Co-oligomerization of Diphenylketene and Ethylene promoted by (η^5-Cyclopentadienyl)bis(ethylene)cobalt(I): Synthesis and *X*-Ray Structure of a Heterocycle containing Cobalt(III) †

Sandro Gambarotta
Dipartimento di Chimica e Chimica Industriale, Università di Pisa, 56100 Pisa, Italy
Sergio Stella and Carlo Floriani *
Chemistry Department, Columbia University, New York, N.Y. 10027, U.S.A.
Angiola Chiesi-Villa and Carlo Guastini
Instituto di Strutturistica Chimica, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Università di Parma, 43100 Parma, Italy

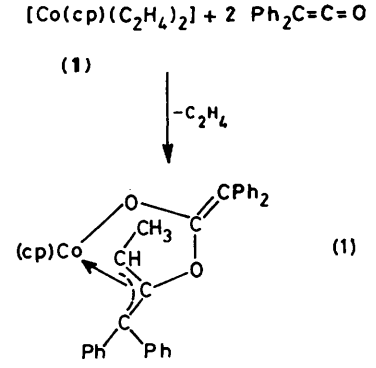
The complex $[\mathrm{Co(cp)(C_2H_4)_2}]$ (cp = η^5-$\mathrm{C_5H_5}$) promotes the co-cyclization of two diphenylketenes and one ethylene molecule to form a chelate ring which is a structural model for some precursors of metal-catalyzed co-cyclization of different functionalities. The *X*-ray structure of the resulting complex $[\overline{\mathrm{Co\{[Ph_2C{\cdots}C{\cdots}CH(CH_3)]OC({=}CPh_2)O}}\}\mathrm{(cp)}]$, (**2**), shows the sequence of co-oligomerization of the three molecules. The cobalt is η^5 bonded to cp, η^3 bonded to an allyl group (arising from the rearrangement of an ethylene residue), and bonded to an oxygen atom. Complex (**2**) crystallizes in the triclinic space group $P\bar{1}$, with a = 12.664(4), b = 16.637(5), c = 10.378(4) Å, α = 93.60(4), β = 113.27(3), γ = 93.83(4)°, Z = 2, R = 0.065.

There is currently great interest in the organometallic chemistry of ketenes.[1] The ketene functionality undergoes a variety of fixation, fragmentation, and coupling reactions by metal complexes. Some ketenes have been used as modelling the behaviour of other cumulenes, and mainly for carbon dioxide.[2] The metal-promoted fragmentation into a carbene and CO[3a] and the reverse reaction emphasize[3b] the intermediacy of metal–ketene complexes in the catalytic and stoicheiometric reduction of carbon monoxide.[4] In this context the conversion of an η^2-C,O acyl into the corresponding η^2-C,O metal-bonded ketenes[5] has a significant relevance. This latter type of complex may undergo insertion of another molecule of ketene,[2a] olefin,[5b] or acetylene[5b] to form five-membered chelate rings. Here we wish to report the formation of a seven-membered chelate ring in a rearranged form. This result was achieved by reacting diphenylketene, $\mathrm{Ph_2C{=}C{=}O}$, with $[\mathrm{Co(cp)(C_2H_4)_2}]$ (**1**) (cp = η^5-$\mathrm{C_5H_5}$),[6] which promotes the co-cyclization of two $\mathrm{Ph_2C{=}C{=}O}$ and one ethylene molecule.

Results and Discussion

A toluene solution of complex (**1**) reacts at room temperature with $\mathrm{Ph_2C{=}C{=}O}$ according to equation (1) with a partial loss of ethylene. The resulting complex, (**2**), is a diamagnetic derivative of cobalt(III), and the ^{1}H n.m.r. spectrum confirms the ethylene rearrangement present in the ligand around cobalt. Reaction (1) is further proof that, due to the lability of two co-ordination sites, complex (**1**) can drive the reaction between different functionalities.[7]

