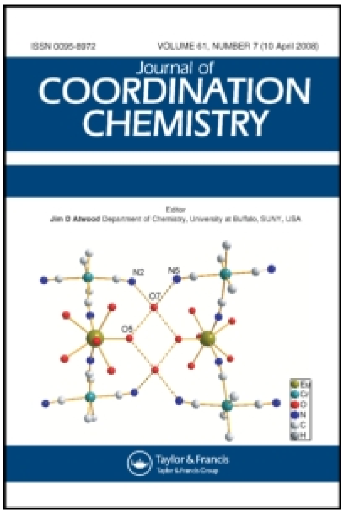

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Facile synthesis and reactions of some olefin-substituted acetylacetonate complexes

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Facile synthesis and reactions of some olefin-substituted acetylacetonate complexes

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Synthesis of transition metal complexes of olefin-substituted acetylacetones has been effected by reaction of nonaqueous solutions of substituted acetylacetones with the metal salt in the presence of Zn or Mg. 3-Allylacetylacetonates of Be(II), Cu(II), Ni(II), Fe(III), Co(II), Pd(II) and Zn(II) have thus been synthesized in quantitative yields. 3-Propylideneacetylacetone, which exists mainly in the keto form, afforded the corresponding 3-propenylacetylacetonates in which 3-propylideneacetylacetone has rearranged to 3-propenylacetylacetone which has a greater probability of existing in the enol form, thus making its reaction with metal ions favorable. Metal–metal exchange reactions of transition metal salts with olefin-substituted Zn or Mg acetylacetonates provide yet another route for the synthesis of transition metal olefin-substituted acetylacetonates. The homogeneous catalytic hydrogenation of the olefin moiety in olefin-substituted metal acetylacetonates could be achieved by a Pt/Sn catalyst.

Keywords: Olefin-substituted metal acetylacetonates; Catalytic hydrogenation; Synthesis

1. Introduction

Olefinic substitution on the 3-position of acetylacetone (2,4-pentanedione) affords 3-olefin substituted acetylacetones which may further react with transition metal ions to afford 3-olefin-substituted metal acetylacetonates that lend themselves to various interesting reactions of the coordinated ligands. 3-Bromo-acetylacetonates of Cr(III) and Co(III) afforded several phenyl-substituted Cr(III) and Co(III) acetylacetonates upon coupling with phenylboronic acid catalyzed by $Pd(PPh_3)_4$ [1]. 3-Allyl-, and 3-propenylacetylacetonates of Be(II), Cu(II), Ni(II) and Fe(III) have also been reported [2]. Substituents on acetylacetone in metal acetylacetonates modify the electronic environment on the metal atom in a way that may enhance activity as oxidation catalysts [3, 4] and in other applications [5]. Substitution of the olefins on the acetylacetonate ligand may afford organometallic monomers that could be polymerized to yield polymers with electric and/or magnetic properties that may find important practical applications.

A simple synthetic route for the synthesis of substituted acetylacetonates will have the way for further investigation of the chemistry and applications of such compounds.

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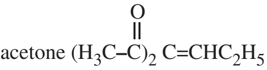
Hence, the present work reports a facile procedure for the synthesis of olefin- and alkyl-substituted metal acetylacetonates of some transition metal ions, and some chemical manipulation of these compounds.

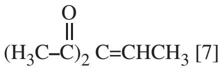
2. Experimental

2.1. *Preparation of substituted acetylacetones*

The following olefin-substituted acetylacetones were prepared and characterized according to literature methods [6, 7]:

3-Allylacetylacetone 
$(H_3C\text{–}\overset{\overset{O}{\|}}{C})_2CHCH_2CH=CH_2$ [6],

3-Propylideneacetylacetone 
$(H_3C\text{–}\overset{\overset{O}{\|}}{C})_2\ C=CHC_2H_5$ [7], and

3-Ethylideneacetylacetone 
$(H_3C\text{–}\overset{\overset{O}{\|}}{C})_2\ C=CHCH_3$ [7].

2.2. *Reactions of substituted acetylacetones with metal ions*

The three olefin-substituted acetylacetones were reacted with several metal ions. Similar procedures were used for the same metal salt in its reactions with each of the substituted acetylacetones: allylacac, propylideneacac and ethylideneacac. Slightly different procedures were applied for different metal salts. Both 3-allylacac and 3-propylidene-acac afforded well-characterized products; but 3-ethylideneacac did not react with the tested metal salts under the reaction conditions used for allyl- and propylideneacac.

