Synthesis, Crystal and Molecular Structure of Acetonitrilecarbonyldichloro(cyclo-octa-1,5-diene)ruthenium(II)

By **Robert O. Gould,* C. Lynn Jones, Donald R. Robertson, and T. Anthony Stephenson *** Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

Reaction of $[RuCl_2CO(C_8H_{12})]_2$ with acetonitrile gives $[RuCl_2CO(MeCN)C_8H_{12}]$ (Ia), shown by *X*-ray diffraction analysis to have octahedral stereochemistry with a *trans*-OC–Ru–MeCN arrangement. Crystals are monoclinic, space group $P2_1/c$, with a = 12.933(2), b = 7.641(8), c = 13.435(3) Å, β = 104.36(2)°, and contain one molecule per asymmetric unit. The structure was solved by use of 1 086 film data, and refined to R 0.09. The related complexes $[RuCl_2CO(L)C_8H_{12}]$ (L = acrylonitrile and cyclopropyl cyanide) have also been synthesised.

ALTHOUGH the carbonyl diene complexes $[RuX_2CO(diene)]_n$ {X = Cl or Br, diene = bicyclo[2.2.1]hepta-2,5-diene (norbornadiene) or cyclo-octa-1,5-diene} were first reported in 1966,[1] surprisingly little work on the reactions of these compounds has been published. Thus, Robinson and Wilkinson [1] showed that with pyridine, bridge splitting and diene displacement occur giving $[RuCl_2CO(C_5H_5N)_3]$, whereas with quinoline (quin) *trans*-$[RuCl_2(CO)_2(quin)_2]$ is formed. More recently, cleavage of the halide bridges with halide ion to give the $[RuX_3CO(C_7H_8)]^-$ anion has been achieved [2] and there has been a detailed study of the reactions of $[Ph_3(PhCH_2)P][RuCl_3(CO)(C_7H_8)]$ with various Lewis bases.[3]

In contrast, the chemistry of the related $[RuX_2\text{-}diene]_n$ compounds has been extensively investigated.[2] Very recently, Ashworth and Singleton [4] reported that the cationic $[RuCl(C_8H_{12})(MeCN)_3][PF_6]$ complexes can be readily synthesised by heating under reflux $[RuCl_2(C_8H_{12})]_n$ with acetonitrile, followed by precipitation with $[NH_4][PF_6]$. In an attempt to prepare the analogous cation $[RuCl(C_8H_{12})CO(MeCN)_2]^+$ we have examined the reaction of $[RuCl_2CO(C_8H_{12})]_n$ with excess of acetonitrile. However, the main product from this reaction was a crystalline orange compound with analysis corresponding closely to $[RuCl_2(CO)(MeCN)(C_8H_{12})]$ (I). Unfortunately, although the i.r. spectrum of this material showed the presence of carbonyl, acetonitrile, and cyclo-octadiene groups, it was too insoluble and involatile for n.m.r., mass spectroscopy, or molecular-weight studies. Therefore, an *X*-ray structural determination of (I) was undertaken both to verify the formulation and to ascertain the detailed geometry.

RESULTS

Crystal Data.—$C_{11}H_{15}Cl_2NORu$, M = 349.2, Monoclinic, a = 12.993(2), b = 7.641(8), c = 13.435(3) Å, β = 104.36(2)°, U = 1 292 Å^3, D_m = 1.77, Z = 4, D_c = 1.795 g cm^{-3}. Cu-K_α radiation, λ = 1.541 8 Å; μ(Cu-K_α) = 138.1 cm^{-1}. Space group $P2_1/c$.

Intensity data were derived from multiple-packs of Weissenberg films by use of an SAAB Mark II automatic film scanner. Layers $h0$—$4l$ and 0—$2kl$ were measured for a small plate-like crystal of diameter 0.2 mm and thickness 0.1 mm. No absorption corrections were made. Cell dimensions were derived from the films by an adaptation of the method of Main and Woolfson.[5]

From the Patterson function, the ruthenium atom could be placed near $\frac{1}{4}$,0,0, where it contributes significantly only to reflections $h = 2n$, $k + l = 2n$. The rest of the structure was found by the DIRDIF procedure,[6] by use of phased difference-structure factors for those reflections with a ruthenium contribution, two origin-fixing reflections, and a permutation of signs for two other reflections, giving a fourfold solution. The correct solution could easily be distinguished, and all non-hydrogen atoms were located in a second difference-Fourier synthesis. No attempt was made to locate hydrogen atoms.