The structure of complex (**2**) was established by *X*-ray analysis and is shown in the Figure. Bond distances and angles are given in Table 1. Cobalt is η^5 bonded to the cp ring at a normal distance of 1.694(7) Å,[7] and to an oxygen and an allylic group, which are the ends of a ligand formed from the co-oligomerization of two $\mathrm{Ph_2C{=}C{=}O}$ and one ethylene unit. The plane of the allylic group C(9), C(8), C(10) is perpendicular to the plane defined by Co, O(1), C(7), O(2), C(8), the dihedral angle between the two planes being 87.6(5)°. Cobalt lies 1.654(2) Å from the allylic plane, the three related Co–C bonds being very close, in agreement with an η^3 interaction [Co–C(8), 2.019(9); Co–C(9), 2.188(10), Co–C(10), 2.084(10) Å], as are the related C–C bonds (Table 1). A significant difference is observed among the C–O bond distances, with C(7)–O(1) maintaining a significant double bond character.



(**1**)

(**2**)

(1)

A plausible mechanism for the formation of (**2**) can be based on previous information on the dimerization of $\mathrm{Ph_2C{=}C{=}O}$,[1,2a] on the chemistry of $[\mathrm{Co^I(cp)}]$,[7] and on structural evidence. It must be emphasized that complex (**2**) resembles a plausible precursor for a metal-catalyzed co-cyclization of two $\mathrm{Ph_2C{=}C{=}O}$ and $\mathrm{C_2H_4}$. Reductive elimination of the organic fragment was not observed under the mild reaction conditions we used, nor in the presence of $\mathrm{P(C_6H_{11})_3}$. Two basic pathways [(*a*) and (*b*) in the Scheme] can be suggested for reaction (1), leading to the same precursor of (**2**).

Monosubstitution of $\mathrm{C_2H_4}$ by different ligands is a known process;[7c] co-ordination of $\mathrm{Ph_2C{=}C{=}O}$ through the C=O group

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

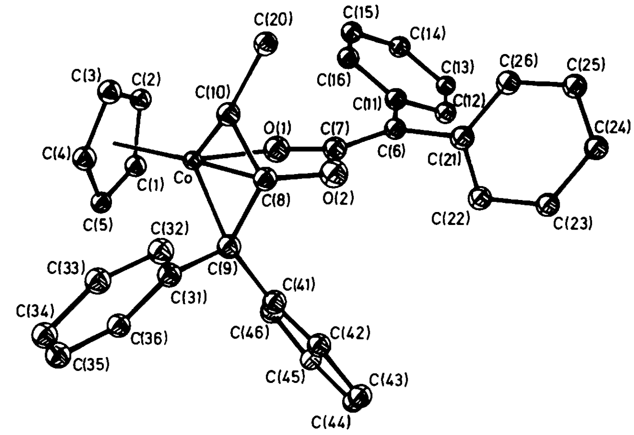


Figure. Molecular structure of complex (**2**). Non-hydrogen atoms are shown with arbitrary radii

