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# Synthesis of New Ferrocenyl-β-diketone Ligands and Studies on their Complexation with Cu(II), Ni (II) and Zn(II) Metals

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## ABSTRACT

Ferrocenyl-β-diketone ligands have been synthesised by the reaction of (ferrocenyl methyl) trimethyl ammonium iodide ($FcCH_2N^+Me_3I^-$), where $Fc=C_5H_5FeC_5H_4^-$ with sodium salt of -β-diketone [$Na^+CH^-(COR^1)$ $(COR^2)$, where $R^1= R^2=CH_3$, $R^1= CH_3$, $R^2=Ph$, $R^1= R^2=CMe_3$]. The formula of the ligands (1-3) are $FcCH_2CH(COCH_3)(COCH_3)$, $FcCH_2CH(COCH_3)(COPh)$ and $FcCH_2CH(COCMe_3)_2$ respectively. The work also synthesised some complexes of Cu(II), Ni (II) and Zn(II) by the reaction of ferrocenyl methyl β-diketones with corresponding metal acetate in a mixture of water and dichloromethane ($CH_2Cl_2$). The formula of the complexes are $[Zn\{FcCH_2CH(COCH_3)_2\}_2]$, $[Cu\{FcCH_2CH(COCH_3)\}_2]$, $[Ni\{FcCH_2CH(COCH_3)(COPh)\}_2]$ and $[Cu\{FcCH_2CH(COCH_3)(COPh)\}_2]$. The ligands and complexes have been characterizied on the basis of infrared spectra, UV-visible spectroscopic studies, Elemental analysis, Magnetic moment, Conductance measurement, Metal estimation, Melting point, NMR spectra and other physical properties.

**Key words:** Ferrocenyl-β-diketone, Complexation and Metals.

## INTRODUCTiON

The molecule $(C_5H_5)Fe(C_5H_5)$, known as ferrocene, has a sandwich structure where the metal lies between two planer cyclopentadienyl ring (Fig.1) in which the 6π electron system ion $C_5H_5$ is bound to the metal ion.

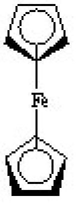
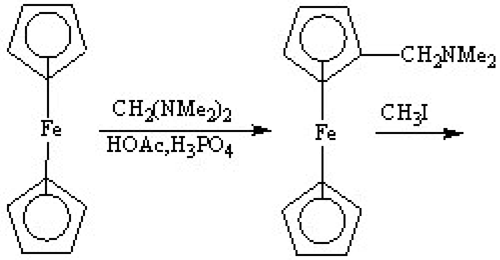
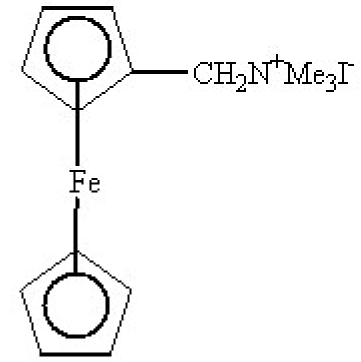


Fig.1

The rotational freedom of cyclopentadienyl rings in ferrocene was experiment by wood ward[1]. Under the Manich reaction condition first produces a Manich base [$CH_2=N^+(CH_2)_2$] and after alkylation produces a quarternary ammonium salt reported[2].





In the derivative chemistry of ferrocene, an important synthetic intermediate is the salt ($FcCH_2N^+Me_3I^-$) this reacts with a wide range of nucleophiles. The aim is to produce a range of nucleophiles which will react with the ($FcCH_2N^+Me_3I^-$) these nucleophiles will be in the form of anion derivatives from acyclic diketones, cyclic diketones and di, tri keto ester. Once a suitable method to produce these nucleophiles has been found, the reaction between these salts and the ($FcCH_2N^+Me_3I^-$) will then be carried out[3]. The resulting compounds will then be caracterised by IR, UV, NMR spectra, X-ray crystrallography and by conductance measurement. One point interest in these substituted ferrocene compound comes from the fact they may enolies.

