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Reactions of Bis(2,4-pentanedionato)nickel(II) with Isocyanates and Other Electrophiles. Electrophilic Addition to 2,4-Pentanedione Catalyzed by Ni(acac)$_2$

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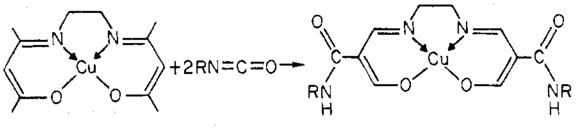
Bis(2,4-pentanedionato)nickel(II), Ni(acac)$_2$, reacts quickly and in high yield with electrophiles at the methine position. Reactions of isocyanates produce diamides; diethyl azodicarboxylate produces a dihydrazine and dimethyl acetylenedicarboxylate produces a diolefin. The ligands have been displaced intact from the metal with H_2S and are identical with those prepared catalytically. Ni(acac)$_2$ also catalyzes the addition of these electrophiles to free Hacac and it is demonstrated that catalysis proceeds via reaction of a coordinated ligand. Other metal 2,4-pentanedionates, Mg(II), Cd(II), Zn(II), Co(II), Li(I), Mn(III), Cu(II), and Fe(III), also catalyze the reaction of PhN=C=O with Hacac, but Cr(acac)$_3$, Pd(acac)$_2$, and Al(acac)$_3$ do not. The relative catalytic efficiency of these 2,4-pentanedionates was determined. The new compounds were fully characterized by elemental analyses, melting points, and infrared, electronic, and NMR spectroscopy. A mechanism for these reactions is proposed and discussed. A facile synthetic route to a variety of substituted acetoacetamides is available via the catalyzed RN=C=O reactions.

Introduction

It is well known that numerous transition-metal β-diketonates undergo a wide range of substitution reactions common to aromatic systems[2] despite the realization that these β-diketonates possess little or no aromatic character.[3] The methine protons on the complexes' chelate rings can be displaced by many different electrophilic groups.[2] Recent work[4] in our laboratories has established that copper(II) complexes of the Schiff base condensation products of 2,4-pentanedione and diamines such as I react quickly and quantitatively with isocyanates in a fashion similar to that of β-diketone complexes to yield the diamides II according to reaction 1.



(1)

I, Cu[baen] II, Cu[baen]·2RNCO

When copper(II) is replaced by nickel(II) in reaction 1, reactions with isocyanates proceed slowly[5] and only with reactive[6] isocyanates containing electron-withdrawing substituents such as R = tosyl, phenyl, and 1-naphthyl. In contrast to the behavior of Ni[baen], anhydrous Ni(acac)$_2$ reacts quickly and essentially quantitatively with both alkyl and aryl isocyanates as well as with the electrophiles diethyl azodicarboxylate and dimethyl acetylenedicarboxylate yielding respectively diamide, dihydrazine, and diolefin derivatives of the parent β-diketone complex. Also, Ni(acac)$_2$ and other M(acac)$_n$ complexes effectively catalyze these addition reactions to free 2,4-pentanedione. These reactions and their products are described in this paper.

Experimental Section

Anhydrous bis(2,4-pentanedionato)nickel(II) was dried under vacuum at 75 °C for 48 h prior to use. All solvents were dried by standard procedures and distilled immediately before use. The various electrophiles were obtained from commercial sources and used as received.

Nuclear magnetic resonance, infrared, electronic, and mass spectra and melting points were obtained as previously described.[4,7] Magnetic susceptibilities were determined at room temperature on a Faraday apparatus employing a Cahn electrobalance, with Hg[Co(CN)$_4$] used as calibrant;[8] ligand diamagnetic corrections were estimated from Pascal's constants.[9] Elemental analyses were performed by Chemalytics, Inc., Tempe, Ariz., or Galbraith Laboratories, Knoxville, Tenn.

All reactions were run in oven-dried glassware. Addition reactions to Ni(acac)$_2$ were run in refluxing benzene while catalyzed additions were run either in benzene or dichloromethane at ambient temperature. The following are exemplary.