Reactions with $CuCl_2 \cdot 2H_2O$. $CuCl_2 \cdot 2H_2O$ (1.71 g, 0.01 mol) was dissolved in 200 mL of ethyl alcohol. To the solution, magnesium metal (0.243 g, 0.01 mol), and substituted acetylacetone (4.20 g, 0.03 mol) were added. The mixture was refluxed with stirring for 30 min. The solution was then filtered, and ethyl alcohol was completely evaporated. The residue was washed with distilled water and excess low-boiling petroleum ether. The product was re-crystallized from ethyl alcohol.

3-Allylacetylacetone (allylacac) gave a grey compound (3.10 g, 91% yield), m.p., 192°C (with decomposition), which was identified as bis(allylacetylacetonato) copper(II), Cu(allylacac)$_2$, while 3-propylideneactylacetone gave a green compound, (3.14 g, 92%) m.p., 160–162°C (with decomposition), which was identified as bis(propenylacetylacetonato)copper(II), Cu(propacac)$_2$. Identification of the compounds was done by comparison of their colors with those of authentic samples prepared by different literature methods [2]. The identity of the coordinated ligands was confirmed by decomposing the metal acetylacetonate, isolating the substituted acetylacetone and identifying it by comparing its gas chromatograph (GC) retention time, and the NMR and IR spectra with those of authentic ligands.

Olefin-substituted acetylacetones behaved in an identical manner when Zn metal was used instead of Mg metal in their reactions with $CuCl_2 \cdot 2H_2O$.

Reactions with $BeCl_2$. Beryllium chloride, $BeCl_2$, (0.79 g, 0.01 mol) was dissolved in 200 mL of ethyl alcohol. To the solution, magnesium metal (0.243 g, 0.01 mol) and substituted acetylacetone (4.20 g, 0.03 mol), were added and the solution was refluxed with stirring for 30 min. The solution was filtered to remove any excess magnesium metal, and ethyl alcohol was evaporated completely. The yellow residue was dissolved in 10 mL of benzene and filtered to remove any benzene-insoluble material. The product was precipitated from the benzene solution by addition of excess low-boiling petroleum ether.

Allylacac gave a yellow crystalline product, (2.71 g, 94% yield) m.p., 48–50°C, which was identified as $Be(allylacac)_2$; while 3-propylideneacac gave a white powder (2.70 g, 94% yield), m.p., 52°C, which was identified as $Be(propacac)_2$. Identification of the compounds was done by comparison of their colors, m.p., and IR spectra with those of authentic samples prepared by different literature methods [2]. The identity of the co-ordinated ligands was confirmed by decomposing the metal acetylacetonate, isolating the substituted acetylacetone and identifying it by comparing its gas chromatograph (GC) retention time, and the NMR and IR spectra with those of authentic synthesized ligands. Olefin-substituted acetylacetones behaved in an identical manner when Zn was used instead of Mg in reactions with $BeCl_2$.

Reactions with $FeCl_3 \cdot 6H_2O$. Iron(III) chloride hexahydrate, $FeCl_3 \cdot 6H_2O$, (2.66 g, 0.01 mol) was dissolved in 200 mL of ethyl alcohol. To the solution, magnesium metal (0.243 g, 0.01 mol) and substituted acetylacetone (5.60 g, 0.04 mol) were added. The mixture was refluxed with stirring for 30 min. The solution was filtered to remove any unreacted material. The solvent was evaporated completely. The deep red residue was purified by dissolution in methanol, and precipitation by addition of water. It was dried under vacuum.

Allylacac gave a red product, (3.54 g, 85% yield) m.p., 67°C, which was identified as $Fe(allylacac)_3$; while 3-propylideneacac afforded a deep red product (3.62 g, 87% yield), m.p., 115°C, which was identified as $Fe(propacac)_3$. Identification of the compounds was done by comparison of their colors, m.p., and IR spectra with those of authentic samples prepared by different literature methods [2]. The identity of the co-ordinated ligands was confirmed by decomposing the metal acetylacetonate, isolating the substituted acetylacetone and identifying it by comparing its gas chromatograph (GC) retention time, and the NMR and IR spectra with those of authentic synthesized ligands.