Table 1. Selected bond distances (Å) and angles (°)*

Co–O(1)	1.925(4)	Co–C(1)	2.095(7)
Co–C(8)	2.019(9)	Co–C(2)	2.075(8)
Co–C(9)	2.188(10)	Co–C(3)	2.063(7)
Co–C(10)	2.084(10)	Co–C(4)	2.076(6)
Co–cp	1.694(7)	Co–C(5)	2.095(7)
O(1)–C(7)	1.303(10)	C(8)–C(9)	1.435(12)
O(2)–C(7)	1.391(10)	C(8)–C(10)	1.411(13)
O(2)–C(8)	1.404(8)	C(9)–C(31)	1.484(8)
C(6)–C(7)	1.365(9)	C(9)–C(41)	1.516(9)
C(6)–C(11)	1.488(10)	C(10)–C(20)	1.496(15)
C(6)–C(21)	1.507(10)	C(10)–H(10)	1.14
O(1)–Co–cp	123.8(3)	Co–C(8)–O(2)	111.3(5)
O(1)–Co–C(10)	96.2(3)	O(2)–C(8)–C(10)	116.9(7)
O(1)–Co–C(9)	96.8(3)	O(2)–C(8)–C(9)	117.2(7)
O(1)–Co–C(8)	79.6(3)	Co–C(8)–C(10)	72.4(5)
cp–Co–C(10)	122.8(3)	Co–C(8)–C(9)	76.6(5)
cp–Co–C(9)	130.8(3)	C(9)–C(8)–C(10)	124.2(8)
cp–Co–C(8)	155.8(3)	Co–C(9)–C(8)	63.8(5)
C(9)–Co–C(10)	72.1(4)	Co–C(9)–C(31)	121.8(7)
C(8)–Co–C(10)	40.2(4)	Co–C(9)–C(41)	118.5(7)
C(8)–Co–C(9)	39.6(3)	C(8)–C(9)–C(31)	121.8(7)
Co–O(1)–C(7)	118.8(5)	C(8)–C(9)–C(41)	115.8(7)
C(7)–O(2)–C(8)	114.8(6)	C(31)–C(9)–C(41)	115.0(7)
C(7)–C(6)–C(11)	121.1(7)	Co–C(10)–C(8)	67.4(5)
C(7)–C(6)–C(21)	119.5(7)	C(8)–C(10)–C(20)	122.2(8)
C(11)–C(6)–C(21)	119.4(7)	Co–C(10)–C(20)	119.9(7)
O(2)–C(7)–C(6)	118.4(7)	C(8)–C(10)–H(10)	102.4
O(1)–C(7)–C(6)	127.6(8)	Co–C(10)–H(10)	87.0
O(1)–C(7)–O(2)	113.9(6)	C(20)–C(10)–H(10)	133.6
C(1)–Co–C(2)	39.8(3)	C(9)–C(31)–C(32)	121.0(6)
C(1)–Co–C(5)	39.7(3)	C(9)–C(31)–C(36)	119.0(6)
C(2)–Co–C(3)	40.2(3)	C(9)–C(41)–C(42)	116.6(6)
C(3)–Co–C(4)	40.1(3)	C(9)–C(41)–C(46)	123.3(6)
C(4)–Co–C(5)	39.8(3)		
		C(6)–C(11)–C(12)	119.5(6)
		C(6)–C(11)–C(16)	120.7(6)
		C(6)–C(21)–C(22)	122.0(6)
		C(6)–C(21)–C(26)	118.0(6)

* The rigid body refinement of the cyclopentadienyl and phenyl rings of the complex molecule resulted in C–C mean distances of 1.42(1) and 1.394(8) Å respectively. For the undisordered toluene molecule the mean distance in the ring is 1.39(3) Å.

rather than C=C is assumed on the basis of the final compound containing the head-to-tail dimer of the C=O functionality; insertion of C_2H_4 into the Co–C bond, which has precedents,[5b] leads to (**4**), while the head-to-tail dimerization of $Ph_2C=C=O$ leading to (**5**) has been reported in titanium chemistry.[2a] Results from the recent literature seem to confirm the preference of C_2H_4 to insert into a M–C bond,[5b] while $>C=O$ functionalities seem to prefer the M–O bond;[8] thus the insertion of $Ph_2C=C=O$ into (**4**) and C_2H_4 into (**5**) lead to the same precursor, (**6**). A seven-membered ring is not unusual in metal-promoted cyclization of unsaturated substrates.[7,9] The precursor (**6**) can rearrange easily *via* β-hydrogen elimination to form (**2**).

Experimental

Preparation of Complex (**2**).—A toluene solution (50 cm^3) of diphenylketene (2.5 cm^3, 14.0 mmol) was treated with $[Co(cp)(C_2H_4)_2]$[6] (1.19 g, 6.60 mmol). The colour of the solution changed quickly from orange to green, then to deep red. On allowing the solution to stand at room temperature for 24 h a dark red crystalline solid formed (1.8 g, yield 37%) (Found: C, 81.05; H, 6.75; Co, 8.95. Calc. for $C_{35}H_{29}CoO_2 \cdot 2C_7H_8$: C, 81.20; H, 6.25; Co, 8.15%). ^1H N.m.r. (300 Mz, C_6D_6): δ 7.90—6.60 (m, 20 H), 4.80 (q, 1 H, *J* 6.8), 4.02 (s, 5 H), and 1.73 (d, 3 H, *J* 6.8 Hz) (not including toluene).