Table I. Physical Properties of the Complexes [Ni(acac·RNCO)$_2$]$_3$

R	Mp, °C	μ_{eff}, μ_B[a]	Ligand[b] mp, °C	% yield Complex	% yield Ligand[b]
CH_3	188–191	3.30	83–85	95	89
C_2H_5	180–182	3.53	49–51	75	81
i-C_3H_7	168–171	3.43	94–95	76	87
C_6H_5	193–195	3.35	117–119[c]	90	93
p-$CH_3C_6H_4$	183–186	3.48	109–110	97	83
p-$CH_3OC_6H_4$	184–187	3.46	100–102	92	98
p-ClC_6H_4	206–210	3.29	144–145	95	87
p-$CH_3C_6H_4SO_2$	172–175	3.43	128–130	94	85

[a] At 293 K. [b] Catalytically prepared, the H_2S-displaced ligands are identical with the catalytically prepared products. [c] Lit.[15] mp 118–119 °C.

I. Addition Reactions of Ni(acac)$_2$. (A) Ni(acac)$_2$ + 2PhNCO. Phenyl isocyanate, 4.15 mL (0.0382 mol), was slowly added (*CAUTION*: isocyanates are both toxic and lacrymatory) to a solution containing 4.93 g (0.0191 mol) of anhydrous Ni(acac)$_2$ in 50 mL of dry benzene in a 100-mL round-bottom flask. The reaction mixture was stirred magnetically and topped with a condenser and a CaCl$_2$-containing drying tube. No change in the green homogeneous solution was observed before refluxing commenced. About 10 min after refluxing commenced, a pale green precipitate appeared in the reaction flask, which increased in quantity until the mixture had solidified to a light green mass (after 10 h of heating). The product was isolated by filtration, washed with hexane, and dried in vacuo. After recrystallizing once from chloroform/hexane a 90% yield of green microcrystalline product mp 193–195 °C was obtained. Anal. Calcd for $C_{24}H_{24}N_2NiO_6$: C, 58.24; H, 4.85; N, 5.66; Ni, 11.86. Found: C, 58.04; H, 4.82; N, 5.61; Ni, 11.80. The physical properties of the isocyanate adducts are given in Table I.

(B) Ni(acac)$_2$ + 2C$_2$H$_5$CO$_2$N=NCO$_2$C$_2$H$_5$. Similarly 3.67 g (0.02 mol) of 95% diethyl azodicarboxylate (*CAUTION*, concentrated solutions of azocarboxylates will explode if heated) and 2.58 g (0.01 mol) of Ni(acac)$_2$ were refluxed in dry benzene for 24 h. Recrystallization from chloroform/hexane and vacuum drying produced a 53% yield of a mustard yellow microcrystalline product, mp 204–207 °C. Anal. Calcd for $C_{22}H_{34}N_4NiO_{12}$: C, 43.68; H, 5.62; N, 9.26; Ni, 9.70. Found: C, 43.62; H, 5.54; N, 9.16, Ni, 9.56.

(C) Ni(acac)$_2$ + 2CH$_3$CO$_2$C≡CCO$_2$CH$_3$. Similarly 2.84 g (0.02 mol) of dimethyl acetylenedicarboxylate and 2.58 g (0.01 mol) of Ni(acac)$_2$ were reacted under reflux in dry benzene for 20 h. Upon addition of hexane to the brown benzene solution a golden brown powder precipitated. Two recrystallizations from chloroform/hexane produced a yellow microcrystalline product, mp 176–180 °C, in 86% yield. Anal. Calcd for $C_{22}H_{26}NiO_{12}$: C, 48.85; H, 4.81; Ni, 10.85. Found: C, 48.51; H, 5.03; Ni, 10.65.