Olefin-substituted acetylacetones behaved in an identical manner when Zn was used instead of Mg in reaction with $FeCl_3 \cdot 6H_2O$.

Reactions with $NiCl_2 \cdot 6H_2O$. Nickel(II) chloride hexahydrate, $NiCl_2 \cdot 6H_2O$, (2.37 g, 0.01 mol) was dissolved in 200 mL of ethyl alcohol. To the solution, magnesium metal (0.243 g, 0.01 mol) and 3-allylacetylacetone (4.20 g, 0.03 mol) were added. The mixture was refluxed with stirring for one hour. When the solution was filtered and evaporated completely, $NiCl_2 \cdot 6H_2O$ was recovered.

However, when the solution was treated with concentrated aqueous ammonia (10 mL), a greenish-blue precipitate was obtained after the evaporation of ethyl alcohol. The residue was washed with distilled water and low-boiling petroleum ether. The product was re-crystallized from methanol and dried under vacuum.

Allylacac afforded a greenish blue product (3.84 g, 89% yield), m.p., 178°C, which was identified as Ni(allylacac)$_2$(NH$_3$)$_2$; while 3-propylideneacac afforded a greenish blue product, (3.87 g, 90% yield) m.p., 164°C, which was identified as Ni(propacac)$_2$(NH$_3$)$_2$. Identification of the compounds was done by comparison of their colors, m.p., and IR spectra with those of authentic samples prepared by different literature methods [2]. The identity of the co-ordinated ligands was confirmed by decomposing the metal acetylacetonate, isolating the substituted acetylacetone and identifying it by comparing its gas chromatograph (GC) retention time, and the NMR and IR spectra with those of authentic synthesized ligands.

3-Allylacac and 3-propylideneacac showed identical behavior, when Zn was used instead of Mg, in reaction with $NiCl_2 \cdot 6H_2O$.

Reactions with $CoCl_2$. Cobalt(II) chloride, $CoCl_2$, (0.650 g, 0.005 mol) was dissolved in 200 mL of ethyl alcohol. To the solution, magnesium metal (0.122 g, 0.005 mol) and 3-allylacetylacetone (2.10 g, 0.015 mol) were added. The mixture was refluxed with stirring for about 15 min. Pyridine (py) (10 mL) was added to the solution. The green solution obtained was refluxed for 15 min. The solution was then cooled to room temperature. Any solid material that formed or remained in the mixture was removed by filtration. The brown solution obtained was evaporated completely and the product was dried under vacuum.

Allylacac afforded a brown product, (2.39 g, 93% yield) m.p., 86–88°C. Anal. Calcd for Co(allylacac)$_2$(py)$_2 \cdot H_2O$, $C_{26}H_{34}O_5N_2Co$(%): C, 60.81; H, 6.66, N, 5.45. Found: C, 61.05; H, 6.30; N, 5.69. 3-Propylideneacac afforded a deep brown product, (2.25 g, 88% yield) m.p., 92°C. Anal. Calcd for Co(propacac)$_2$(py)$_2 \cdot H_2O$, $C_{26}H_{34}O_5N_2Co$(%): C, 60.81; H, 6.66; N, 5.45. Found: C, 60.51; H, 6.42; N, 5.75. The identity of the coordinated ligands was confirmed by decomposing the metal acetylacetonate, isolating the substituted acetylacetone and identifying it by comparing its gas chromatograph (GC) retention time, and the NMR and IR spectra with those of authentic synthesized ligands.

When Zn was used instead of Mg in the reactions of $CoCl_2$, no products were formed.

Reactions with $PdCl_2$. Palladium(II) chloride, $PdCl_2$, (0.887 g, 0.005 mol) was added to 200 mL of ethyl alcohol. To the mixture, magnesium metal (0.122 g, 0.005 mol) and 3-allylacetylacetone (2.10 g, 0.015 mol) were added. The mixture was refluxed for two hours. The solution was cooled to room temperature and filtered to remove any unreacted magnesium metal or any precipitate formed. The clear solution was evaporated completely. The yellow residue was washed with distilled water and low-boiling petroleum ether, respectively. Allylacac gave a yellow product, (1.77 g, 90% yield), m.p., 185°C (with decomposition). Anal. Calcd for Pd(allylacac)$_2$, $C_{16}H_{22}O_4Pd$(%): C, 49.95; H, 5.76. Found: C, 50.16; H, 6.16. 3-Propylideneacac gave a yellow product (1.87 g, 89% yield), m.p., 127–130°C (with decomposition). Anal. Calcd for Pd(propacac)$_2 \cdot 2H_2O$, $C_{16}H_{26}O_6Pd$(%): C, 45.67; H, 6.22. Found: C, 45.53, H, 5.95. The identity of the coordinated ligands was confirmed by decomposing the metal acetylacetonate, isolating the substituted acetylacetone and identifying it by comparing its gas chromatograph (GC) retention time, and the NMR and IR spectra with those of authentic ligands.

