

Hetero- and Homobimetallic Complexes of New Hard-Soft Binucleating Ligands

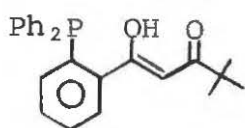
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Final Seminar

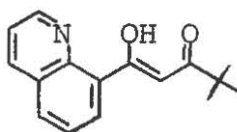
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In recent years considerable inorganic research has been directed toward the preparation of binucleating ligands designed to hold two metals in close proximity. Reasons for continued interest in this area include the fact that complexes of this type are of potential importance in the development of new industrial catalysts [1] and in the simulation of biological catalytic systems [2]. Early researchers including Robson [3], Kida [4], Lintvedt and Glick [5], and Fenton [6] studied the coordination chemistry of ligands derived from the Schiff base condensation of either 3-formylsalicylic acid or 1,3,5-triketones with diamines. These ligands contain nitrogen and oxygen donor atoms which typically coordinate to "hard" 1st-row transition metals. More recently, researchers have prepared a number of bimetallic complexes using unsymmetrical "soft" ligands such as $\text{Ph}_2\text{PC}_5\text{H}_4\text{N}$ [7] and $\text{Ph}_2\text{PC}_5\text{H}_4^-$ [8,9,10]. Others have synthesized phosphine ligands incorporating crown ether-like [11,12] and Schiff-base [13] type sites which contain both "hard" and "soft" donor sites.

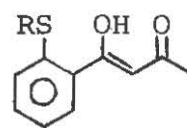
A unique feature of our unsymmetrical ligand systems is the arrangement of hard and soft donor atoms in a manner to preclude its functioning as a tridentate chelating agent. We have prepared a series of functionalized β -diketone ligand systems via the Claisen condensation of ortho-substituted methyl benzoate compounds with the potassium enolate of methyl ketones. The new binucleating ligands prepared in this work include phosphine, thioether and quinoline substituted β -diketones along with the Schiff-base derivatives of the thioether β -diketone, as shown below.



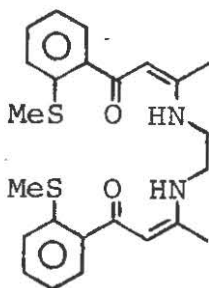
HacacP



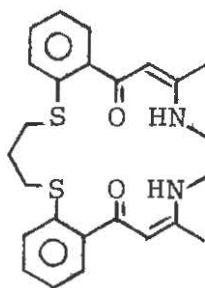
Quinoline
 β -diketone



Thioether β -diketone
 $2\text{R} = 2\text{Me}, (\text{CH}_2)_3$



$\text{S}_2\text{O}_2\text{N}_2\text{H}_2$

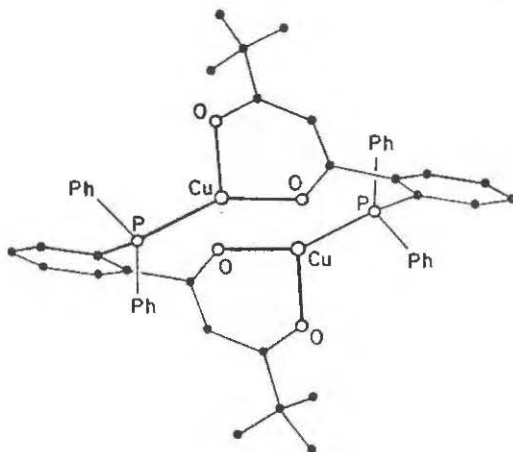


cyclo- $\text{S}_2\text{O}_2\text{N}_2\text{H}_2$

With these ligand systems we can exploit the extensive transition metal coordination chemistry of β -diketonates and of "soft" donor groups to prepare complexes containing two different metals.

Studies of monometallic complexes between acacP^- and Ir(I)L_2 [$\text{L}_2 = \text{cyclooctadiene}$ or $(\text{CO})_2$] [14] or $\text{Ni(II)(C}_8\text{H}_{13})$ have demonstrated the dependence of the site selectivity of acacP^- on the π basicity of the metal ion. ^{31}P NMR spectroscopy established that the Ir(COD) moiety occupies the P,O site while the Ir(CO)_2 moiety occupies the O,O site. The $\text{Ni(II)(C}_8\text{H}_{13})(\text{acacP})$ compound exhibits a third type of bonding; the ligand forms a P,C chelate in which the methine carbon bonds to nickel.

$\text{Cu}_2(\text{acacP})_2$ was prepared and its structure was shown to consist of two trigonally coordinated coppers situated in a face-to-face orientation [15]. This coordinatively unsaturated binuclear complex



undergoes le^- oxidative addition with peroxy acids and peroxides [16] and readily reacts with molecular oxygen to give a stable crystalline derivative. Both of these processes give mixed valence compounds of the general type $[\text{Cu}_2(\text{acacP})_2(\mu\text{-O}_2\text{CR})]$.

Heterobimetallic complexes containing two acacP ligands [14] can be prepared systematically by two reaction sequences. One method involves insertion of the hard metal into the O_4 compartment followed by coordination of a second, soft metal to the phosphine donors. Because of the incompatibility of phosphines with cupric salts, a second method must be employed for the preparation of $\text{M-Cu}(\text{acacP})_2$ complexes. This involves coordination of the phosphines to the soft metal followed by metalation of the O_4 site. In this way the following heterobimetallic compounds were prepared: $\text{ML}_2\{\text{M}'(\text{acacP})_2\}$, $\text{M} = \text{Pt, Pd, Ru, Ir}$, $\text{M}' = \text{Cu, Zn, TiCl}_2$. An examination of this series by NMR, EPR and optical spectroscopy has been valuable in the assignment of structures as well as in determining the extent to which these two metals interact with one another.

Monometallic Ni(II) and Cu(II) derivatives of the new Schiff-base thioether ligand, $\text{S}_2\text{O}_2\text{N}_2^{2-}$ and cyclo- $\text{S}_2\text{O}_2\text{N}_2^{2-}$ have been prepared along with a new binuclear copper complex.

References

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