Crystal-structure Determination of Complex (**2**).—*Crystal data.* $C_{35}H_{29}CoO_2 \cdot 2C_7H_8$, $M = 724.8$, triclinic, $a = 12.664(4)$, $b = 16.637(5)$, $c = 10.378(4)$ Å, $\alpha = 93.60(4)$, $\beta = 113.27(3)$, $\gamma = 93.83(4)^\circ$, $U = 1\,995(1)$ Å^3, $Z = 2$, $D_c = 1.207$ g cm^{-3}, $F(000) = 764$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 4.64 cm^{-1}, space group $P\bar{1}$.

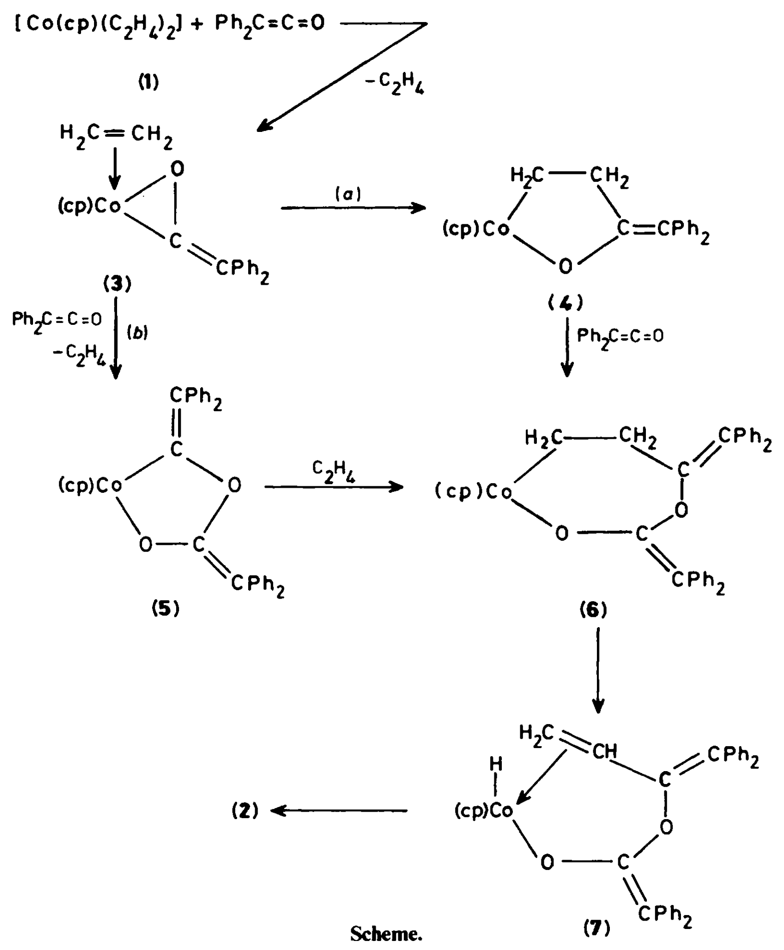
The intensities of 4 091 unique intensity data lying in the quadrant $\pm h, k, l$ with $6 < 2\theta < 44^\circ$ were measured on a Philips PW 1100 four-circle automatic diffractometer using graphite-monochromatized Mo-K_α radiation.

The structure was solved by the heavy-atom method starting from a three-dimensional Patterson map. Refinement was first isotropic, then anisotropic for the non-H atoms, by blocked full-matrix least squares. Solution and refinement were based on 2 552 observed reflections [$I > 3\sigma(I)$]. Data reduction, structure solution, and refinement were carried out on a GOULD SEL 32/77 computer, using the SHELX 76[10] system of programs. The *X*-ray analysis revealed the presence of two toluene molecules of crystallization. One appears to be affected by disorder. Several attempts were made to interpret it in terms of 'partial' atoms. Only the model in which this molecule was statistically distributed over two positions [C(61)–C(67), C(71)–C(77)] converged in successive refinement. The 14 'partial' atoms were refined isotropically with site occupancy factors of 0.5. The remaining non-hydrogen atoms were refined anisotropically applying 'rigid body' constraints to the cyclopentadienyl and phenyl rings. The hydrogen atoms associated to the complex molecule were located in a ΔF map and introduced as fixed-atom contributions ($U_{iso} = 0.08$ Å^2) prior to the final refinement. The refinement converged with $R = 0.065$, $R' = 0.067$, and g.o.f. = 1.7.*