Identical behavior of 3-allylacac and 3-propylideneacac with $PdCl_2$ was observed when Zn was used instead of Mg.

Reactions with $ZnCl_2$. Zinc chloride, $ZnCl_2$ (1.36 g, 0.01 mol) was dissolved in 15 mL of distilled water; the solution was treated with 10 mL of concentrated aqueous ammonia and stirred until a clear solution was obtained. To the resulting solution of $Zn(NH_3)_4^{++}$, 3-allylacetylacetone (2.80 g, 0.02 mol) was added drop-wise with stirring. The precipitate formed was filtered and re-crystallized from ethyl alcohol.

Allylacac afforded a white product (3.97 g, 95% yield), m.p., 98°C. Anal. Calcd for $Zn(allylacac)_2 \cdot 4H_2O$, $C_{16}H_{30}O_8Zn$(%): C, 46.23; H, 7.27. Found: C, 45.59; H, 6.96. 3-Propylideneacac afforded a white product, (3.93 g, 94% yield) m.p., 105–107°C. Anal. Calcd for $Zn(propacac)_2 \cdot 4H_2O$, $C_{16}H_{30}O_8Zn$(%): C, 46.23; H, 7.27. Found: C, 46.49; H, 6.87. The identity of the coordinated ligands was confirmed by decomposing the metal acetylacetonate, isolating the substituted acetylacetone and identifying it by comparing its gas chromatograph (GC) retention time, and the NMR and IR spectra with those of authentic ligands.

Reactions of 3-ethylideneacetylacetone. The reactions of 3-ethylideneacetylacetone were attempted with each of the metal salts investigated for 3-allylacac and 3-propylideneacac, under similar reaction conditions, but no identifiable reaction products could be isolated.

2.3. *Metal–metal exchange in the reactions of metal chlorides with $Zn(allylacac)_2 \cdot 4H_2O$ and $Zn(propacac)_2 \cdot 4H_2O$*

The olefin-substituted acetylacetonates $Zn(allylacac)_2 \cdot 4H_2O$ and $Zn(propacac)_2 \cdot 4H_2O$ were reacted with some metal chlorides, by the following general procedure:

The metal chloride (0.001 mol) was dissolved in 100 mL of ethyl alcohol. To the solution, $Zn(allylacac)_2 \cdot 4H_2O$ or $Zn(propacac)_2 \cdot 4H_2O$ (0.001 mol) was added. The mixture was refluxed with stirring for 30 min and the solvent was then evaporated. The residue obtained was washed with distilled water and low-boiling petroleum ether and dried under vacuum. Variations in the general procedure involved: re-crystallization of the product from benzene in the case of the reactions of $BeCl_2$, and purification of the product by dissolution in ethanol followed by precipitation by addition of water for reactions of $FeCl_3 \cdot 6H_2O$. Reactions of $Zn(allylacac)_2 \cdot 4H_2O$ with $CuCl_2 \cdot 2H_2O$, $BeCl_2$, $FeCl_3 \cdot 6H_2O$ and $PdCl_2$ afforded the corresponding $Cu(allylacac)_2$, $Be(allylacac)_2$, $Fe(allylacac)_3$, and $Pd(allylacac)_2$, respectively. Likewise, reactions of $Zn(propacac)_2 \cdot 4H_2O$ with these metal chlorides produced the corresponding metal propenylacetylacetonates. Cobalt(II) chloride and $NiCl_2$ failed to react with $Zn(allylacac)_2 \cdot 4H_2O$ or $Zn(propacac)_2 \cdot 4H_2O$ under the above-mentioned reaction conditions. Reaction products were characterized by the normal procedures described under 2.2 above.