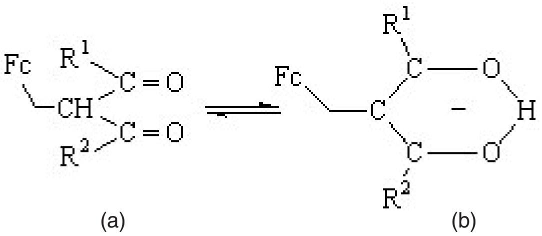
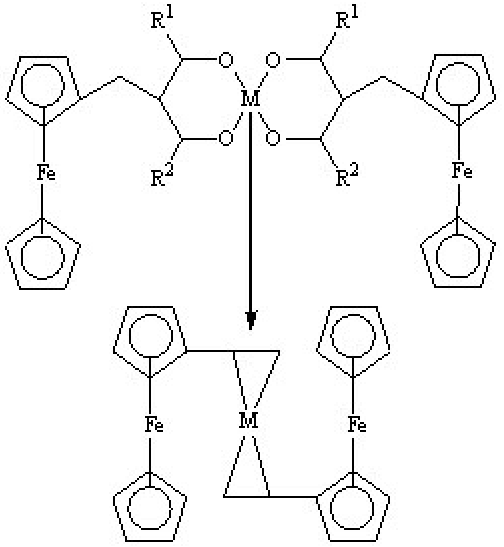


**Fig. 2: (a)represents keto form and (b) the enol form**

Thus, in general enolisation requires close proximity of the oxygen atoms. So the intramolecular hydrogen bond can form. Factors affecting enolisation depend on the size of the R groups, if these groups are bulky they may twist the two carbonyl group out of the C-C-C plane. If this happens then enolisation cannot move too far apart and the hydrogen and that is shown form. Once it has been established that these compounds can be formed, then their ligating properties will be investigated and complexation will be attempted between them and suitable metal centers. Complexation of metal cation by b-diketones is well established for simple non redox-active ligands, but few extensions have been made in systems which incorporate redox-active electrochemical function[4]. Neutral 2:1 complexes were reported[5] many years ago complexes were formed from the mono-anion [$FcCOCHCOCH_3$] with metal ions ($Mn^{2+}$,$Co^{2+}$,$Ni^{2+}$,$Cu^{2+}$,$Zn^{2+}$) but no redox properties for such complexes have been reported, nor have ferrocenyl bis-diketone been the subject of any systematic complexation study. However, Beer has reported[6,4] extensive studies which demonstrate that the observed redox potential of pendant ferrocenyl groups on crown ether cores can be used as a sensitive electrochemical probe for the selective complexation of simple redox-inactive guest cation by the crown ether moiety. This work has opened up the possibility of using the environment sensitive redox properties of ferrocenyl groups as a sensitive probe in molecular recognition studies then developed recently used ferrocene based polyaza macrocycles[7] . Using the range of new ferrocenyl β-diketone in Fig-2 above our first objective is the synthesis and structural characterization of simple metal complexes derived from these β-diketone ligands. e.g.



Where, M=$Mn^{2+}$,$Co^{2+}$,$Ni^{2+}$,$Cu^{2+}$,$Zn^{2+}$ etc

**Fig. 3: Proposed structure of heterometal complex and picotorial representation**

## EXPERIMENTAL

### Reagents

All the chemicals were used of reagent grade and were used as supplied by Fluka.

### Physical measerments and Elemental analysis

IR Spectra (as KBr pellets) were recorded on a SHIMADZU FIIR-8101 infrared spectrophotometer. The spectra were recorded for the range of 4000-400 $cm^{-1}$. Conductivities of $10^{-3}$ M solutions in dimethyl sulfoxide (DMSO)were measured at $26^0C$ using a CG857 No 71798 SCHOTT-GREAT Gmbh. Germany, digital Conductivity meter and a dip type cell with a polarized electrodes. Micro analysis for Carbon and hydrogen were performed by Carlo Erbal 1108. The absorbance of the compounds were recorded on SI06 spectrophotometer, WPA instrument.

