The Crystal Structures of Ethylene and Tetrafluoroethylene Complexes of Rhodium(I)

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Summary The molecular geometries of acetylacetonatodiethylenerhodium(I) and acetylacetonatoethylenetetrafluoroethylenerhodium(I) show that C_2F_4 is more closely bound to rhodium than C_2H_4, a consequence of increased π-bonding.

ALTHOUGH the Chatt–Dewar scheme provides a good conceptual description of the bonding of olefins to transition metals, the relative importance of the σ- and π-contributions to the bond is a controversial topic. We have determined the crystal structures of two bis-olefin-rhodium(I) complexes, $(C_2H_4)_2Rh(acac)$ (**1**) and $(C_2H_4)(C_2F_4)Rh(acac)$ (**2**), [(acac) = acetylacetonato], for in the latter complex it should be possible to make direct comparisons of rhodium–alkene geometry within the same molecule.

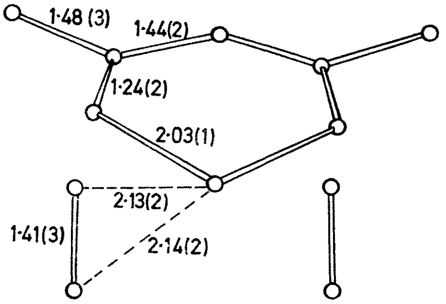

FIGURE 1. *The molecular structure of* $(C_2H_4)_2Rh(C_5H_7O_2)$. *Bond-lengths in* Å, *e.s.d.'s of last figure in parentheses.*

The two molecules have similar geometry. As expected the Rh(acac) unit is nearly planar, and the C=C bonds of the two olefin groups are approximately perpendicular to this plane [87·4° in (**1**), 84·2° and 87·8° for C_2F_4 and C_2H_4 respectively in (**2**)]. The detailed geometry (Figures 1 and 2) reveals that in (**2**) the tetrafluoroethylene carbon atoms are significantly (10σ) closer to the rhodium atom than the ethylene carbon atoms. A comparison of the Rh–C distances with those of compound (**1**) (the two ethylene ligands are equivalent in this molecule by a crystallographic mirror plane) suggests that in (**2**) C_2F_4 is *more* strongly bound, and C_2H_4 *less* strongly bound, than are the two C_2H_4 groups in the bisethylene complex (**1**). This trend is in line with the predicted π-acceptor properties of C_2F_4 and C_2H_4, and the reverse of that predicted for their σ-donor properties. It follows that the π-acceptor properties of olefins dominate in metal–olefin bonding, at least within this system. A similar conclusion has been reached by Cramer[1] from thermodynamic measurements on the substitution of olefins in compound (**1**), and, in the related system $(\pi\text{-}Cp)Rh(C_2F_4)(C_2H_4)$ (Cp = cyclopentadienyl), the activation energy to rotation of the ethylene group is lower than in (π-Cp)Rh(C_2H_4)$_2$, and C_2F_4 is not observed to rotate below 110 °C.[2]

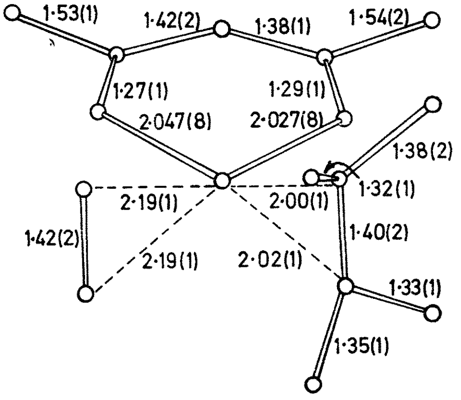

FIGURE 2. *The molecular structure of* $(C_2H_4)(C_2F_4)Rh(C_5H_7O_2)$ *Bond-lengths in* Å, *e.s.d.'s of last figure in parentheses.*

The olefin C–C bond lengths should also reflect the changing contributions of the π^* orbital in the metal–olefin bond. Allowing for the errors in these distances, it is unlikely that any of the olefin bond lengths in the two compounds differs by more than 0·03 Å (2σ) from the mean value of 1·41 Å; this is surprising in view of the large differences in Rh–C bond-lengths. However, since the C–C bond length in free C_2H_4 (1·336 Å)[3] is longer than in C_2F_4 (1·31 Å[4] or 1·27 Å[5]), the complexed olefin C–C bond lengths observed here are consistent with an increased population of π^* orbitals. Nevertheless, the small differences in olefin C–C bond lengths, coupled with their inevitably higher standard deviations, suggest that the C=C bond length alone is not a good criterion of bond-type; other guides such as metal–carbon distance, or the extent of distortion of the alkene from planarity, are more accurate. Thus, in the structure of acetylacetonatobis(tetramethylallene)rhodium(I),[6] a complex with an "unsymmetrical" olefin, the metal–carbon distances (2·18 and 2·03 Å, the shorter distance involves the more electronegative, originally *sp* hybridised carbon atom) differ by a significantly larger amount than the differences between co-ordinated and "free" C=C bond-lengths within the allene groups.

There is a slight *trans*-influence evident from the Rh–O distances in (**2**); the longer bond is *trans* to C_2F_4 and may be associated with the shorter metal–alkene distance. In other respects the co-ordinated C_2F_4 geometry is very similar to that observed in $(Ph_3P)_2(C_2F_4)RhCl$.[7]

Both structures were determined by conventional *X*-ray methods using Stoe Weissenberg diffractometer data. *R* for (**1**) is 0·079 (533 reflexions); for (**2**) *R* is 0·069 (2014 reflexions). We thank the S.R.C. for support.

(*Received, December* 16*th*, 1970; *Com.* 2176.)

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