The function minimized during the least-squares refinement was $\Sigma w|\Delta F|^2$. Weights were applied according to the scheme $w = k/[\sigma^2(F_o) + |g|(F_o)^2]$. At the end of refinement the values of *k* and *g* were 1.4354 and 0.001 171 respectively. Anomalous scattering corrections were included in all structure factors calculations.[11b] Scattering factors for neutral atoms were taken from ref. 11*a* for non-hydrogen atoms and from ref. 12 for H.

---

* $R = \Sigma||F_o| - F_c||/\Sigma|F_o|$, $R' = \Sigma\sqrt{w}||F_o| - |F_c||/\Sigma\sqrt{w}|F_o|$, g.o.f. = $[\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{\frac{1}{2}}$.



Scheme.

Table 2. Fractional atomic co-ordinates (× 10^4)*

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Co	1 678(1)	1 468(1)	853(1)	C(35)	5 685(3)	957(4)	1 716(5)
O(1)	179(4)	1 357(3)	−683(5)	C(36)	4 501(3)	893(4)	884(5)
O(2)	1 010(4)	2 182(3)	−1 740(5)	C(41)	2 302(5)	926(3)	−1 757(5)
C(1)	1 299(6)	495(4)	1 838(6)	C(42)	2 679(5)	1 145(3)	−2 790(5)
C(2)	994(6)	1 225(4)	2 320(6)	C(43)	2 354(5)	642(3)	−4 034(5)
C(3)	2 009(6)	1 775(4)	2 943(6)	C(44)	1 652(5)	−80(3)	−4 246(5)
C(4)	2 942(6)	1 384(4)	2 846(6)	C(45)	1 275(5)	−299(3)	−3 214(5)
C(5)	2 503(6)	593(4)	2 163(6)	C(46)	1 600(5)	205(3)	−1 969(5)
C(6)	−1 031(6)	1 943(5)	−2 740(8)	C(51)	2 777(12)	3 958(13)	5 098(25)
C(7)	3(6)	1 806(5)	−1 719(8)	C(52)	3 349(12)	3 365(13)	5 927(25)
C(8)	2 003(6)	2 165(5)	−498(8)	C(53)	4 317(12)	3 082(13)	5 794(25)
C(9)	2 693(7)	1 506(5)	−432(8)	C(54)	4 713(12)	3 392(13)	4 833(25)
C(10)	2 095(7)	2 679(6)	684(10)	C(55)	4 142(12)	3 984(13)	4 004(25)
C(20)	1 251(8)	3 283(6)	595(10)	C(56)	3 173(12)	4 267(13)	4 136(25)
C(11)	−2 142(4)	1 634(4)	−2 688(6)	C(57)	4 527(20)	4 301(15)	3 108(28)
C(12)	−3 086(4)	1 365(4)	−3 939(6)	C(61)	1 521(24)	5 051(17)	6 635(27)
C(13)	−4 143(4)	1 095(4)	−3 911(6)	C(62)	3 204(50)	4 840(34)	8 848(55)
C(14)	−4 258(4)	1 093(4)	−2 632(6)	C(63)	3 712(36)	5 536(29)	9 775(48)
C(15)	−3 314(4)	1 362(4)	−1 382(6)	C(64)	3 537(37)	5 959(29)	10 379(44)
C(16)	−2 257(4)	1 632(4)	−1 409(6)	C(65)	2 109(43)	6 200(25)	10 584(42)
C(21)	−1 049(5)	2 441(3)	−3 911(5)	C(66)	1 579(35)	5 772(24)	9 767(42)
C(22)	−333(5)	2 321(3)	−4 621(5)	C(67)	636(29)	4 553(19)	7 691(31)
C(23)	−373(5)	2 801(3)	−5 689(5)	C(71)	2 353(37)	5 699(22)	9 819(37)
C(24)	−1 129(5)	3 402(3)	−6 047(5)	C(72)	1 098(27)	5 409(20)	9 152(33)
C(25)	−1 846(5)	3 522(3)	−5 337(5)	C(73)	331(37)	5 018(27)	8 348(47)
C(26)	−1 806(5)	3 042(3)	−4 269(5)	C(74)	1 344(38)	4 349(19)	7 606(34)
C(31)	3 954(3)	1 588(4)	442(5)	C(75)	2 243(40)	4 725(23)	8 364(38)
C(32)	4 591(3)	2 347(4)	833(5)	C(76)	2 849(31)	5 228(21)	9 092(33)
C(33)	5 774(3)	2 411(4)	1 665(5)	C(77)	3 018(37)	6 311(20)	10 727(32)
C(34)	6 321(3)	1 716(4)	2 107(5)				

