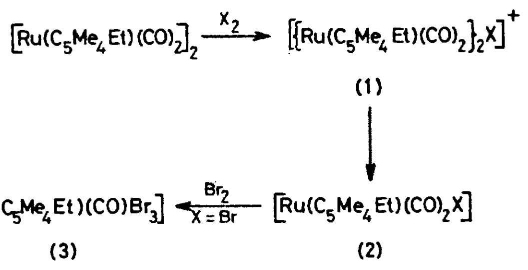
Halogenation of Bis[dicarbonyl(ethyltetramethylcyclopentadienyl)ruthenium(I)]; *X*-Ray Structure of Tribromocarbonyl(ethyltetramethylcyclopentadienyl)ruthenium(IV)

By IAN W. NOWELL*
(*Chemistry Department, Sheffield City Polytechnic, Sheffield* S1 1WB)
and KHALIL TABATABAIAN and COLIN WHITE*
(*Department of Chemistry, The University, Sheffield* S3 7HF)

Summary. Halogens react with the compound $[Ru(\eta^5\text{-}C_5Me_4Et)(CO)_2]_2$ to give first the halogeno-bridged cation $[\{Ru(\eta^5\text{-}C_5Me_4Et)(CO)_2\}_2X]^+$ and then $[Ru(\eta^5\text{-}C_5Me_4Et)(CO)_2X]$ (X = Cl, Br, or I); the bromide reacts further with bromine to give $[Ru(\eta^5\text{-}C_5Me_4Et)(CO)Br_3]$ whose *X*-ray structure is reported.

ORGANOMETALLIC compounds of ruthenium in which the ruthenium atom has a formal oxidation state of IV have often been proposed as catalytic intermediates.[1] To our knowledge the only isolated compounds of this type are $[RuH_4(PPh_3)_3]$[2] and the diallyldichloro-compounds isolated as intermediates in the $RuCl_3$-promoted trimerization of butadiene[3] and dimerization of isoprene.[4] In this communication we report the preparation and crystal structure of a stable ruthenium(IV) carbonyl compound $[Ru(\eta^5\text{-}C_5Me_4Et)(CO)Br_3]$.

Bis[dicarbonyl(ethyltetramethylcyclopentadienyl)ruthenium(I)][5] reacts with halogens in dichloromethane to give first the bridged halogeno-compounds (**1**) (isolated as the PF_6 salts) and then the neutral dicarbonyl halides (**2**).† The compound $[Ru(C_5H_5)(CO)_2]_2$ has been reported[6] to undergo similar reactions with halogens but in contrast to the cyclopentadienyl compound, the bromide (**2**, X = Br) reacts further with bromine to give the tribromide (**3**) (Scheme).



SCHEME

Evidence for the high positive charge on the metal atom in compound (**3**) comes from the ^{13}C n.m.r. spectrum in which the signals of the ring carbon atoms occur at considerably lower field than those of $Ru(C_5Me_4Et)(CO)_2Br$ (Table). In addition, the tribromide exhibits a single carbonyl absorption band at 2050 cm^{-1} (CH_2Cl_2), significantly higher than the carbonyl bands observed for $[Ru(C_5Me_4Et)(CO)_2Br]$ (2030 and 1982 cm^{-1}).

Crystal data: Compound (**3**), $C_{12}H_{17}Br_3ORu$, *M* 518·1, crystallises from dichloromethane–ether as dark-red crystals. The crystals are orthorhombic with $a = 14{\cdot}196(3)$, $b = 16{\cdot}107(3)$, $c = 13{\cdot}367(3)$ Å, space group *Pbca* (D_{2h}^{15} No. 61),

TABLE. $^{13}C\{H\}$ N.m.r. data.[a]

Compound	C(1)	C(2,5)	C(3,4)	Me_4	CH_2Me	CH_2Me	CO
$[Ru(C_5MeEt)(CO)_2Br]$	103·4	100·1,	101·0	10·0	19·4	14·9	199·4
$[Ru(C_5Me_4Et)(CO)Br_3]$	113·9	113·0,	118·2	10·4, 10·9	18·7	12·9	193·7

[a] δ scale; recorded in $CDCl_3$.

