

07-Crystallography of Organometallic and Coordination Compounds

maps, the multipole model deformation density maps, and the theoretical deformation maps employing the ab initio HFSCF and CASSCF methods. A better understanding of the charge distribution and bond order of all chemical bonds will be discussed through ab initio calculations via Natural Bond Orbital analysis. With such combined studies we wish to shed some light on the metal-metal bond problem.

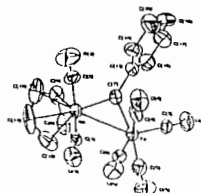


Fig. 1

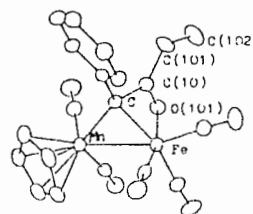


Fig. 2

PS-07.03.06 THE STRUCTURES OF HETERONUCLEAR DIMETAL COMPLEXES WITH BRIDGING CARBENE LIGANDS, [FeRe(μ -CHC₆H₅)(CO)₆(η -Cp)] and [MnFe(η -Cp)(η , μ -C(COCH₂-CH₃)C₆H₅)(CO)₅] (Cp=C₅H₅). By Jian Chen*, Pei-Ju Zheng, Research Center of Analysis & measurement, Fudan University, Shanghai, P.R.China, 200433; Jia-Bi Chen, Yong Yu, Shanghai Institute of Organic chemistry, Chinese Academy of Sciences.

[η -Cp(CO)₂ReCC₆H₅]BBr₄ reacted with Na₂Fe(CO)₄ in THF at low temperature giving the novel bridging carbene complex (A), [FeRe(μ -CHC₆H₅)(CO)₆(η -Cp)], instead of the expected non-bridging carbene complex (Chen, Yu, Liu, Wu, Chen and Zheng, to be published). Similarly, the reaction of [η -Cp(CO)₂Mn \equiv CC₆H₅]BBr₄ with Na₂Fe(CO)₄ gives complex (B), [MnFe(η -Cp)(η , μ -C(COCH₂CH₃)C₆H₅)]. It was the first time that such complexes have been synthesized by the reaction of cationic carbene complexes of transition metals with a nucleophile containing carbonyl metal anion, though a series of such complexes have been obtained from the reaction of carbene complexes with low-valent metal species or the carbyne complexes with metal hydrides.

The complex (A) crystallized in space group P2₁/c with a=7.903(1), b=29.912(3), c=8.856(3)Å, β =110.21(2), Z=4, R=0.030 for 2315 observed ($I > 3\sigma(I)$) reflections; and complex (B) in space group P2₁/c, a=9.894(3), b=10.455(2), c=20.683(5)Å, β =114.35(4), Z=4, R=0.045 for 2839 observed reflections.

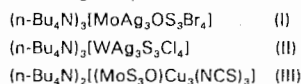
In complex (A), as shown in Fig.1, the iron atom is ligated by the terminally bonded CO ligands and the μ -CHC₆H₅ group to form an approximately octahedral environment; whereas, in complex (B), as illustrated in Fig.2, the Fe atom is surrounded by η , μ -C(COCH₂CH₃)C₆H₅ group besides the CO ligands to display pentagonal bipyramidal configuration. The atom Re and Mn have similar bonded ligands to adopt the pseudo-trigonal bipyramid coordination geometry, if the C(η)-bonded Cp ligand is regarded as occupying a single polyhedral vertex. It is clear that the ligations of all the metals atoms satisfy the 18-electron rule.

The bond distances of 2.583(4)Å for Fe-Mn in (B) and 2.758(1)Å for Re-Fe in (A) are slightly shorter than the 2.823(1)Å for Fe-Mo in [MoFe(μ -CC₆H₅Me-4)(CO)₆(η -C₅H₅)] (Garcia, Jeffery, etc., J. Chem. Soc. Dalton Trans., 1987, 1209), taking into account the difference of the atomic radii. The μ -C-M lengths (2.12(5)Å for M=Re, and 2.097(5)Å for M=Fe in (A), and 2.021(3)Å for M=Mn, and 2.021(4)Å for M=Fe in (B)) compare reasonably with those in [MoFe(μ -CC₆H₅Me-4)(CO)₆(η -C₅H₅)]. In (B), the bonds Fe-C(10)(2.135(5)Å) and Fe-O(101)(2.003(3)Å) are somewhat longer than the average Fe-C_(CO) (C_(CO) = the carbon of the terminal carbonyl group) distance (1.788Å), but close to those of μ -C-Fe and Mn-C(Cp) (C(Cp)=the carbon of Cp ring). It is interesting that μ -C and C(10) and O(101) of the bridging carbene group are attached to the iron atom. The establishment of the structures of these complexes will shed new light on the mechanism of these novel reactions.

PS-07.03.07 STUDIES ON SOLID STATE REACTIONS OF COORDINATION COMPOUNDS. SOLID STATE SYNTHESSES AND CRYSTAL STRUCTURES OF M-Cu(Ag)-S (M=Mo,W) CLUSTERS. By Cai Jinhua*, Weng Linghong, Kang Beisheng (Fujian Institute of Research on the Structure of Matter, and Fuzhou Laboratory of Structural Chemistry, Chinese Academy of Sciences, Fuzhou, 350002, China) and Lang Jianping, Zhu Huizhen, Xin Xinquan (Coordination Chemistry Institute, Nanjing University, Nanjing, 210008, China)

The chemistry of the M-Cu(Ag)-S compounds have been well developed because of the multifunctional ligation of the [MS₄]²⁻ (M=Mo,W) ligands and the high tendency of Cu(I) towards forming metal-sulfur bonds.

The well-ground mixture of the reactant was sealed under argon and heated at 100-110°C for a few hours. The dark product was extracted with DMF and filtered. On standing in air for a few days, crystals of the following compounds were obtained:



(I) and (II) are isostructural crystals of space group of P $\bar{4}$ 3m. (I): a=b=c=12.093(4) Å, V=1768.3 Å³, Z=1, D_c=1.48 g/cm³. (II): a=b=c=12.059(2) Å, V=1753.4 Å³, Z=1, D_c=1.43 g/cm³. (III): monoclinic space group P2₁/n, a=16.672(9), b=16.278(6), c=19.608(8) Å, β =110.05(4)°, V=4999.0 Å³, Z=4. Data were collected on diffractometer using Mo K α radiation and the structures were solved by directed methods. Final R=0.076(I), 0.075(II), 0.068(III) for 154, 152, 4668 reflections with $I > 3\sigma(I)$, respectively.

The anions of (I) and (II) possess $\bar{4}3m$ symmetry. The cores of (MoAg₃S₃Br)⁺ and (WAg₃S₃Cl)⁺ can be viewed as cubes with four metal and four non-metal atoms statistically distributed, respectively. The tetrahedrons of MAG₃, S₃X and SX₃ (or OX₃) (M=Mo,W; X=Cl,Br) are also disordered. The distances Mo...Ag and W...Ag are 3.225(2) and 3.158(5)Å, respectively. All bond lengths in the cluster anions are evidently averaged.

(III) is a new cluster complex of a 'nido' conformation with an MoCu₃S₃ core. The overall Mo-S-Cu framework is like a nest constructed by condensing three roughly planar MoS₂Cu prisms via adjacent edges to form a cube-like body with a sulphur atom missing at a corner. The Mo atom at the bottom of the nest is coordinated by one oxygen and three sulphur atoms. The Mo-O bond length (1.704(6)Å) is close to an Mo=O double bond length. The mean distance of the Mo-S bond length is 2.256Å. The copper atoms are coordinated by the N atoms of the three SCN ligands.