2.4. *Catalytic hydrogenation of Cu(allylacac)$_2$*

To 200 mL of dichloromethane, Cu(allylacac)$_2$ (8.0 g, 0.0234 mol), $Pt(PPh_3)_2Cl_2$ (1.0 g, 0.00126 mol), and $SnCl_2 \cdot 2H_2O$ (2.5 g, 0.0111 mol) were added. The mixture was placed in a Parr pressure reactor under 400 psi hydrogen gas. The mixture was stirred for 8 h at 75°C and then cooled and removed from the reactor. The solution was evaporated under vacuum to 1/3 volume and low-boiling petroleum ether was added in excess, with stirring. The mixture was filtered. The filtrate was decomposed by aqueous KCN according to the procedure described in section 2.5 below. The recovered substituted acetylacetone was purified by distillation. The fraction with b.p. 86°C (20 mm Hg) was collected. Its NMR chemical shifts did not show any peaks corresponding to olefinic hydrogen.

The NMR chemical shifts are identical to those of 3-*n*-propylacetylacetone prepared by the reaction of n-propylbromide and sodium acetylacetone: ppm downfield from TMS: CH_3CH_2–1.17(t) (3H); $(CH_3CO)_2$ 1.79(s) (6H); $CH_3CH_2CH_2$–3.18–3.36 (m) (4H); –CH of the acac 5.2(t) (1H).

The IR spectrum of the recovered 3-*n*-propylacac showed a strong absorption at 1700 cm^{-1}, but no absorption in the 1610–1700 cm^{-1} range.

2.5. *Decomposition of olefin-substituted acetylacetonates*

In order to identify coordinated substituted acetylacetonates, some complexes containing them were decomposed with aqueous potassium cyanide and the olefin-substituted acetylacetone was extracted with anhydrous ether by the following general procedure:

Potassium cyanide, KCN, (1.0 g) was dissolved in 25 mL of water. To the solution, 1.0 g of the complex was added with stirring until a clear solution was obtained. The solution was extracted with two 25 mL portions of anhydrous ether. The ether solution was dried over sodium sulfite. Ether was evaporated, and the ligand was recovered and identified by comparison of its NMR and IR spectra, and GC retention time to those of authentic samples of the corresponding substituted acetylacetones.

Substituted acetylacetones recovered by decomposition of their corresponding complexes are: 3-allylacac, 3-propenylacac and 3-propylacac. The NMR chemical shifts of 3-propylacac have already been described in 2.4 above.

The NMR chemical shifts for 3-propenylacac are in ppm downfield from TMS: $CH_3CH=1.32$ (d) (3H); $(CH_3CO)_2$ 1.81 (s) (6H); –CH = CH–4.5–4.70 (m) (2H); CH of acac 5.44 (d) (1H).

Those of 3-allylacac are: $(CH_3CO)_2$ 1.86 (s) (6H); $-CH_2$ –2.92 (m) (2H); $CH_2=CH$– 4.71–4.89 (m) (3H); CH of the acac 5.57 (t) (1H).

The three ligands can be differentiated from one another with respect to their NMR chemical shifts by recognizing that one of them, allylacac, does not have a unique methyl group (other than those bonded to the carbonyl carbons). The other two can be differentiated by the fact that allylacac shows a chemical shift due to olefinic hydrogens, while the other, propylacac is saturated. Differention by GC retention time is also feasible. Using a $5' \times 1/8''$ stainless steel column with 20% diethyleneglycol succinate on 60–80 chromosorb at 142°C, the retention times of propylidenacac, propenylacac and propylacac were 3.75, 4.50 and 5.50 min., respectively. The retention time of allylacac was 8.50 min using a 10′ × 1/4″ Cu-column with 20% diethyleneglycol adipate on 60–80 chromosorb at 160°C.

2.6. *Instrumental*

Infrared spectra were run using a Nicolet-impact 410 FT-IR spectrophotometer, NMR shifts were determined using a Bruker advanced DPX 300 mHz instrument, and gas chromatographic identification was carried out using a Varian CP3800 gas chromatograph. Hydrogenation experiments were performed using a Parr Instruments stirring pressure reactor with temperature control.

