9.3-18 SYNTHESIS AND MOLECULAR STRUCTURES OF RELATED TRI-NUCLEAR RHODIUM COMPLEXES

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Reaction of the unsaturated, 32 valence electron species \([\text{Rh}_2(\text{CO})_2(\text{n}-\text{C}_5\text{H}_5\text{Me})_2]\) with \([\text{Rh}(\text{C}_2\text{H}_4)(\text{n}-\text{C}_5\text{H}_5\text{Me})_2]\) gives the trinuclear compound \([\text{Rh}_3(\mu^2-\text{CO})(\mu-\text{C}_2\text{H}_2)(\mu-\text{H})(\text{n}-\text{C}_5\text{H}_5\text{Me})_3][\text{I}]\) containing \(\mu\)-bridging carbonyls on either face of an \(\text{Rh}_2\) triangle (\(\text{Rh}-\text{Rh}\) distances 2.553, 2.572, 2.639 Å).

Acetylene reacts with (I) at room temperature displacing one CO ligand. The product, \([\text{Rh}_3(\mu^2-\text{C}_2\text{H}_2)(\mu^2-\text{CO})](\mu^2-\text{H})(\text{n}-\text{C}_5\text{H}_5\text{Me})_3][\text{T}]\) (III), isolated as its tetrafluoroborate, contains \(\mu\)-bound acetylene above the \(\text{Rh}_2\) plane and a bridging hydride. Reaction of (I) with dihydrogen affords \([\text{Rh}_3(\mu^2-\text{CO})(\mu^2-\text{H})(\text{n}-\text{C}_5\text{H}_5\text{Me})_3][\text{H}]\) (III) where insertion of two bridging hydrides forces one carbonyl to become \(\mu\)-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.


9.3-19 ORDER PHENOMENA IN \(\text{EP}_1\,\text{I}_{1.6}\) (\(\text{N},\text{N}'-\text{DIHYDRO-}N',\text{N}'-\text{DIETHYLPHENAZINIUM IODIDE}\). 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 \(\text{EP}_1\,\text{I}_{1.6}\) 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 inclinations 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 \(\text{I}\)-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.,1982,739) in their interpretation of the same diffuse layers it was confirmed that the iodine modulation with a doubled cell is due to interactions between and within two sublattices which are incommensurate with one another. One is of different nature.

To extend the chemistry to Group VA-metal diene bond. To extend the chemistry to Group VA-metal we have prepared a series of tantalum-diene complexes and determined their structures.

1: \((\text{n}^5-\text{C}_5\text{H}_5)\text{TaCl}_2\) (butadiene), monoclinic, \(\text{P2}_1/\text{n}\), \(a=6.615(1), b=10.962(1), c=14.388(2)\), \(\beta=97.02(2)^\circ\), \(Z=4\), \(N=0.048\).

2: \((\text{n}^5-\text{C}_5\text{H}_5)\text{Ta}(2,3\text{-dimethylbutadiene})\), orthorhombic, \(\text{Pnma}\), \(a=8.947(1), b=12.291(2), c=13.512(2)\), \(Z=4\), \(N=0.061\).

3: \((\text{n}^5-\text{C}_5\text{H}_5)\text{Ta}(2,3\text{-dimethylbutadiene})\), monoclinic, \(\text{P2}_1/\text{n}\), \(a=10.468(2), b=12.442(2), \beta=80.020(1)\), \(Z=2\), \(N=0.049\).

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°).