

PS07.00.50 STRUCTURE OF A NEW HYDRIDO-(METHOXO)-IRIDIUM(III) COMPLEX RELATED TO CATALYTIC REDUCTION OF ALKYNES. Tsuneaki Yamagata, Kazuhide Tani, Department of Chemistry, Faculty of Engineering Science, Osaka University

Hydrido(alkoxo) complexes of transition metals play important roles of catalytic processes involving hydrogen transfer and alcohol homologation. Here we will report the preparation and structural characterization of a new dinuclear hydrido(methoxo)iridium(III) complex.

The hydrido(methoxo) complex, $[\{\text{Ir}\{(\text{R})\text{-binap}\}(\text{H})_2(\mu\text{-OMe})_2(\mu\text{-Cl})\} + \text{Cl} \cdot \text{CH}_3\text{OH} (1)]$ was prepared by treating "Ir{(R)-binap}Cl" {(R)-binap = (R)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl} in absolute methanol-toluene (1:1). The structure of 1 was determined by an X-ray crystallography and NMR investigation. The cationic part of 1 has a dinuclear iridium. The coordination environment of both iridium atoms can be described as a distorted octahedron with two bridging methoxy and a chloride ligands and a terminal hydride ligand. The bridging chlorine atom of the cationic part and the oxygen and carbon atoms of the solvating methanol lay on a 2-fold axis. The chloride counter anion locates near the methanol. The dihedral angle between two least-squares planes defined by two phosphorus atoms of BINAP and two oxygen atoms of bridging methoxide ligands is $142.0(1)^\circ$. A terminal hydride ligand occupied *trans* position to the μ -chloro ligand and *cis* position to the methoxy groups. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows two doublets (AB coupling pattern) at δ -1.75 and -15.22 ($J = 19$ Hz). The ^1H NMR spectrum showed the terminal hydride at δ -23.10 (doublet of doublets, $J = 18, 23$ Hz) and the methoxy groups at δ 2.63 (triplet, $J = 3.4$ Hz). These results are consistent with the X-ray structure and show that 1 is prepared by oxidative addition of methanol to the neutral Ir(I) complex.

The hydrido(alkoxo)iridium(III) complex is effective as a catalyst precursor for transfer hydrogenation of acetylenic compounds in methanol-toluene (1:1). Diphenylacetylene was smoothly transformed into *trans*-stilbene (100% conversion and quantitative yield) with a catalytic amount of 1 ($[\text{sub}]/[\text{Ir}] = 50/1$) at 80°C for 48 h.

PS07.00.51 STRUCTURE OF TWINNED $[\text{Fe}(\text{heed3a})\text{H}_2\text{O}]$. Gernot Zahn¹, Martin Boddin², Roland Meier², Peter Paufler¹, ¹Institut für Kristallographie und Festkörperphysik, Technische Universität Dresden, D 01062 Dresden, German, ²Fachgruppe Chemie, Hochschule für Technik, Wirtschaft und Kultur Leipzig, D 04251 Leipzig, Germany

The X-ray single-crystal structure analysis revealed that iron is sevenfold coordinated in the yellow N-hydroxyethyl-ethylendiamine-triacetato iron(III) monohydrate ($P 2_1/c$, $a = 7.375(2)$, $b = 13.062(2)$, $c = 13.856(6)$ Å, $\beta = 101.91(1)^\circ$). Evidently yellow phase differs from brown phase in a different packing of complex and its enantiomorphous mirror image in the unit cell. The observed twinning can be described by two laws 1. rotation about [100] or 2. reflection through (001), which is in accordance with the centrosymmetrical space group and results in coinciding 0kl, separated 2kl, 3kl, 6kl, 7kl and overlapping 1kl, 4kl, 5kl reflections.