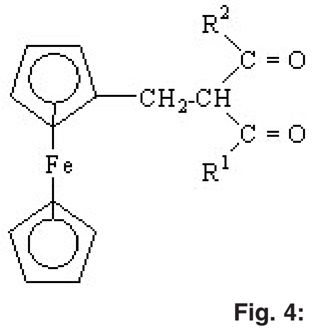
### Preparation of ligands

Three ferrocenyl β-diketone ligands have been prepeared by the direct reaction with (Ferrocenyl methyl) (trimethyl) ammonium iodide ($FcCH_2N^+Me_3I^-$) and Sodium salt of acetyl acetonate [$NaCH(COCH_3)(COCH_3)$] benzoyl acetonate [$NaCH(COCH_3)(COPh)$], 2,2,6,6 trimethyl -3,5- haptane dione $NaCH(COCMe_3)_2$ by refluxing 16 hours in acetonitrile ($CH_3CN$) solution. The ligands are $FcCH_2CH(COCH_3)(COCH_3)$, $FcCH_2CH(COC\ H_3)(COPh)$ and $FcCH_2CH(COCMe_3)_2$ were formed.

### Preparation of complexes containig ferrocenyl β-diketone as ligands

Five complexes have been prepeared using two ligands $FcCH_2CH(COCH_3)_{2,}$ $FcCH_2CH(COCH_3)(COPh)$ with Cu(II),Ni(II) and Zn(II) metals. Ligands are dissolve in a water. The two solution then poured in a 500 ml conical flask and (2L:1M)and stired 4 days by using magnetic stirrer. The organic layer was then seperated by separating funnel and dried over $Cacl_2$. In this way we have prepeared(**4-8**)

4. $[Zn\{FcCH_2CH(COCH_3)_2\}_2]$
5. $[Cu\{FcCH_2CH(COCH_3)_2\}_2]$
6 $[Ni\{FcCH_2CH(COCH_3)_2\}_2]$
7. $[Ni\{FcCH_2CH(COCH_3)(COPh)\}_2]$ and
8. $[Cu\{FcCH_2CH(COCH_3)(COPh)\}_2]$ complexes



a. $R^1 = R^2 = CH_3$
b. $R^1 = CH_3$, $R^2 = Ph$
c. $R^1 = R^2 = Me_3C$
d. $R^1 = Ph.\ R^2 = CH_3$

**Fig. 4:**

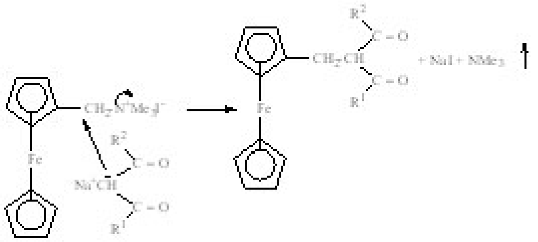


**Fig. 5: Reaction of (Ferrocenyl methyl) (trimethyl) ammonium iodide and the salt of b-diketone**

## RESULTS AND DISCUSSION

(Ferrocenyl methyl)(trimethyl) ammonium iodide $[C_5H_5FeC_5H_4N^+Me_3]\ I^-$ which was synthesised reacts very readily with the mono sodium salt of a β-diketone. $Na^+CH^-(COR^1)\ (COR^2)$ which is act as a good neocleophilic agent produces the ferrocenyl methyl-1,3 - diketones according to equation in Fig. 5.