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† Satisfactory elemental microanalytical data were obtained for all new compounds.

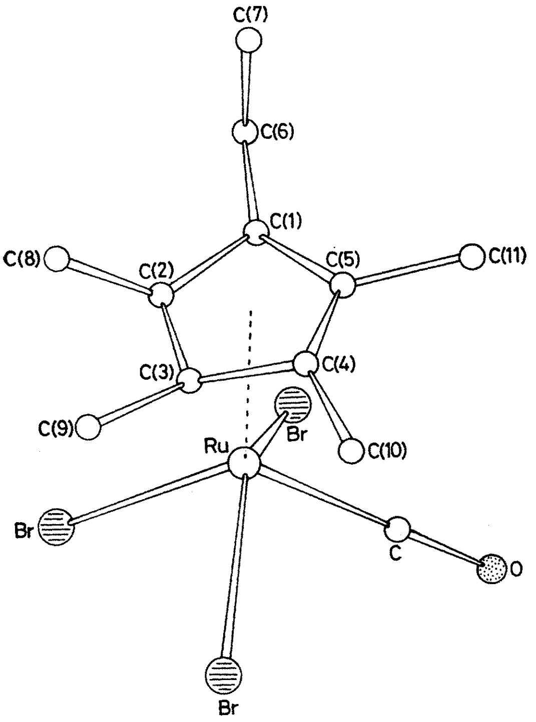

FIGURE. Molecular structure of $[Ru(\eta^5\text{-}C_5Me_4Et)(CO)Br_3]$. Important parameters: Ru–Br, 2·538, 2·546, and 2·557(6); and Ru-ring mean plane, 1·91 Å; ∠Br–Ru–Br, 80·1, 82·1, and 130·6(2)°.

$Z = 8$. R for 1201 reflections having $I/\sigma(I) \geqslant 3$, is currently 0·088.‡

Although the $(C_5Me_4Et)Ru$ fragment of the molecule is readily identifiable, the $Br_3(CO)$ grouping is disordered. The principal rotamer is shown in the Figure, the Ru–C and C–O bond distances being fixed at values of 1·87 and 1·16 Å, respectively. The five-membered ring is effectively planar, the substituent carbon atoms lying out of the mean plane in a direction away from the ruthenium atom, by an average of 0·14 Å. The Ru–Br distances (mean 2·547 Å) are significantly shorter than the values of 2·610(5) and 2·615(5) Å reported[7] for tris(*o*-diphenylarsinophenyl)arsineruthenium(II) dibromide. It seems likely that the carbonyl group is distributed over the four basal positions, but can only be readily identified in the orientation shown.

The corresponding iodide $[Ru(C_5Me_4Et)(CO)_2I]$ is not oxidized by iodine but appears to form an unstable tri-iodide of the type $[Ru(C_5Me_4Et)(CO)_2(I_3)]$ and the reaction of chlorine with $[Ru(C_5Me_4Et)(CO)_2Cl]$ gives a mixture of products that we have not yet fully identified. The tribromo-compound (**3**) is stable in air and in non-polar solvents; this is in marked contrast to the corresponding molybdenum(IV) compounds $[Mo(C_5H_4)(CO)_2X_3]$ (X = Cl, Br, or I).[8] As expected, it is much more reactive than the ruthenium(II) compound (**2**) and we are currently investigating reactions of $[Ru(C_5Me_4Et)(CO)Br_3]$ in order to explore the organometallic chemistry of ruthenium(IV).

We thank the Pahlavi Foundation for the award of a scholarship (To K. T.) and the S.R.C. for an equipment grant (to I. W. N.).

(*Received*, 21*st March* 1979; *Com.* 298.)

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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