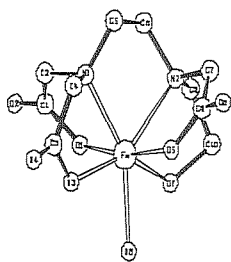


Fig. 1: Coordination polyhedron

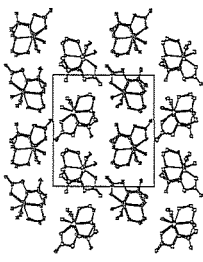
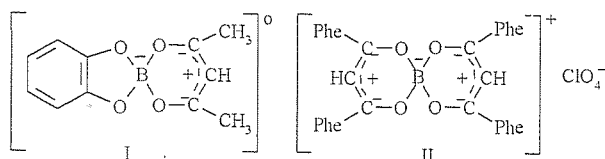


Fig. 2: Cell projection along [100]

PS07.00.52 THE NEUTRAL MULTILIGAND AND CATION COMPLEXES WITH BORON; $\text{C}_{11}\text{H}_{11}\text{O}_4\text{B}$, $\text{C}_{30}\text{H}_{22}\text{O}_4\text{BClO}_4$. I.Zviedre, J.Schwartz, V.Belsky, Institute of Inorganic Chemistry, Latvian Academy of Sciences, Latvia

In contrast to the anionic coordination compounds, a series of compounds exists derived from β -diketones in which the boron atom forms cation or neutral complexes. We have determined two crystal structures which contain the central BO_4 -tetrahedron.

I 2,4-Pentanedion-2,3-phenyldioxoborate $\text{C}_6\text{H}_4\text{O}_2\text{BO}_2\text{C}_3\text{H}(\text{CH}_3)_2$, II bis(1,3-diphenyl-1,3-propanedion)boro(III)perchlorate $((\text{C}_6\text{H}_5)_2\text{C}_3\text{HO}_2)_2\text{B} \cdot \text{ClO}_4$.



In complex I the boron atom is coordinated to one diol ligand and one β -diketone ligand. The boron-oxygen tetrahedron is, due the unequal B-O bond lengths, symmetrical distorted. Bond lengths are B-O(alkyl) 1.445(4) and B-O(keto) 1.495(4) Å; C-O(alkyl) 1.370(3) and C-O(keto) 1.296(4) Å. Bond angles on B are from $107.6(2)^\circ$ to $110.7(3)^\circ$.

In the structure II the four O atoms adopt an almost perfect tetrahedral arrangement about the boron with bond lengths B-O mean 1.46(1) Å, bond angles OB-O are between $107.7(2)^\circ$ and $112.5(3)^\circ$. Bond lengths C-O are 1.31(2) Å. All heterocycles in both compounds are non-planar.

Crystal data: I - $a = 10.059(2)$, $b = 12.617(2)$, $c = 8.502(10)$ Å, $\gamma = 95.44(2)^\circ$, $Z = 4$, sp.gr. $P2_1/n$, II - $a = 22.724(4)$, $b = 13.740(3)$, $c = 8.763(2)$ Å, $\gamma = 99.06(1)^\circ$, $Z = 4$, sp.gr. $P2_1/a$ [1].

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[1] Zviedre I., Belsky V./Thes.VII Conf.SSSR, Khim.Dicarb.S., 1991, 93.

PR07.00.53 METAL-ION COMPOUNDS OF 2,2,4,10,10,12-HEXAMETHYL-1,5,9,13-TETRA-AZACYCLOHEXANE (L). Olga Gladkikh*, Neil F. Curtis*, Graeme A. Gainsford** and David A. Rae***, *Victoria University of Wellington, Wellington, New Zealand, **Industrial Research Ltd, Gracefield, Wellington, New Zealand, ***Australian National University, Canberra, Australia

A series of new complexes of divalent Co, Ni and Cu with the macrocyclic ligand L have been synthesized and analysed by both experimental (X-ray single crystal analysis) and theoretical (molecular mechanics) methods.

Tetra-coordinate coordination compounds of (L) with cobalt(II), nickel(II) and copper(II) have coordination geometries intermediate between tetrahedral and square planar. The extent of the twisting of the coordination plane increases from $S = 0$ nickel(II) through copper(II) to $S = 4$ Co(II), which is close to tetrahedral. It also varies significantly with the counter-ion for the perchlorate and tetrachlorozincate salts.