3:83.0°) with terminal carbons toward the Cp ring and the second diene is nearly parallel with the Cp plane (2:35.0°, 3:18.5°) with terminal carbons away from the Cp ring. Complex 1, the starting material for a series of bis(diene) complexes as 2 and 3, includes the first type of diene. In all the complexes, the terminal C-C bonds are longer than the central C-C bonds. The bent angles of the pentacycles of Ta and diene (1:94.9°, 2:102.5, 100.4°) are intermediate in value   between the corresponding angles in Group IVA- and VIII-metal-diene complexes. The extended Hückel calculations on $CpTaCl_2$(butadiene) and $CpTa$(butadiene)$_2$ have corroborated these features characteristic of the Ta-diene bonding in 1, 2, and 3.

$\underline{1}$ $\underline{2}$
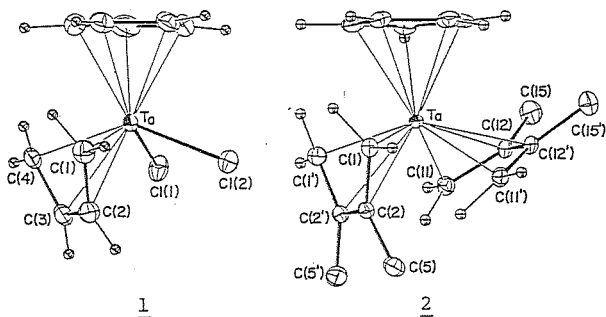
09.3—22   ASYMMETRIC BONDING OF THE 1-SYN SUBSTITUTED ALLYL MOIETY IN 4 CO-ORDINATE PALLADIUM(II) COMPLEXES

Nicholas W. Murrall and Alan J. Welch
Department of Chemistry, University of Edinburgh,
West Mains Road, Edinburgh. EH9 3TT U.K.

The complexes [Pd(TMEDA)(1-syn-Ph-C_3H_4)]BF_4 and {Pd(TMEDA)(1-syn-C(O)OEt-C_3H_4)] see Fig. 1. (TMEDA=N,N,N¦N'-Tetramethylethylenediamine) have been structurally characterised.
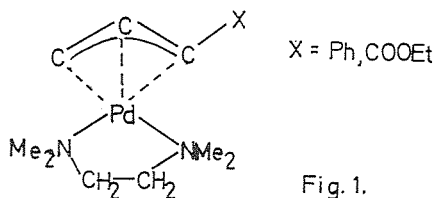

Fig. 1.

Despite the similar steric requirements of the two substituents the bonding of the two η³-Allyl fragments is not identical. In the 1-Ph derivative the end carbon bearing the substituent is further from the metal, whereas the X = C(O)OEt it is more closely bound. The origins of this will be traced to the modifications in the allyl frontier orbitals as a function of substituent.

09.3—23   CRYSTAL AND MOLECULAR STRUCTURES WITH A DIIRON CEN-
TER. By M. Font-Altaba, X. Solans, J. Ros and R. Mathieu. Dept. de
Cristal.lografia, Univ. Barcelona, GranVia 585 (Barcelona-11) and
Dept. Química Inorgànica, Univ. Autònoma Barcelona, Bellaterra
(Barcelona).

Five crystal structures with a diiron centre have been solved from X-ray diffraction data.

1. $(Fe_2(CO)_6)(\mu$-C(C(O)OCH$_3$)C(C(O)OCH$_3$C(O)C(C$_6$H$_5$)C(C$_6$H$_5$)H))(P(C$_6$H$_5$)$_4$) $0.5CH_2Cl_2$. Monoclinic, P2$_1$/n, a=17.244(6), b=23.419(7), c=12.218(5) β=94.31(4)°, V=4920(5) A^3, Z=4. Solved by direct methods using the MULTAN system of computer programs and refined by full-matrix least square. R final 0.080 (Rw=0.090).

2. $(Fe_2(CO)_6(\mu$-C(C$_6$H$_5$)C(C$_6$H$_5$)C(CF$_3$)C(CF$_3$)H)(P(C$_6$H$_5$)$_4$). Triclinic, P$\bar{1}$, a=15.397(5), b=14.495(4), c=11.258(4), α=107.3(3)°, β=96.9(2)°, γ=110.8(3)°, V=2168(2) A^3, 3572 reflections. Solved by direct methods with the MULTAN system of computer programs and refined by full-matrix least squares. R final 0.075 (Rw=0.077).

3. $(Fe_2(CO)_6(\mu$-COC$_2$H$_5$)(μ-C(C$_6$H$_5$)C(C$_6$H$_5$)H). Monoclinic, P2$_1$/n. a= 17.801(3), b=10.006(2), c=12.971(2), β=106.0(2)°, V=2220(1) A^3, Z=4, 2325 reflections. Solved by heavy atom method and refined by full-matrix least squares. R final 0.051 (Rw=0.054).

4. $(Fe_2(CO)_6(\mu$-C(CH$_2$OCH$_3$)CC(CF$_3$)C(CF$_3$). Monoclinic, P2$_1$/n. a=17.438 b=13.776(2), c=7.703(1), β=106.7(2), V=1773(4) A^3, Z=4, 1701 reflections. Solved by heavy atom method and refined by full-matrix least squares. R final 0.069 (Rw=0.066).

5. $(Fe_2(CO)_5(\mu$-C(OC$_2$H$_5$)C(CO$_2$CH$_3$)C(CO$_2$CH$_3$))(μ-C(C$_6$H$_5$)C(C$_6$H$_5$)H).0.5 H_2O. Monoclinic, C2/c, a=32.138(2), b=8.559(1), c=22.203(3), β=107.2(2)°, Z=8, 1331 reflections. Solved by direct methods using the MULTAN system of computer programs and refined by full-matrix least squares. R final 0.055 (Rw=0.053).

The Fe-Fe bond distance varies from 2.457(1) in structure 5) to 2.635(1) in 3); bond interactions has been observed in the five structures.