### Formation of Carbonanions of β-diketone

Initial reaction were using the hydroxide as a nucleophile. Which deprotonates the β-diketones at their α-carbon atom. The reaction involves takaing a mixture of methanol in aqueous sodium hydroxide and mixing this with the β-diketone. Stirring the mixture for about half an hour and living it until the sodium salt of the β-diketone pecipitates out. This method worked reasonably well for acylic β-diketone but gave no pecipitate for the range of cyclic β-diketone. It was suggested that this may be due to the salt being soluble in the aqueous solvent, or it could be that there is some electronic effects from the R groups on the diketone. This would make the α-hydrogen less acidic.

Therefore the hydroxide ion is not a strong enough base here. This reaction was also favourable since it carried out as a one pot reaction.

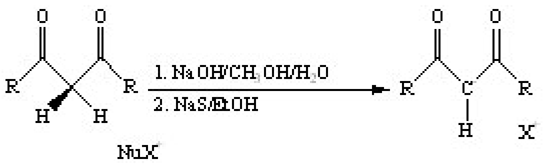


**Fig. 6: Method 1 and Method 2 of carbocation production here is a summary of β-diketone that was investigated**

### Acyclic diketones

These compounds may also be referred in as b-dicarbonyl compounds and have the general form:

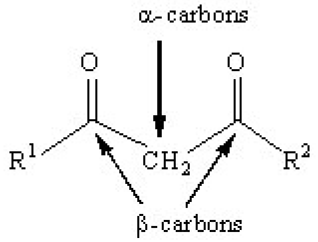
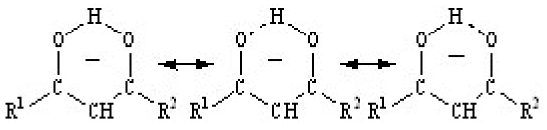


**Fig. 7:**

The two carbonyl groups are separated by an intervening carbon and the two hydrogen on this carbon tend to be more acidic than any other hydrogen in the molecule. pKa is in the region of 9 for these hydrogen's ions. The acidity of this hydrogen leads to the easy conversion of the compounds in to an enolate ion e.g.



Resonance hybride

**Fig. 8: Enolisation of an acyclic diketone**

### Ferrocenyl methyl and diketone coupling reaction

The reaction of the (Ferrocenyl methyl)(trimethyl) ammonium iodide with carbocation of the diketone is a simple substitution reaction. Where trimethylamine is substituted with the carbocation (see Fig.5). The trimethyl amine is simple lost from the reaction as a gas. Sodium iodides is the other side product which is lost in the work up. The reaction was initialy carried out in acetonitrile with the (Ferrocenyl methyl)(trimethyl) ammonium iodide and sodium salt of 2,2,6,6 tetramethyl-3,5-heptanedione. Acetyl acetonate and benzoyl acetonate being reflux for approximately 16 hours. Then left to cool. Initial seperation of the product was done by column chromatography. The eluent was dichloromethane which carried the product down the column ahead of the other more polar side products. This procedure worked well for 2,2,6,6- tetramethyl-3,5-heptanedione and dibenzylmethane. X-ray quality crystals were grown of the ferrocenyl methyl 2,2,6,6- tetramethyl-3,5-heptanedione acetyl acetonate and benzoyl acetonate from a 30/40 petroleum ether and dichloromethane mixture. The ferrocenyl -1,3-diketone ligands and its metal complexation are characterized by Infrared spectra, conductance, melting point, magnetic moments, electronic spectra, elemental analysis and others analytical and physical studies.

