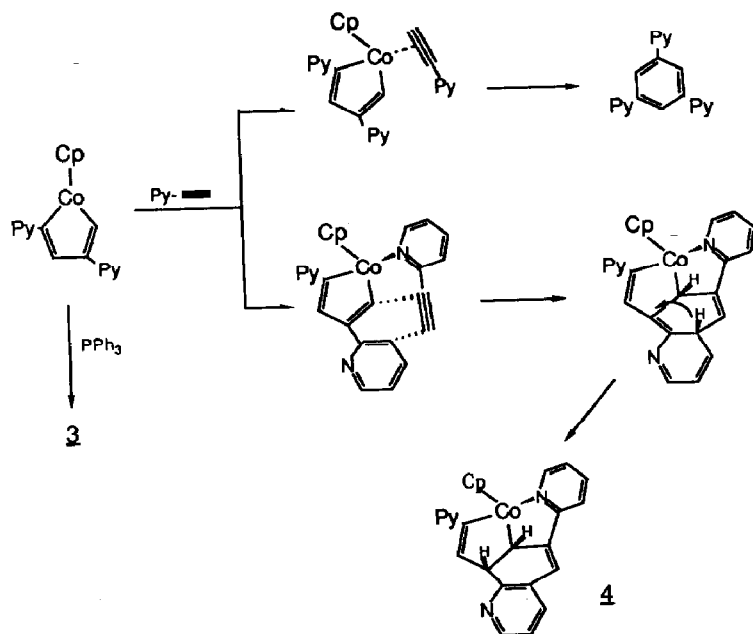
Scheme 1

Some comments on the reaction mechanism

Since the formation of analogous cobaltacyclopentene with phenylacetylene has not been observed, coordination of the nitrogen in the pyridylacetylene to cobalt must have played an important role. As illustrated in Scheme 1 we assume that this coordination of nitrogen to the metal center of 2,4-dipyridylcobaltacyclopentadiene must take place. This anchoring effect places the acetylenic moiety in the correct spatial disposition for the Diels–Alder reaction, such that one double bond of the cobaltacyclopentadiene and one double bond in pyridyl ring cooperate as a diene system. The subsequent 1,3-hydrogen shift to regain aromaticity of the fused pyridyl ring completes the reaction to give **4**. Coordination by the acetylenic part instead of the pyridyl nitrogen leads to the formation of 1,3,5-tris(2-pyridyl)benzene.

A similar reaction by the acetylenic bond with the 2,5-dipyridylcobaltacyclopentadiene should give 1,2,4-tris(2-pyridyl)benzene. The η^2-coordination of the triple bond is difficult here because of steric repulsion by the two pyridyl groups at α-positions. Since the spatial requirements for the pyridyl group-assisted Diels–Alder reaction are not satisfied either, the 2,5-dipyridylmetallacycle intermediate merely accepts coordination of the phosphine to give **2**.

Experimental

Reaction of [CoCp(PPh₃)₂] with 2-ethynylpyridine

The reaction was carried out at room temperature under nitrogen. To a solution of $[CoCp(PPh_3)_2 \cdot C_6H_6]$ (1.45 g) in benzene (30 mol) was added 2-ethynylpyridine (0.4 ml) dropwise with stirring. After 18 h, the dark brown solution was concentrated under vacuum and chromatographed on alumina (Sumitomo KCG-30, deactivated beforehand by adding 5 wt% of water, 18 × 20 cm). The first band

(orange-brown) and the second band (orange) were eluted with benzene. The first eluate was concentrated and hexane was added to give brown crystals of **2** (133 mg); decomp. 129–132°C. ^{1}H NMR (CD$_2$Cl$_2$): δ 5.18 (s, 5H, C$_5$H$_5$); 6.47 (d, J(PH) 6.8 Hz, 2H, metalloring-H); 6.65 (d, J(HH) 8.0 Hz, 2H, pyridyl-H(3)); 6.93 (dd, J(HH) 6.8 and 3.9 Hz, 2H, pyridyl-H(5)); 7.08–7.40 (m, 17H, phenyl and pyridyl-H(4)); 8.515 (dd, J(HH) 3.9 and 1.7 Hz, 2H, pyridyl-H(6))ppm. Analysis. Found: C, 74.74; H, 5.09; N, 4.63. C$_{37}$H$_{30}$CoN$_2$P calc: C, 75.00; H, 5.10; N, 4.73%. The second eluate was treated similarly but it remained a brown oil (210 mg). Prolonged storage of this oily complex **3** under nitrogen resulted in some decomposition. ^{1}H NMR (CD$_2$Cl$_2$): δ 4.92 (s, 5H, C$_5$H$_5$); 6.81 (dd, J(PH) 6.8, J(HH) 3.2 Hz, 1H, metalloring-H); 6.9–7.5 (m, 22H, pyridyl and phenyl); 8.36 (broad-d, J(HH) 3.7 Hz, 1H, pyridyl-H(6)); 8.61 (broad-d, J(HH) 3.9 Hz, 1H, pyridyl-H(6′)) ppm. The third fraction (colorless) was eluted with benzene/dichloromethane (1/1) which on concentration gave colorless crystals of 1,3,5-tris(2-pyridyl)benzene (73 mg); mp. 224°C. ^{1}H NMR (CD$_2$Cl$_2$) δ 7.30 (dd, J(HH) 7.7 and 5.0 Hz, 3H, pyridyl-H(5)); 7.83(triplet of