3. Results and discussion

Substitution of acetylacetone would effect electronic and steric changes on the metal atom in its complexes and in the steric requirements of its complexes as a whole. This will provide a tool to enhance the reactivity and selectivity of acetylacetonate metal complexes in their catalytic reactions, thus simplifying and improving such reactions. The purpose of the present work has been to: (a) find a simple route for the synthesis of some already known olefin-substituted metal acetylacetonates; (b) extend the list of known olefin-substituted acetylacetonates, and (c) investigate the catalytic hydrogenation of a representative olefin-substituted metal acetylacetonate.

3.1. *Synthesis of olefin-substituted acetylacetonate metal complexes*

The preparation of olefin-substituted acetylacetonates of Cu(II), Be(II), Fe(III) and Ni(II) by conventional methods which involve reacting the metal salt with the ligand in an aqueous medium has been reported [2]. A facile route has been applied in the present work for the synthesis of these complexes involving the reaction of the metal chloride with olefin-substituted acetylacetone in the presence of Mg or Zn in ethanolic solution. The method gives almost quantitative yields of the products. The following overall reaction has been observed:

$$M' + M^{2+} + 2\ \text{olefacacH} \rightarrow (M')^{2+} + M(\text{olefacac})_2 + H_2$$

where $M' = $ Zn or Mg metal, olefacacH = olefin-substituted acetylacetone; $M^{2+} = Cu^{2+}$, Be^{2+}, Ni^{2+}, Co^{2+} and Pd^{2+}. The ferric complexes $Fe(olefacac)_3$ have also been prepared by the same method.

The formation of Ni(II) and Co(II) complexes was only possible when NH_3 or pyridine, respectively, were included in the system. The complexes $Ni(olefacac)_2(NH_3)_2$ and $Co(olefacac)_2(py)_2$ were thus isolated.

In addition to the known $Cu(allylacac)_2$, $Be(allylacac)_2$, $Ni(allylacac)_2(NH_3)_2$ and $Fe(allylacac)_3$, $Cu(propacac)_2$, $Be(propacac)_2$, $Ni(propacac)_2(NH_3)_2$, the compounds $M(allylacac)_2$ and $M(propacac)_2$ (M=Pd(II) and Zn(II)); and $Co(allylacac)_2(py)_2 \cdot H_2O$ and $Co(propacac)_2(py)_2 \cdot H_2O$ were synthesized. When 3-ethylideneacetylacetone was used as a ligand, no product was formed. 3-Propenylacetylacetonate complexes, M(propacac)$_2$, were isolated in the case of 3-propylideneacetylacetone. This suggests that substituted acetylacetones have to be in the enol form in order to bond to the metal. When enolization is not favored as in 3-ethylideneacetylacetone, no product is formed. However, a Pt(0) complex $Pt[(C_6H_5)_3P]_2L$ where L is benzylideneacetylacetone, in which the ligand behaves as a diketone, has been reported [8]. The identity of the ligand in the reaction of 3-propylideneacetylacetone with metal salts was confirmed as 3-propenylacetylacetone by the decomposition of its coordination compound and the isolation, and identification of the ligand.

The reactions of metal ions with olefin-substituted acetylacetones in the presence of Zn or Mg metals apparently proceed through the formation of Zn(olefacac)$_2$ or Mg(olefacac)$_2$ which then reacts in a metal–metal exchange process with the metal salt to form M(olefacac)$_2$ and $ZnCl_2$ or $MgCl_2$, respectively. The driving force for such reactions is the lower stability of Zn(olefacac)$_2$ or Mg(olefacac)$_2$ with respect to M(olefacac)$_2$, and the high stability of $MgCl_2$ and $ZnCl_2$. The failure to isolate the olefin-substituted acetylacetonate of either Mg or Zn by boiling an ethanolic suspension of either Mg or Zn metal with either 3-allylacetylacetone or 3-propylideneacetylacetone is indicative of the low stability of these complexes in ethanolic solutions.