Refinement to a final R 0.092 based on 1 086 data was carried out by full-matrix least squares with the weighting scheme $W = X^2Y^2$, where $X = \sin\theta/0.54$ for $\sin\theta < 0.54$ (otherwise $X = 1$) and $Y = 37/|F_o|$ for $|F_o| > 37$ (otherwise $Y = 1.0$). Latterly, anisotropic thermal parameters were used for the ruthenium and chlorine atoms only. On the final cycle of refinement, no parameter shifted by $>0.1\sigma$. Final atomic parameters are given in Table 1, and structure factor tables are deposited as Supplementary Publication No. SUP 21843 (4 pp., 1 microfiche).*

DISCUSSION

Bond lengths and angles for (I) are given in Table 2, and a view of the molecule in the Figure. They show unequivocally that the product is (Ia). The co-ordination of the ruthenium is essentially octahedral, with the CO and MeCN ligands *trans*. The greatest deviation

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue. (Items less than 10 pp. are supplied as full-size copies.)

[1] S. D. Robinson and G. Wilkinson, *J. Chem. Soc.* (*A*), 1966, 300.

[2] T. A. Stephenson, E. S. Switkes, and L. Ruiz-Ramírez, *J.C.S. Dalton*, 1973, 2112, and refs. therein.

[3] L. Ruiz-Ramírez and T. A. Stephenson, *J.C.S. Dalton*, 1974, 1640.

[4] T. V. Ashworth and E. Singleton, *J. Organometallic Chem.*, 1974, **77**, C31.

[5] P. Main and M. M. Woolfson, *Acta Cryst.*, 1963, **16**, 731.

[6] R. O. Gould, Th. E. M. van den Hark, and P. T. Beurskens, *Acta Cryst.*, 1975, **A31**, 813.

is shown by the N(1)–Ru–C(1) angle (167°). The cyclo-octadiene ligand is in the normal tub conformation, and the carbonyl is approximately and the acetonitrile ligand is accurately collinear with the ruthenium atom.

TABLE 1

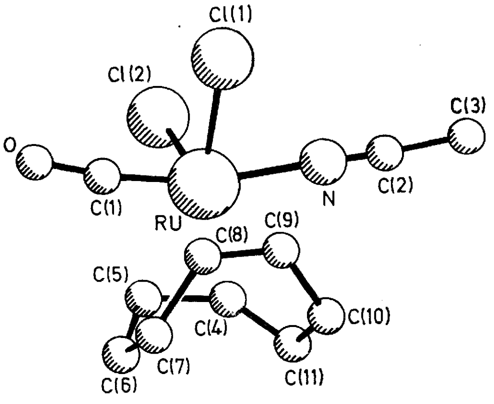
Positional and thermal parameters for (I)

Atom	10^4x	10^4y	10^4z	$10^3U/$ Å^2
Ru	2 510(1)	256(2)	−51(1)	*
Cl(1)	1 910(5)	381(10)	1 499(4)	*
Cl(2)	3 781(4)	2 535(9)	507(4)	*
C(1)	1 531(21)	1 933(41)	−480(19)	49
O	885(15)	3 126(25)	−664(14)	56
N	3 714(14)	−1 494(27)	813(13)	31
C(2)	4 302(15)	−2 390(31)	1 230(14)	29
C(3)	5 067(23)	−3 583(44)	1 845(21)	57
C(4)	3 339(14)	−614(30)	−1 287(13)	22
C(5)	2 546(17)	763(36)	−1 711(16)	37
C(6)	1 506(25)	186(47)	−2 464(22)	66
C(7)	748(22)	−828(44)	−2 073(20)	57
C(8)	1 017(18)	−1 200(36)	−927(17)	40
C(9)	1 734(17)	−2 432(35)	−447(15)	35
C(10)	2 426(21)	−3 482(43)	−983(19)	51
C(11)	3 205(26)	−2 453(51)	−1 480(23)	69