Table 3

Crystal data

Formula	C$_{26}$H$_{20}$CoN$_3$
M	433.4
Crystal size, mm	0.35×0.23×0.19
Space group (crystal system)	$P\bar{1}$ (triclinic)
a, Å	12.925(3)
b, Å	13.664(3)
c, Å	12.349(3)
α, deg	103.78(2)
β, deg	98.07(2)
γ, deg	71.32(2)
V, Å^3	2001.7(8)
Z	4
$D_{\rm m}$ (floatation), g cm^{-3}	1.44(5)
$D_{\rm c}$, gcm^3	1.438
$F(000)$	896
μ, cm^{-1}	8.71
Radiation (λ/Å)	Mo-K_α(0.7107)
Diffractometer	Rigaku-AFC
Scan speed, deg·min^{-1}	constant, 3.6
2θ scan limits, deg	$2 < 2\theta < 55$
Scan method	ω-2θ
Data collection	$\pm h$, $\pm k$, $+l$
Standard reflections	3 std/150 reflections (var. <1%)
Unique data	9620
Unique data used in refinement $F_{\rm o} \geq 3\sigma(F_{\rm o})$	4636
R	0.042
$R_{\rm w}$ ($w = 1/\sigma(F)$)	0.033
Number of parameters	702
GOF	1.95
Maximum residual electron density (eÅ^{-3})	0.26

doublet, J(HH) 7.7 and 1.7 Hz, 3H, pyridyl-H(4)); 7.97 (doublet of broad triplet, J(HH) ca. 8 Hz, 3H, pyridyl-H(3)); 8.74 (broad-d, J(HH) ca. 5 Hz, 3H, pyridyl-H(6)); 8.76 (s, 3H, benzene-H) ppm. Analysis. Found: C, 81.55; H, 4.90; N, 13.52. $C_{21}H_{15}N_3$ calc: C, 81.53; H, 4.89; N, 13.58%. The fourth band (red-purple) was eluted with dichloromethane. Concentration of the eluate and addition of hexane gave dark-purple crystals of **4** (97 mg); mp. 188°C dec. ^{1}H NMR (CD_2Cl_2) δ 4.33 (dd, J(HH) 6.3 and 1.7 Hz, 1H, H(C4)); 4.79 (s, 5H, Cp); 5.90 (doublet of broad triplet, J(HH) 6.3, 2.4, and 1.7 Hz, 1H, H(C3)); 6.01 (t, J(HH) 1.7 Hz, 1H, H(C6)); 6.61 (d, J(HH) 2.4 Hz, 1H, H(C2)); 6.85–6.95 (m); 7.1–7.15 (m); 7.28–7.35 (m); 7.4–7.5 (m); 8.35–8.42 (m) ppm. Analysis. Found: C, 71.79; H, 4.67; N, 9.62. $C_{26}H_{20}CoN_3$ calc: C, 72.06; H, 4.65; N, 9.70%.

Crystal structure determination

The crystal and refinement data are summarized in Table 3. The coordinates of the cobalt were determined from a Patterson map. The remaining atoms were located from subsequent difference Fourier syntheses. Nonhydrogen atoms were refined anisotropically and hydrogen atoms were refined with isotropic thermal parameters, by block-diagonal least-squares. Anomalous dispersion effects for Co were included in the calculation by use of Δf and $\Delta f''$ values taken from ref. 7. Atomic scattering factors were taken from the "International Tables" [8]. Tables of anisotropic temperature factors, hydrogen atom coordinates, and structure factors are available from the authors.

References

1 (a) Y. Wakatsuki and H. Yamazaki, J. Chem. Soc., Chem. Commun., (1973) 280; (b) Y. Wakatsuki T. Kuramitsu and H. Yamazaki, Tetrahedron Lett., (1974) 4549; (c) Y. Wakatsuki and H. Yamazaki, ibid., (1973) 3383; (d) Y. Wakatsuki and H. Yamazaki, J. Organomet. Chem., 149 (1978) 385.
2 H. Yamazaki and Y. Wakatsuki, J. Organomet. Chem., 139 (1977) 157.
3 Y. Wakatsuki, O. Nomura, K. Kitaura, K. Morokuma, and H. Yamazaki, J. Am. Chem., Soc., 105 (1983) 1907.
4 D.L. McAlister, J.E. Bercaw and R.G. Bergman, J. Am. Chem. Soc., 99 (1977) 1666.
5 Y. Wakatsuki, K. Aoki, and H. Yamazaki, J. Am. Chem. Soc., 101 (1979) 1123.
6 A.M. Stolzenberg, M. Scozzafava, and B.M. Foxman, Organometallics, 6 (1987) 769.
7 D.T. Cromer, Acta Crystallogr., 18 (1965) 17.
8 International Tables for X-ray Crystallography, Vol. 3, Kynoch Press, Birmingham, England, 1962.