To test the assumption that a metal–metal exchange process is involved in the reaction, Zn(allylacac)$_2$ and Zn(propacac)$_2$ were prepared in aqueous media, and then reacted with other metal salts. On boiling an ethanolic solution of either Cu(II), Be(II), Fe(III) or Pd(II), in the form of metal chloride, with either Zn(allylacac)$_2$ or Zn(propacac)$_2$ in the same solvent, the olefin-substituted acetylacetonates of these metals were isolated.

$$\mathrm{Zn(allylacac)_2} + \mathrm{M^{2+}} \xrightarrow[\text{Reflux}]{\mathrm{C_2H_5OH}} \mathrm{Zn^{2+}} + \mathrm{M(allylacac)_2}$$

$$\mathrm{Zn(propacac)_2} + \mathrm{M^{2+}} \xrightarrow[\text{Reflux}]{\mathrm{C_2H_5OH}} \mathrm{Zn^{2+}} + \mathrm{M(propacac)_2}$$

M = Cu(II), Be(II), Pd(II) and Fe(III) (with the necessary changes in the stoichiometry of the reaction for the case of Fe(III).

3.2. *Stability of olefin-substituted metal acetylacetonates*

Although ν_{M-O} is a good probe for the stability of acetylacetonate–metal coordination compounds, its occurance in the skeletal vibrational region of the IR spectrum makes its assignment rather ambiguous. Thus, $\nu_{C=O}$ was used instead as such a criterion. The stretching frequencies in the investigated metal allyl- and propenylacetylacetonates and their shifts from the values of the free ligands are listed in table 1.

These values suggest that for both 3-allyl and 3-propenyl metal acetylacetonates the stability of the M–O bonds varies in the order Zn(II) < Co(II) < Ni(II) < Be(II) < Cu(II) $\simeq$ Fe(II) < Pd(II). This order of stability supports the metal–metal exchange mechanism. Thus, the low stability of Zn(allylacac)$_2 \cdot 4H_2O$ and Zn(propacac)$_2 \cdot 4H_2O$ with respect to other metal-olefin-substituted acetylacetonates favors the formation of olefin-substituted acetylacetonates of these metals upon mixing the metal salt with Zn(allylacac)$_2 \cdot 4H_2O$ or Zn(propacac)$_2 \cdot 4H_2O$. Moreover, it should not be surprising

Table 1. Carbonyl vibrations in the IR spectra of substituted metal acetylacetonates.

Compound	$\nu_{C=O}$ Stretching frequency (cm^{-1})	$\Delta\nu_{C=O}$*
3-Allylacetylacetone	1715	0
$Cu(allylacac)_2$	1570	145
$Be(allylacac)_2$	1580	135
$Fe(allylacac)_3$	1570	145
$Ni(allylacac)_2(NH_3)_2$	1585	130
$Co(allylacac)_2(py)_2 \cdot H_2O$	1595	120
$Zn(allylacac)_2 \cdot 4H_2O$	1605	110
$Pd(allylacac)_2$	1560	155
3-Propylideneacetylacetone	1700	0
$Cu(propacac)_2$	1565	135
$Be(propacac)_2$	1575	125
$Fe(propacac)_3$	1565	135
$Ni(propacac)_2(NH_3)_2$	1580	120
$Co(propacac)_2(py)_2 \cdot H_2O$	1590	110
$Zn(propacac)_2 \cdot 4H_2O$	1600	100
$Pd(propacac)_2 \cdot 2H_2O$	1555	145

*$\Delta\nu_{C=O} = \nu_{C=O}$(ligand) − $\nu_{C=O}$(complex).

that no product could be isolated upon mixing Co(II) or Ni(II) with either $Zn(allylacac)_2 \cdot 4H_2O$ or $Zn(propacac)_2 \cdot 4H_2O$ in ethanolic solution. This can be attributed to the small difference in the stability constants of these metal complexes and those of Zn(II).

3.3. *Catalytic hydrogenation of Cu(allylacac)$_2$*

It is known that a mixture of $PtCl_2(Ph_3P)_2$ and $SnCl_2$ catalyses the hydrogenation of polyolefins to mono-olefins [9]. The reaction proceeds through a mechanism, which involves double-bond-migration isomerization whereby the double bonds move to a conjugated position before being hydrogenated. It was hoped that double-bond migration may be effected in olefin-substituted metal acetylacetonates, if they were exposed to mild catalytic hydrogenation conditions. However, the mild catalytic hydrogenation of bis(3-allylacetylacetonato)-copper(II) led to the hydrogenation of the allyl group and the formation of bis(3-propylacetylacetonato)copper(II), as evidenced by the absence of olefinic protons in the NMR chemical shifts of the substituted acetylacetone recovered from the decomposition of the hydrogenated Cu-substituted acetylacetonate. The result is not surprising, since terminal double bonds are known to have a great tendency to be hydrogenated.

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