* Anisotropic parameters (Å² × 10³). The temperature factor is of form exp $(2\pi^2\Sigma_i\Sigma_j h_i h_j a^4{}_i a^*{}_j U_{ij})$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru	21	21	22	2	−2	3
Cl(1)	52	51	34	18	12	6
Cl(2)	35	31	47	−19	−15	4

The deviation of the N–Ru–C(1) angle from 180° may be associated with the inclination of the acetonitrile group away from the cyclo-octadiene, shown by the mean N–Ru–Cl and N–Ru–X angles (96.5 and 85.3°). Even so, the contact distances N ··· C(10) and N ··· C(11) are 3.01 and 3.07 Å. The distortion is somewhat less marked for the more closely bound carbonyl group where the mean C(1)–Ru–Cl and C(1)–Ru–X angles are 85.8 and 93.0°, and the C(1) ··· C(6) and C(1) ··· C(7) contacts 2.97 and 3.02 Å. Here, however, the Ru–C(1)–O angle is directed away from the cyclo-octadiene, as shown by an angle of 105° between the lines O–C(1) and Ru ··· X(3) where X(3) is the midpoint of the cyclo-octadiene ring.



Projection of a single molecule of (I)

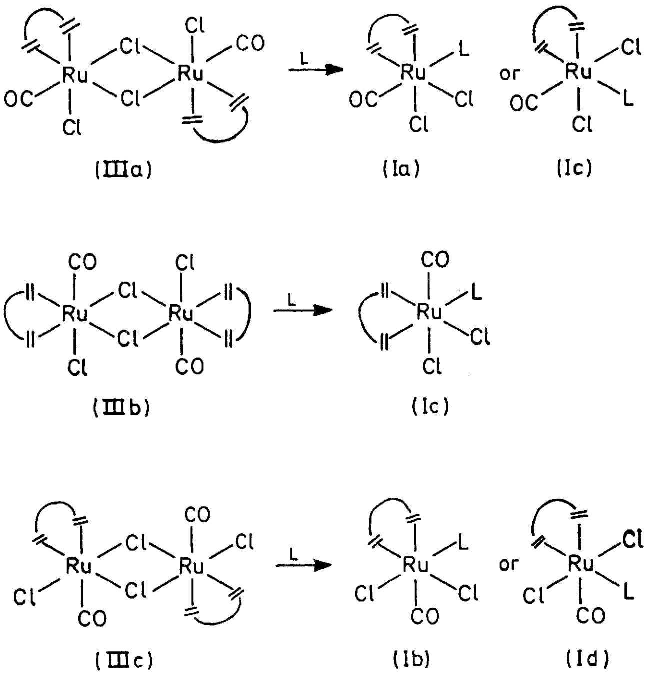
At first sight, the results are rather surprising, since earlier work on reactions of [Ph$_3$(PhCH$_2$)P][RuCl$_3$CO-(C$_7$H$_8$)] with various Lewis bases also gave [RuCl$_2$CO-(L)(C$_7$H$_8$)] (L = AsPh$_3$, SbPh$_3$, or C$_5$H$_5$N) and detailed ^{1}H n.m.r. studies revealed that these compounds had either structure (Ib) or (Ic) but not (Ia) or (Id)[3] (see Scheme 1).

