^{1}H and ^{13}C Nuclear Magnetic Resonance Spectra and *X*-ray Crystal Structure of [1-Methyl-3-ethyl-(σ-1,3-h^2,π-1,2,3-h^3)-allyl]nonacarbonyltriruthenium: the Allyl Group as a Five-electron Donor

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Summary The reaction of *cis,trans*- or *trans,trans*-hexa-2,4-diene and $Ru_3(CO)_{12}$ is shown, by ^{1}H and ^{13}C n.m.r. spectra and *X*-ray crystal structure to give a product in which the diene ligand has undergone a skeletal rearrangement producing a π-allyl group, a metal hydride bond, and two metal–carbon σ-bonds.

There are numerous examples of the rearrangement of olefinic ligands to satisfy the electronic requirements of binuclear and trinuclear metal carbonyls.[1] Bruce and his co-workers have recently reported[2] the structure of the ruthenium cluster compound $HRu_3(CO)_9C_{12}H_{15}$ (I) where one of the enyl-groups in the original ligand, cyclododeca-1,5,9-triene, is rearranged to a π-bonded allyl group, accompanied by the formation of two metal–carbon σ-bonds to the 1 and 3 allyl carbons and a metal hydride bond. We report here another example of this unusual rearrangement which takes place on reaction between *cis,trans*- or *trans,trans*-hexa-2,4-diene with dodecacarbonyltriruthenium to give $HRu_3(CO)_9C_6H_9$ (II).[3]

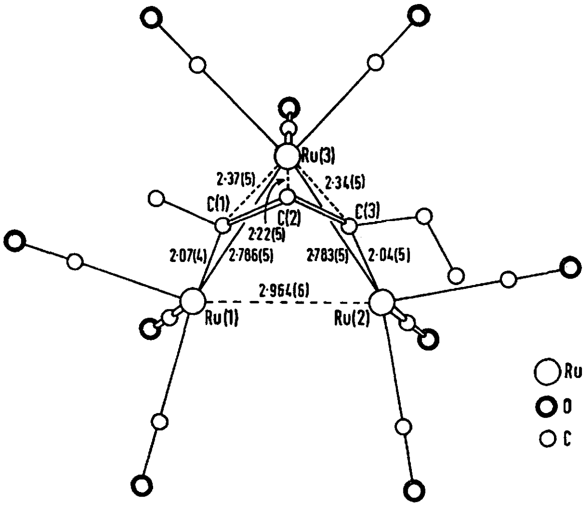

Figure. *The molecular structure of* $Ru_3(CO)_9C_6H_{10}$

The ^{1}H n.m.r. spectrum of (II) is: τ 3·36 (d), 7·16 (m), 7·21 (s), 8·58 (t), and 30·1 (d). The high-field doublet at τ 30·1 couples (2·0 Hz) to a proton giving a low field doublet at τ 3·36. A similar long-range coupling of 2·7 Hz was observed between the enyl proton at τ 3·81 and the metal-hydride resonance at τ 30·2 in (I).[2] Double irradiation in the region of the complex multiplet at τ 7·21 collapses the triplet at τ 8·58 but leaves both the high- and low-field doublets unchanged. This suggests that the olefinic doublet is separated from the rest of the ligand hydrogens by at least four bonds. The second order nature of the multiplet at τ 7·21 along with the superposition of the singlet at τ 7·16 makes definitive analysis of the proton data difficult although the integration ratio of 1:5:3:1 along with the ^{1}H chemical shifts suggests the presence of a methyl group, an ethyl group, and an olefinic methinyl group.

The proton noise decoupled ^{13}C n.m.r. and the off-resonance spectrum make interpretation more definite. A triplet resonance at 47·2 p.p.m. (±0·1 p.p.m., downfield with respect to internal Me_4Si), two quartets at 39·8 and 20·0 p.p.m., and a doublet at 119·8 p.p.m. confirm the presence of the methyl, ethyl, and methinyl groups and strongly suggests an allyl arrangement of the ligand as shown in the Figure. We have not observed ^{13}C-resonances for the two quaternary carbons required for this structure, probably due to the poorer signal to noise ratio (no Overhauser enhancement) and the longer relaxation times expected for these resonances.

The metal carbonyl region of (II) consists of three resonances at 192·1, 198·9, and 199·5 p.p.m. At narrower sweep widths (1·25 kHz) these are resolved into five resonances at 192·1, 196·6, 198·5, 199·3, and 199·7 p.p.m. A spectrum obtained without the use of proton noise decoupling showed all the resonances except the one at 198·5 p.p.m. split into doublets with J (H–M–$C{\equiv}$O) values of 17·0, 8·5, 4·0, and 4·0 Hz (±1 Hz) respectively. Although these data are consistent with the structure shown in the Figure, with the hydride bridging Ru(1) and Ru(2), not enough is known about the variation of ^{13}C-chemical shifts and ^2J(H–M–CO) in cluster compounds to make any meaningful assignments. Thus the structure shown in the Figure is based on the ^{1}H and ^{13}C n.m.r. assignments of the hydrocarbon region. We are currently investigating a series of ruthenium cluster compounds of known structure in the hope of definitively assigning the CO resonances and the location of the hydrogen in the metal cluster.

Crystals of (II) are triclinic, $a = 9{\cdot}809$, $b = 9{\cdot}448$, $c = 10{\cdot}88$ Å, $\alpha = 93{\cdot}2$, $\beta = 100{\cdot}8$, $\gamma = 90{\cdot}4°$, space group $P\bar{1}$ with $Z = 2$. The intensities of 1044 reflections out to a 2θ limit of 100° were measured on a G.E.XRD6 manual diffractometer, using the stationary crystal–stationary counter technique and Cu-K_α radiation. The structure was solved by standard heavy atom methods and the present R factor (with isotropic temperature factors and data uncorrected for absorption) is 0·115. The structure found is shown in the Figure, which includes some of the relevant bond parameters.

This structure is consistent with there being π-bonding between Ru(3) and the allylic carbon atoms C(1), C(2), and

C(3) with C(1) and C(3) being σ-bonded to Ru(1) and Ru(2), and a hydride bridging Ru(1) and Ru(2) directly analogous to the bonding picture suggested for (I). Indeed, the dimensions for the Ru(CO) fragment in our compound are almost identical to those in (I). The allyl and the hydride ligands provide the total of six electrons required for the $Ru_3(CO)_9$ group. That two different olefin ligands can give the same bonding scheme is surprising and suggests a common mechanism for the formation of complexes (I) and (II).

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