

## 09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

## 09.3-18 SYNTHESIS AND MOLECULAR STRUCTURES OF RELATED TRI-NUCLEAR RHODIUM COMPLEXES

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Reaction of the unsaturated, 32 valence electron species  $[\text{Rh}_2(\mu\text{-CO})_2(\eta^5\text{-C}_5\text{Me}_5)_2]$  with  $[\text{Rh}(\text{C}_2\text{H}_4)_2(\eta^5\text{-C}_5\text{Me}_5)]$  gives the trimetal compound  $[\text{Rh}_3(\mu^3\text{-CO})_2(\eta^5\text{-C}_5\text{Me}_5)_3]^+ \text{ (I)}$  containing  $\mu^3$ -bridging carbonyls on either face of an  $\text{Rh}_3$  triangle (Rh-Rh distances 2.553, 2.572, 2.639 Å). Acetylene reacts with (I) at room temperature displacing one CO ligand. The product,  $[\text{Rh}_3(\eta^2\text{-C}_2\text{H}_2)(\mu^3\text{-CO})(\mu^2\text{-H})(\eta^5\text{-C}_5\text{Me}_5)_3]^+ \text{ (III)}$ , isolated as its tetrafluoroborate, contains  $\eta^2$ -bound acetylene above the  $\text{Rh}_3$  plane and a bridging hydride. Reaction of (I) with dihydrogen affords  $[\text{Rh}_3(\mu^3\text{-CO})(\mu^2\text{-CO})(\mu^2\text{-H})(\eta^5\text{-C}_5\text{Me}_5)_3] \text{ (III)}$  where insertion of two bridging hydrides forces one carbonyl to become  $\mu^2$ -bridging.

We report the single crystal X-ray structure determination of compounds I-III and compare the geometry of the  $\text{Rh}_3$  moiety in each one.

I. M. Green, D.R. Hankey, J.A.K. Howard, P. Louca, and F.G.A. Stone, *J.Chem.Soc., Chem.Comm.*, (1983), 757.

09.3-19 ORDER PHENOMENA IN  $\text{E}_2\text{PI}_{1.6}$  (N,N'-DIHYDRO-N,N'-DIETHYLPHENAZINIUM IODIDE). By E. Rosshirt, F. Frey, H. Boysen and H. Jagodzinski, Institut für Kristallographie der Universität, München, W-Germany

X-ray diffraction patterns of the organometallic compound  $\text{E}_2\text{PI}_{1.6}$  reveal long-range-, short-range and disorder phenomena due to different interactions between and within two sublattices which are incommensurate with one another. One of them, chain-like inclusions of polyiodide anions has a 1-d liquid like character. At room temperature two superperiods along the chains with a doubled and a sixfold period, respectively, are superposed. Both are of different origin. The modulation with a doubled cell is due to a displacement of the iodine perpendicular to the wavevector. A modulation with a fourfold superperiod exists along the stacking direction of the  $\text{E}_2\text{P}$  molecules. These superordering may be -at least in part- of common origin. The longitudinal modulations become more pronounced at low temperatures (190 K). Lateral correlations are both of short- and long-range type and concern the actual iodine positions. S.r.o. correlations exist between the I-chains within (110) planes. Satellite reflections within the diffuse layers indicate, in addition, correlations along [100] via interactions between the organic stacks and the I-chains. The description in frame of uncorrelated sublattices becomes worse at lower temperatures. In comparison with the results of Endres, Pouget and Comes (*J.Phys.Chem.Sol.* 43 (1982) 739) we conclude that  $\text{E}_2\text{PI}_{1.6}$  may exist in different states of order as far as superstructures are concerned. Work was supported by the BMFT under 03-102A04

09.3-20 LINEAR CHAIN DISORDER IN  $\text{E}_2\text{PI}_{1.6}$ 

(N,N'-DIHYDRO-N,N'-DIETHYLPHENAZINIUM IODIDE) By E. Rosshirt, H. Boysen, F. Frey and H. Jagodzinski, Institut für Kristallographie der Universität, München, W-Germany

A system of diffuse layer lines observed with X-rays in the title compound has been analysed in terms of one dimensional liquid models involving  $\text{I}_3$ -molecules. For a quantitative analysis accurate microdensitometer scans across NOROMO-SIC photographs taken with an equi-inclination technique have been recorded. Various detailed corrections for absorption, instrumental resolution and contaminating satellite layers and reflections (cf. Rosshirt, Frey, Boysen and Jagodzinski, this conf.) were applied. Using the paracrystal method three different distribution functions of next nearest  $\text{I}_3$ -units have been considered:

$$\text{M1: } h_i(z) = \frac{1}{\sigma_i} e^{-\frac{(z-c_i)}{\sigma_i}} \text{ for } z \geq c_i; \quad \text{M2: } h_i(z) = \frac{1}{\sigma_i} e^{-\frac{(z-c_i)}{2\sigma_i}}; \quad \text{M3: } h_i(z) = h_i(z) * h_i(z);$$

The first model M1 reproduces the well known classical Zernike-Prins model, while M2 has been used by Endres, Pouget and Comes (*J.Phys.Chem.Sol.* (1982) 43, 739) in their interpretation of the same diffuse layers. Clearly the best fit was obtained for M3, which in intermediate form accounts for a flexible rigid body model (two interaction forces of different strength). The result will be discussed in comparison with other polyiodide compounds. The temperature dependence was studied between 183 and 333K showing an increasing ordering with decreasing temperature.