### Characterization of new ferrocenyl 1,3 diketones as ligands

The synthesis of new ferrocenyl diketones ligand have been described in the experimental section. The infrared spectra data are illustrted in the table-3. The infrared spectra of the ligand (1-3) showed bands in the region range 3350cm$^{-1}$suggest for the $\nu$ (=CH) stretching frequencies arromatic cyclopentadinyl ring. Bands at 2920 and 2855cm$^{-1}$ suggest the presence of different aliphatic ν(C-H) stretching frequencies in the compounds. A strong band appears at 1707,1709 and 1709cm$^{-1}$ due to the presence of ν(RC=O) stretching frequencies of ketonic groups[8].Here R is the electron repealing group e.g $CH_3$- or $C_6H_5$- or $Me_3C$. A strong sharp band of the compounds in the range of 1666 to 1624cm$^{-1}$ suggest the presence of ν(C=C) groups. The UV-visible spectra data of the ligands are shown (238 to 283)nm which are asigned respectively to the and n-π* of the C=O and C=C bonds. The conductance of the ligands (1-3) are illustrated in the table-1. There are 5.06, 6,09 and 0.00 ohm$^{-1}$ cm$^{2}$mol$^{-1}$ which reveal that the ligands are non electrolyting nature. The elemental analysis data

**Table 1: Analytical data and physical properties of the ligands (1-3)**

| S. No | Complexes | colour & Yield | %C Calculated (Found) | %H Calculated (Found) | m.p. ($^0$C) | Molar conductance (ohm$^{-1}$ cm$^2$mol$^{-1}$) |
|---|---|---|---|---|---|---|
| 1. | $FcCH_2CH(COCH_3)_2$ | Orange<br>(72) | 64<br>(63.56) | 5.36<br>(5.02) | 90 | 05-06 |
| 2. | $FcCH_2CH(COCH_3)(COPh)$ | O. Yellow<br>(81) | 70<br>(79.81) | 5<br>(4.82) | 82-84 | 16-19 |
| 3. | $FcCH_2CH(COCMe_3)_2$ | Orange<br>(87) | 69.10<br>(68.98) | 7.85<br>(7.53) | 127 | 00 |

**Table 2**: **Analytical data and physical properties of the complexes (4-8)**

| S No | Complexes | %M Calculated (Found) | $m_{eff}$ B.M | Molar conductance (ohm$^{-1}$ cm$^2$mol$^{-1}$) | colour & (%Yield) | m.p. (°C) |
|---|---|---|---|---|---|---|
| 4. | $[Zn\{FcCH_2CH(COCH_3)_2\}_2]$ | 9.88(9.08) | dia | 3.19 | Brown(82) | 298(d) |
| 5. | $[Cu\{FcCH_2CH(COCH_3)_2\}_2]$ | 9.63(8.99) | 1.39 | 10.65 | Gray(76) | 310(d) |
| 6. | $[Ni\{FcCH_2CH(COCH_3)_2\}_2]$ | 4.96(4.12) | dia | 8.52 | G.Black(92) | 290(d) |
| 7. | $[Zn\{FcCH_2CH(COCH_3)(COPh)\}_2]$ | 7.53(7.01) | dia | 3.19 | Gray(82) | 200(d) |
| 8. | $[Cu\{FcCH_2CH(COCH_3)(COPh)\}_2]$ | 8.11(7.87) | 1.53 | 8.52 | Brown(77) | 215(d) |

where, d= decomposition

**Table 3: Infrared and UV-visible spectra of the ligands (1-3)**

| S. No | Complexes | ν(C=O) cm$^{-1}$ of the R-C=O | ν(C=C) cm$^{-1}$ of the ferrocene or benzene | ν(C-H) cm$^{-1}$ | ν(-CH$_2$-) cm$^{-1}$ | ν(C=C) cm$^{-1}$ | $\lambda_{max}$ (nm) |
|---|---|---|---|---|---|---|---|
| 1. | $FcCH_2CH(COCH_3)_2$ | 1709 | 3360 | 2920 | 2855 | 1666 | 283.447 |
| 2. | $FcCH_2CH(COCH_3)(COPh)$ | 1709 | 3355 | 2920 | 2855 | 1684 | 238.320 |
| 3. | $FcCH_2CH(COCMe_3)_2$ | 1707 | 3350 | 2855 | 2855 | 1974 | 241.432 |

