Allene Complexes of Rhodium

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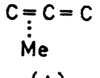
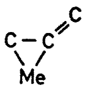
IN the complexes of transition metals with allene[1,2] it is uncertain whether the bonding of the allene to the metal is a simple π-bonding, as in (A), or occurs *via* two σ-bonds, as in (B), though n.m.r. data favour structure (B) as the main contributor to the bonding.



(A)



(B)

We have prepared several allene complexes of Rh and examined some of them by single crystal *X*-ray diffraction methods.

When acetylacetonatobisethylenerhodium, $(C_2H_4)_2$-Rhacac, is introduced into liquid 1,1-dimethylallene (DMA) at 0°, a rapid dissolution of the complex occurs, with evolution of ethylene. Pentane was added and after leaving the mixture at 0°, well-shaped yellow-orange crystals of (I) acac $Rh(CH_2:C:CMe_2)_2$, were deposited. Under the same conditions with tetramethylallene (TMA), an oil (II) acac $Rh(Me_2C:C:CMe_2)_2$ is obtained.

Similarly, when $(C_2H_4)(CO)Rh$ acac reacts in pentane with simple allene or TMA, crystalline complexes of formula $(CO)_2Rh_2$ $acac_2(CH_2:C:CH_2)$ (III) and $(CO)_2Rh_2$ acac $(Me_2$-$C{=}C{=}CMe_2)$ (IV) are obtained upon cooling. In either of these complexes, the allene is rapidly displaced by carbon monoxide or cyclo-octa-1,5-diene, at room temperature.

Single crystals of (I) and (III) have been examined by

X-ray diffraction methods; the intensities were collected by a General Electric XRD 6 diffractometer using Mo-K_α filtered radiation. 2344 independent reflections for complex (I) and 3440 for complex (III) were measured, of which 2094 and 2844, respectively, were used in the refinement. No correction was made for absorption (μ from 0·15 to 0·30). Crystal data, complex (I): $a = 14{\cdot}918 \pm 0{\cdot}042$, $b = 8{\cdot}817 \pm 0{\cdot}023$, $c = 6{\cdot}312 \pm 0{\cdot}019$ Å, $\alpha = 81{\cdot}22 \pm 0{\cdot}20$, $\beta = 98{\cdot}65 \pm 0{\cdot}20$, $\gamma = 97{\cdot}21 \pm 0{\cdot}10°$, $D_c = 1{\cdot}35$, $Z = 2$, space group $P\bar{1}$; complex (III): $a = 11{\cdot}365 \pm 0{\cdot}042$, $b = 8{\cdot}980 \pm 0{\cdot}033$, $c = 8{\cdot}950 \pm 0{\cdot}028$ Å, $\alpha = 86{\cdot}84 \pm 0{\cdot}12$, $\beta = 103{\cdot}93 \pm 0{\cdot}12$; $\gamma = 85{\cdot}14 \pm 0{\cdot}08°$, $D_c = 1{\cdot}69$, $Z = 2$, space group $P\bar{1}$. Both structures have been solved by Patterson and Fourier methods. The atomic parameters were refined by least-squares methods, using anisotropic thermal factors to R 0·058 [complex (I)] and 0·047 [complex (III)].

Valence and dihedral angles (°)

Complex (I)

Valence angles	
C(1)–C(2)–C(3)	152·6
C(2)–C(3)–C(4)	120·2
C(2)–C(3)–C(5)	123·8
C(4)–C(3)–C(5)	116·0
C(1′)–C(2′)–C(3′)	153·3
C(2′)–C(3′)–C(4′)	121·7
C(2′)–C(3′)–C(5′)	121·8
C(4′)–C(3′)–C(5′)	116·4