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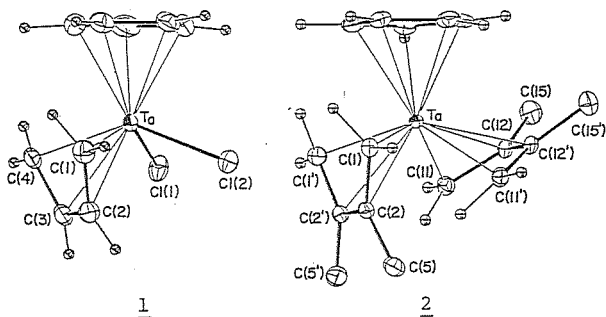
## 09.3-21 STRUCTURE AND PROPERTY OF TANTALUM-DIENE BONDS. By Y. Kai, N. Kanehisa, N. Kasai, H. Yasuda,† T. Okamoto,† K. Tatsumi,† and A. Nakamura,† Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, and †Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan.

Recent development of the early-transition metal chemistry revealed the unique structure and chemical reactivity of Group IVA-metal-diene bonds. To extend the chemistry to Group VA-metal we have prepared a series of tantalum-diene complexes and determined their structures.

1:  $(\eta^5\text{-C}_5\text{H}_5)\text{TaCl}_2$  (butadiene), monoclinic,  $P2_1/n$ ,  $a=6.615(1)$ ,  $b=10.962(1)$ ,  $c=14.348(2)$  Å,  $\beta=97.02(2)^\circ$ ,  $Z=4$ ,  $R=0.048$ . 2:  $(\eta^5\text{-C}_5\text{H}_5)\text{Ta}(2,3\text{-dimethylbutadiene})_2$ , orthorhombic,  $Pnma$ ,  $a=8.947(1)$ ,  $b=12.291(2)$ ,  $c=13.512(2)$  Å,  $Z=4$ ,  $R=0.061$ . 3:  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ta}(2,3\text{-dimethylbutadiene})_2$ , monoclinic,  $P2_1$ ,  $a=10.468(2)$ ,  $b=12.442(2)$ ,  $c=8.020(1)$  Å,  $\beta=106.68(2)^\circ$ ,  $Z=2$ ,  $R=0.049$ .

The coordination geometries of dienes in 2 and 3 are quite unique as compared with the bis(diene) complexes of Mn and Fe. The first diene is nearly perpendicular to the Cp plane ( $2:81.5^\circ$ ,

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<sub>2</sub>(butadiene) and CpTa(butadiene)<sub>2</sub> have corroborated these features characteristic of the Ta-diene bonding in 1, 2, and 3.



09.3-22 ASYMMETRIC BONDING OF THE 1-SYN SUBSTITUTED ALLYL MOIETY IN 4 CO-ORDINATE PALLADIUM(II) COMPLEXES

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The complexes [Pd(TMEDA)(1-syn-Ph-C<sub>3</sub>H<sub>4</sub>)]BF<sub>4</sub> and [Pd(TMEDA)(1-syn-C(O)OEt-C<sub>3</sub>H<sub>4</sub>)] see Fig. 1. (TMEDA=N,N,N',N'-Tetramethylethylenediamine) have been structurally characterised.

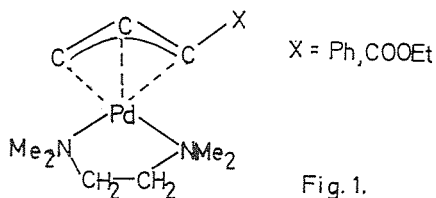


Fig. 1.

Despite the similar steric requirements of the two substituents the bonding of the two η<sup>3</sup>-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 CENTER. By M. Font-Altaba, X. Solans, J. Ros and R. Mathieu. Dept. de Cristallografia, 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<sub>2</sub>(CO)<sub>6</sub>(μ-C(C(O)OCH<sub>3</sub>)C(C(O)OCH<sub>3</sub>)C(C<sub>6</sub>H<sub>5</sub>)C(C<sub>6</sub>H<sub>5</sub>)H))(P(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>)<sub>0.5</sub>CH<sub>2</sub>Cl<sub>2</sub>. Monoclinic, P2<sub>1</sub>/n, a=17.244(6), b=23.419(7), c=12.218(5) Å, β=94.31(4)°, V=4920(5) Å<sup>3</sup>, 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<sub>2</sub>(CO)<sub>6</sub>(μ-C(C<sub>6</sub>H<sub>5</sub>)C(C<sub>6</sub>H<sub>5</sub>)C(CF<sub>3</sub>)C(CF<sub>3</sub>)H))(P(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>). Triclinic, P1̄, 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) Å<sup>3</sup>, 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<sub>2</sub>(CO)<sub>6</sub>(μ-COC<sub>2</sub>H<sub>5</sub>)(μ-C(C<sub>6</sub>H<sub>5</sub>)C(C<sub>6</sub>H<sub>5</sub>)H)). Monoclinic, P2<sub>1</sub>/n, a=17.801(3), b=10.006(2), c=12.971(2), β=106.0(2)°, V=2220(1) Å<sup>3</sup>, 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<sub>2</sub>(CO)<sub>6</sub>(μ-C(CH<sub>2</sub>OCH<sub>3</sub>)C(CF<sub>3</sub>)C(CF<sub>3</sub>)). Monoclinic, P2<sub>1</sub>/n, a=17.438 Å, b=13.776(2), c=7.703(1), β=106.7(2)°, V=1773(4) Å<sup>3</sup>, 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<sub>2</sub>(CO)<sub>6</sub>(μ-C(OC<sub>2</sub>H<sub>5</sub>)C(CO<sub>2</sub>CH<sub>3</sub>)C(CO<sub>2</sub>CH<sub>3</sub>))(μ-C(C<sub>6</sub>H<sub>5</sub>)C(C<sub>6</sub>H<sub>5</sub>)H)). 0.5 H<sub>2</sub>O. 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.