**Table 4: Infrared and UV-visible spectra of the complexes(4-8)**

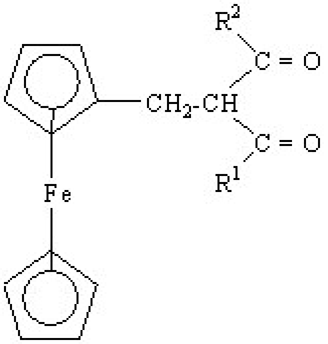
| S. No | Complexes | ν (C=O) cm$^{-1}$ | ν(C=O) cm$^{-1}$ | ν=C-H) cm$^{-1}$ | ν(C=C) cm$^{-1}$ | ν(M-O) cm$^{-1}$ | $\lambda_{max}$ (nm) |
|---|---|---|---|---|---|---|---|
| 4. | $[Zn\{FcCH_2CH(COCH_3)_2\}_2]$ | 1707 | 1590 | 3350 | 1684 | 470 | 510 |
| 5. | $[Cu\{FcCH_2CH(COCH_3)_2\}_2]$ | 1716 | 1597 | 3365 | 1666 | 455 | 550 |
| 6. | $[Ni\{FcCH_2CH(COCH_3)_2\}_2]$ | 1716 | 1610 | 3355 | 1675 | 480 | 510 |
| 7. | $[Zn\{FcCH_2CH(COCH_3)(COPh)\}_2]$ | 1709 | 1600 | 3360 | 1680 | 465 | 560 |
| 8. | $[Cu\{FcCH_2CH(COCH_3)(COPh)\}_2]$ | 1716 | 1597 | 3370 | 1684 | 490 | 530 |

**Table 5: Elmental analysis data of the complexes(4-8)**

| S. No. | Complexes | %C Calculated (Found) | %H Calculated (Found) |
|---|---|---|---|
| 4. | $[Zn\{FcCH_2CH(COCH_3)_2\}_2]$ | 58.06(58) | 5.44(5.06) |
| 5. | $[Cu\{FcCH_2CH(COCH_3)_2\}_2]$ | 58.22(57.87) | 5.45(5.97) |
| 6. | $[Ni\{FcCH_2CH(COCH_3)_2\}_2]$ | 58.65(58.27) | 5.49(5.02) |
| 7. | $Zn\{FcCH_2CH(COCH_3)(COPh)\}_2]$ | 64.72(64.21) | 5.13(5.92) |
| 8. | $[Cu\{FcCH_2CH(COCH_3)(COPh)\}_2]$ | 64.32(63.77) | 5.10(5.06) |

of the ligands are shwon in the Table 1[1-3] reveals that the expected element contain in the ligands.

It appears from the infrared spectral data, UV-visible data and others analytical studies reavls that the ligands may be ferrocenyl β-diketones structure. The analytical data is in good agrement with proposed stoichiometry. On the basis of the above asignment the proposed structure of the ligands (1-3) are shwon in Fig. 9.