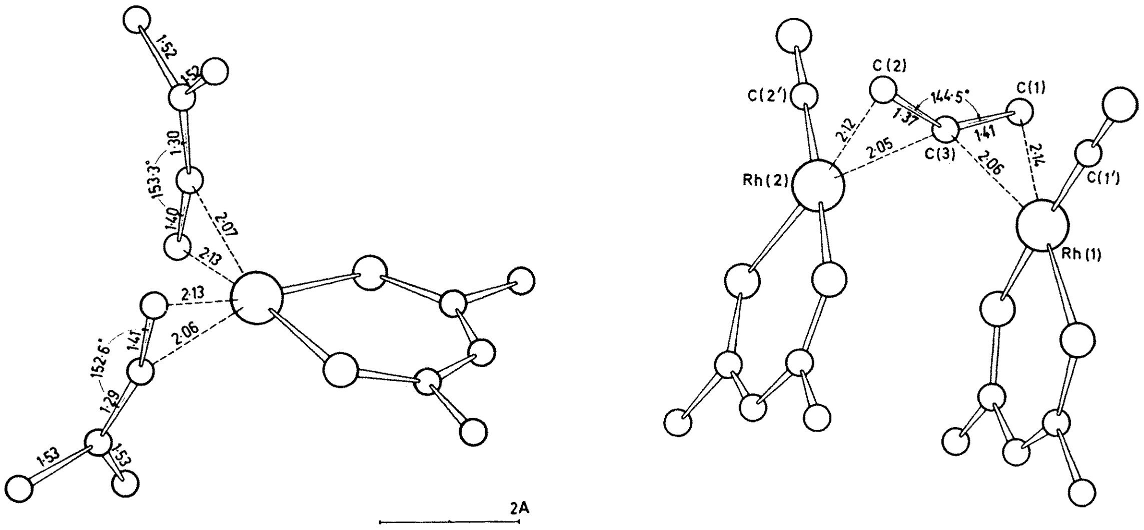
Dihedral angles	
[Rh–acac]–[Rh–C(1)–C(2)]	103·2
[Rh–acac]–[Rh–C(1′)–C(2′)]	102·5
[Rh–C(1)–C(2)]–[Rh–C(1′)–C(2′)]	94·1

Complex (III)

Valence angles	
C(1)–C(3)–C(2)	114·5

Dihedral angles	
[Rh(1)–acac(1)]–[Rh(1)–C(1)–C(3)]	95·5
[Rh(2)–acac(2)]–[Rh(1)–C(1)–C(3)]	85·6
[Rh(1)–C(1)–C(3)]–[Rh(2)–C(2)–C(3)]	94·5

Angles between Rh–CO bonds and some planes	
[Rh(1)–C(1)–C(3)]–[Rh(1)–C(1′)]	93·5
[Rh(2)–C(2)–C(3)]–[Rh(2)–C(2′)]	88·1
[Rh(1)–acac]–[Rh(1)–C(1′)]	181·3
[Rh(2)–acac]–[Rh(2)–C(2′)]	181·4



Projection of the molecules of complex (I) (*left*) *and* (III) (*right*), *with the most significant bond lengths and angles* [σRh–C) ≈ 0·008 Å; σ(C–C) ≈ 0·012 Å; σ(C–C–C) = 0·6°].

The Figure shows the resulting molecular geometries. Valence and dihedral angles are listed in the Table. All the Rh–C distances to the central atom of the allene (2·06 ± 0·1 Å) are significantly shorter than the ones to the terminal C atoms (2·13 ± 0·01 Å); this is likely to be related to the higher π electron density on the central C atom. The DMA skeleton is planar, within experimental error, and the distance from Rh to its plane is very short (0·17 and 0·18 Å for the two crystallographically different DMA groups).

In either complex a distortion of the allene skeleton is observed, which indicates that structure (B) gives some contribution to the allene–rhodium bonding. However, the overall geometry of either complex seems in better agreement with a square-planar co-ordination around Rh, with a π-bonding of the allene to the metal, as in (A).

This type of structure, which also better explains the fact that the allene is easily displaced by carbon monoxide or cyclo-octa-1,5-diene, shows that these complexes are best regarded as derivatives of Rh^{I}, rather than of Rh^{III}.

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[1] S. Otsuka, A. Nakamura, and K. Tani, *J. Organometallic Chem.*, 1968, **14**, 30.

[2] J. A. Osborn, *Chem. Comm.*, 1968, 1231.