TABLE 2

Bond lengths (Å) and bond angles (°) in (I). X(1) and X(2) represent midpoints of the C(4)–C(5) and C(8)–C(9) bonds respectively

(a) Distances			
Ru–Cl(1)	2.400(6)	N–C(2)	1.07(3)
Ru–Cl(2)	2.389(6)	C(2)–C(3)	1.45(3)
Ru–C(1)	1.797(29)	C(4)–C(5)	1.48(3)
Ru–N	2.165(18)	C(5)–C(6)	1.54(4)
Ru–C(4)	2.290(20)	C(6)–C(7)	1.45(5)
Ru–C(5)	2.276(23)	C(7)–C(8)	1.52(4)
Ru–C(8)	2.292(23)	C(8)–C(9)	1.37(3)
Ru–C(9)	2.292(26)	C(9)–C(10)	1.51(4)
Ru–X(1)	2.159(22)	C(10)–C(11)	1.56(5)
Ru–X(2)	2.166(25)	C(11)–C(4)	1.43(4)
C(1)–O	1.22(3)		
(b) Angles			
Cl(1)–Ru–Cl(2)	92.6(2)	N–Ru–X(2)	95.7(8)
Cl(1)–Ru–C(1)	83.9(9)	X(1)–Ru–X(2)	84.4(8)
Cl(1)–Ru–N	84.6(5)	Ru–C(1)–O	173(2)
Cl(1)–Ru–X(1)	176.0(6)	Ru–N–C(2)	179(2)
Cl(1)–Ru–X(2)	92.0(6)	N–C(2)–C(3)	176(3)
Cl(2)–Ru–C(1)	87.7(9)	C(4)–C(5)–C(6)	118(3)
Cl(2)–Ru–N	86.0(5)	C(5)–C(6)–C(7)	119(2)
Cl(2)–Ru–X(1)	90.9(6)	C(6)–C(7)–C(8)	117(2)
Cl(2)–Ru–X(2)	175.2(6)	C(7)–C(8)–C(9)	124(2)
C(1)–Ru–N	166.6(9)	C(8)–C(9)–C(10)	124(2)
C(1)–Ru–X(1)	94.5(10)	C(9)–C(10)–C(11)	118(3)
C(1)–Ru–X(2)	91.5(11)	C(10)–C(11)–C(4)	119(3)
N–Ru–X(1)	97.4(8)	C(11)–C(4)–C(5)	126(2)

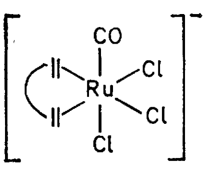
However, this discrepancy is resolved if the possible structures of the two starting materials are examined. Detailed spectroscopic studies on [Ph$_3$(PhCH$_2$)P][RuCl$_3$-COC$_7$H$_8$] show unequivocally that only isomer (II) is present in solution [2] and thus, with the knowledge that



SCHEME 1 Bridge cleavage reactions of the various possible isomers of [RuCl$_2$CO(C$_8$H$_{12}$)]$_2$

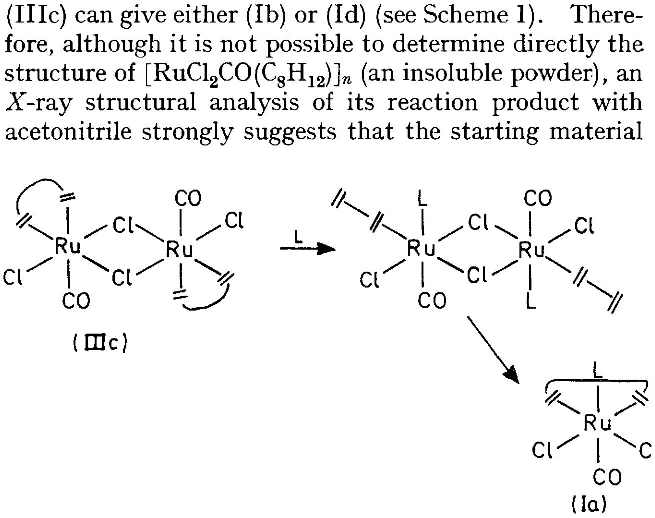
the reaction almost certainly involves initial cleavage of one of the Ru–C bonds (see Scheme 1 of ref. 3), it is impossible to form isomer (Ia).