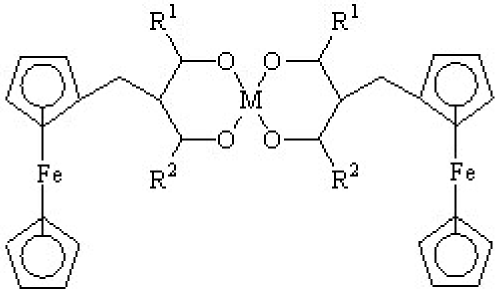


1. $R^1 = R^2 = CH_3$
2. $R^1 = CH_3$, $R^2 = Ph$
3. $R^1 = R^2 = Me_3C$

**Fig. 9: Proposed structure of the ligands (1-3)**

### Transition metal complexes (4-8) containig ligands, ferrocenyl -1,3- diketones

The metal complexes synthesis have been described in the experimental section. The IR spectral data are illustrated in the Table 4. The infrared spectra of the complexes (4-8) showed strong bands in the region (1610-1590) $cm^{-1}$ that attributed to the $\nu$ (C = O) of $FcCH_2CHC=O$ group which are of lower region than the free ligand 1700$cm^{-1}$ due to the coordination through the oxygen atom of the carbonyl group to the metal. The electron density of the C=O bond are withdrawn by the metal as a result, the C=O bond length increases where by the ν(C=O) stretching frequency decreases[9]. The decrease of stretching frequencies of the ligands indicate that complexation have been taken place through oxygen atom[8]. Another strong band in the region (455-490)$cm^{-1}$ is suggested for the n(M-O) of acac complexes are most interesting since they provide direct information about the M-O bond using the metal isotope technique Nakamoto *et al.,*[8]. The UV-visible spectra data are illustrated in the Table-4. The spectral data of the complexes (4-8) showed bands (500, 510, 520, 540, 560) nm. The complexes (4) showed d-d transition at 510 nm ($^1A_{1g}$ $^1B_{1g}$) and other complexes (5-8) reveals absorption at 500, 510, 520, 540, 560 nm due to d-d transition characteristic of square planar Ni(II) , Cu(II), Zn(II) respectively. Other bands for the complexes are due to charge transfer bands. It appears from the magnetic moment data table-2 that the complexes(4), (6), (7) showes diamagnetic property of square planar Zn(II) Ni(II) symmetry[10]. And the others complexes(5) and (8) of Cu(II) containing magnetic moment 1.39M, 1.53M at room temperature typical of square planar Cu(II) having one unpaired electron. The conductance data of the complexes (4-8) in DMSO are given in Table 1. The conductance values of the complexes reveal that these are non electrolytic[11] in nature. It appears from the electronic absorption, conductance measurement, magnetic moments and colour that the complexes (4-8) may have square planar geometry. The elemental analysis data Table-5 and other physical properties are in good agreement with the proposed stiochiometry of the complexes. On the basis of the above assessments the structure of the complexes (4-8) are illustrated in the Fig. 10.



Where, M = Zn(II). $R^1 = R^2 = CH_3$
M = Cu(II). $R^1 = R^2 = CH_3$
M = Ni(II). $R^1 = R^2 = CH_3$
M = Ni(II). $R^1 = CH_3$. $R^2 = Ph$
M = Cu(II). $R^1 = CH_3$. $R^2 = Ph$

**Fig. 10.**

## ACKNOWLEDGMENTS

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## REFERENCES

1. M. Rosenblum and R.B Wood ward, *J, Am Chem. Soc*. **80**: 5443 (1958).
2. Houser, C. R and J. K . Lindsay, *J. Org. Chem.* **21**: 382 (1956).
3. C. Glidewell, C Morrision, and C.M. Zakaria, *J. Organomet. Chem* , **485:** 201-207 (1995).
4. P.D. Beer, H. Sikanika, C. Blackburn.and J. F. Mc Aleer, *J. Chem. Soc. Chem. Common,* 602 (1989).
5. H. Imai and T. Ota, *Bull.Chem. Soc. jpn.*, **47**: 2497 (1994).
6. Review: P. D. Beer, *Chem. Soc .Revs.*,**18:** 409 (1989).
7. P. D. Beer, O.Kocian, R.J. Mortimer, and P. Spencer, *J. Chem. Soc., Chem.*, 602 (1992).
8. Kazuo. Nakamoto, ''Infrared and Raman spectra of Inorganic and coordination" 3rd Edn. John Wiley Sons, N. Y (1978).
9. J. A . Jahagradar,B. G. Patil & B. R Havinali, *Indian J. Chem.* **30A.** 471(1991).
10. F. A Cotton and G. Wilkinsion " Advanced Inorganic Chemistry" 5th Edn (John Wiley, Singapore. (1988).
11. W. J. Geary, ''*Coordination Chemistry Rev."* **7**: 110 (1971).