* The site occupation factor for disordered carbons [C(61)–C(77)] is 0.5.

Among the low-angle reflections no correction for secondary extinction was deemed necessary.

In the final difference map there were no peaks greater than 0.4 e Å^{-3} and no holes less than -0.4 e Å^{-3}.

Final atomic co-ordinates are listed in Table 2.

Acknowledgements

We thank the Office of Naval Research (U.S.A.) and the Consiglio Nazionale delle Ricerche (Rome) for financial support.

References

1 I. Bkouche-Waksman, J. S. Ricci, T. F. Koetzle, J. Weichmann, and W. A. Herrmann, *Inorg. Chem.*, 1985, **24**, 1492; W. A. Herrmann, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 800.

2 (*a*) G. Fachinetti, C. Biran, C. Floriani, A. Chiesi-Villa, and C. Guastini, *Inorg. Chem.*, 1978, **17**, 2995; (*b*) S. Gambarotta, M. Pasquali, C. Floriani, A. Chiesi-Villa, and C. Guastini, *ibid.*, 1981, **20**, 1173 and refs. therein.

3 (*a*) P. Hong, N. Nishii, K. Sonogashira, and N. Hagihara, *J. Chem. Soc., Chem. Commun.*, 1972, 993; T. Yamamoto, A. R. Garber, J. R. Wilkinson, C. B. Boss, W. E. Streib, and L. J. Todd, *ibid.*, 1974, 354; (*b*) W. A. Herrmann, J. Plank, M. L. Ziegler, and K. Weidenhammer, *J. Am. Chem. Soc.*, 1979, **101**, 3133; A. Miyashita and R. H. Grubbs, *Tetrahedron Lett.*, 1981, **22**, 1255; T. W. Bodnar and A. R. Cutler, *J. Am. Chem. Soc.*, 1983, **105**, 5926.

4 W. A. Herrmann, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 117; P. T. Wolczanski and J. E. Bercaw, *Acc. Chem. Res.*, 1980, **13**, 121; G. Erker, *ibid.*, 1984, **17**, 103.

5 (*a*) G. S. Bristow, P. B. Hitchcock, and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 1982, 462; (*b*) D. A. Straus and R. H. Grubbs, *J. Am. Chem. Soc.*, 1982, **104**, 5499; (*c*) E. J. Moore, D. A. Straus, J. Armantrout, B. D. Santarsiero, R. H. Grubbs, and J. E. Bercaw, *ibid.*, 1983, **105**, 2068.

6 K. Jones, E. Deffense, and D. Habermann, *Agnew. Chem., Int. Ed. Engl.*, 1983, **22**, 716.

7 (*a*) K. P. C. Vollhardt, *Acc. Chem. Res.*, 1977, **10**, 1; *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 539; (*b*) H. Bönnemann, *ibid.*, 1985, **24**, 248; 1978, **17**, 505; (*c*) H. Werner, *ibid.*, 1983, **22**, 927; K. Jonas, *ibid.*, 1985, **24**, 295.

8 C. P. Casey, J. M. O'Connor, and K. J. Haller, *J. Am. Chem. Soc.*, 1985, **107**, 3172.

9 J. Browning, M. Green, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1974, 97.

10 G. M. Sheldrick, SHELX 76, system of crystallographic computer programs, University of Cambridge, 1976.

11 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, (*a*) p. 99, (*b*) p. 149.

12 R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

Received 18*th June* 1986; *Paper* 6/1234