For $[RuCl_2CO(C_8H_{12})]_n$ (assuming $n = 2$, as in ref. 1) the



(II)

three chloride-bridged structures (III; a—c) are possible.* Bridge cleavage of isomer (IIIa) with acetonitrile will then give isomer (Ia) if the bond *trans* to CO is broken or (Ic) if that *trans* to the diene group is broken. However, isomer (IIIb) can only give (Ic) and isomer (IIIc) can give either (Ib) or (Id) (see Scheme 1). Therefore, although it is not possible to determine directly the structure of $[RuCl_2CO(C_8H_{12})]_n$ (an insoluble powder), an *X*-ray structural analysis of its reaction product with acetonitrile strongly suggests that the starting material has configuration (IIIa) and that the CO group has a stronger *trans*-labilising effect than does cyclo-octa-1,5-diene.



SCHEME 2 An alternative mechanism for the formation of $[RuCl_2(CO)L(C_8H_{12})]$ (Ia)

This conclusion is, of course, based on the reasonable assumption that (I; b—d) are not initially formed and then undergo isomerisation to give (Ia) as the final product. We have also discounted the alternative mechanism (Scheme 2) which involves initial attack on a Ru–C bond to generate an η^2-C_8H_{12} complex followed by bridge cleavage by the diene to produce $[RuCl_2CO(MeCN)C_8H_{12}]$ (Ia). If this mechanism were correct, then in the presence of excess of acetonitrile, either complete diene displacement or at least the formation of a complex containing two MeCN groups per ruthenium would be expected. The inability [3] of MeCN to displace the diene group in $[Ph_3(PhCH_2)P][RuCl_3CO(C_7H_8)]$ also supports this conclusion.

Finally, reaction of $[RuCl_2CO(C_8H_{12})]_n$ with acrylonitrile and cyclopropyl nitrile (L) gives the related $[RuCl_2(CO)L(C_8H_{12})]$ complexes. The close similarity of the i.r. spectra of these compounds to the acetonitrile analogue suggests they also have configuration (Ia).

EXPERIMENTAL

I.r. spectra were recorded in the region 4 000—250 cm^{-1} on Perkin-Elmer 225 and 457 grating spectrometers for Nujol and hexachlorobutadiene mulls on caesium iodide plates. M.p.s. were determined with a Köfler hot-stage microscope. Standard crystallographic calculations used the *X*-Ray '72 program system.[7]

*Acetonitrilecarbonyldichloro(cyclo-octa-*1,5-*diene)ruthenium*(II).—$[RuCl_2CO(C_8H_{12})]_n$ was heated under reflux under nitrogen in acetonitrile for *ca.* 4 h. The resulting yellow solution was then filtered and concentrated to produce yellow-orange *crystals* (60%), m.p. 180 °C (decomp.) (Found: C, 37.8; H, 4.4; Cl, 20.2; N, 4.0. $C_{11}H_{15}Cl_2NORu$ requires C, 37.8; H, 4.3; Cl, 20.3; N, 4.0%). I.r. spectrum: ν(CN) 2 305, ν(CO) 1 988, and ν(C=C) 1 335 cm^{-1}; combination of symmetric CH_3 deformation and C–C stretching vibrations at 2 340 cm^{-1}.

*Acrylonitrilecarbonyldichloro(cyclo-octa-*1,5-*diene)-ruthenium*(II).—This was prepared similarly as a yellow crystalline *solid*, m.p. 150 °C (decomp.) (Found: C, 39.2; H, 4.3; N, 4.4. $C_{12}H_{15}Cl_2NORu$ requires C, 39.9; H, 4.2; N, 3.9%). I.r. spectrum: ν(CN) 2 153, ν(CO) 2 015, and ν(C=C) 1 333 cm^{-1}.

*Carbonyldichloro(cyclo-octa-*1,5-*diene)(cyclopropyl nitrile) ruthenium*(II).—This was prepared similarly as an orange *solid*, m.p. 190 °C (decomp.) (Found: C, 41.4; H, 4.5; N, 3.8. $C_{13}H_{17}Cl_2NORu$ requires C, 41.6; H, 4.5; N, 3.7%). I.r. spectrum; ν(CN) 2 388, ν(CO) 2 018, and ν(C=C) 1 335 cm^{-1}.

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* It is assumed that (III) contains *trans* CO groups since only one ν_{CO} is observed in the i.r. spectrum (see ref. 1).

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