II. $Ni(acac)_2$-Catalyzed Addition Reactions of 2,4-Pentanedione. (A) 2,4-Pentanedione + PhN=C=O. To a stirring solution containing 4.6 g (0.0046 mol) of 2,4-pentanedione and 0.1 g (0.00039 mol) of $Ni(acac)_2$ in 15 mL of dry dichloromethane was added 5.0 mL (0.0046 mol) of phenyl isocyanate. The reaction flask was topped with a condenser and a $CaCl_2$ drying tube. The reaction was mildly exothermic as the flask became warm to the touch. After 20 h of stirring at ambient temperature, hexane was added and the flask was cooled in a dry ice–acetone bath, which initiated copious precipitation of a white crystalline product. Two recrystallizations from chloroform/hexane afforded white needle-like crystals, mp 117–119 °C, in 93% yield. Anal. Calcd for $C_{12}H_{13}NO_3$: C, 65.70; H, 5.94; N, 6.40. Found: C, 66.17; H, 5.96; N, 6.45. In a similar manner several other 2,4-pentanedionate complexes (0.46 mol) were used as catalysts for the reaction of PhNCO (5 mL) with Hacac (4.72 mL) in C_6H_6 or CH_2Cl_2 (15 mL). The catalysts and isolated yield of product after 20 h at ambient temperature were as follows: $Ni(acac)_2$, 93%; $Mg(acac)_2$, 84%; $Cd(acac)_2$, 72%; $Zn(acac)_2$, 67.4%; $Co(acac)_2$, 66.5%; Li(acac), 56.7%; $Mn(acac)_3$, 54.8%; $Cu(acac)_2$, 50.8%; $Fe(acac)_3$, 23.6%. $Al(acac)_3$, $Pd(acac)_2$, and $Cr(acac)_3$ did not catalyze the reaction.

(B) 2,4-Pentanedione + $C_2H_5CO_2N{=}NCO_2C_2H_5$. To a stirring solution containing 5.0 mL (0.005 mol) of Hacac and 0.1 g (0.00039 mol) of $Ni(acac)_2$ in 15 mL of dry dichloromethane was added 9.16 g (0.005 mol) of 95% diethyl diazodicarboxylate. An exothermic reaction commenced immediately upon addition of the azodicarboxylate, and the reaction mixture refluxed spontaneously for an hour and a white precipitate appeared. After the mixture cooled, the precipitate was collected by filtration, washed with hexane, and recrystallized twice from chloroform/ether to furnish white tubular crystals, mp 114–116 °C, in 78% yield. Anal. Calcd for $C_{11}H_{18}N_2O_6$: C, 48.17; H, 6.62; N, 10.21. Found: C, 48.05; H, 6.62; N, 10.29.

(C) 2,4-Pentanedione + $CH_3CO_2C{\equiv}CCO_2CH_3$. Similarly 7.1 g (0.005 mol) of dimethyl acetylenedicarboxylate, 5 mL (0.005 mol) of Hacac and 0.1 g (0.0039 mol) of $Ni(acac)_2$ were reacted in 15 mL of dry dichloromethane at ambient temperature overnight. Evaporation of the dichloromethane left an amber oil which was distilled in a short-path vacuum apparatus to yield 5.0 mL (50% yield) of a viscous oily product, bp 195–200 °C (10 mm). Anal. Calcd for $C_{11}H_{14}O_6$: C, 54.54; H, 5.83. Found: C, 54.35; H, 5.43.

(D) 2,4-Pentanedione + $C_2H_5N{=}C{=}O$ (No Catalyst). A solution containing 10.27 mL (0.10 mol) of Hacac and 7.87 mL (0.10 mol) of $C_2H_5N{=}C{=}O$ in 50 mL of dry benzene was refluxed for 6 days. An infrared spectrum of the solution at this point demonstrated that considerable unreacted isocyanate remained (ν_{NCO} 2270 cm^{-1} very strong). The unreacted isocyanate, 2,4-pentanedione, and benzene were removed on a rotary evaporator. Crystallization of the residue from ether/hexane produced 0.8 g of yellowish crystals which melted at 30 °C: NMR ($CDCl_3$) δ 1.20 (t, 3, J = 6 Hz, CH_3CH_2N), 2.15 (s, 3, $CH_3C{=}O$), 2.84 (d, 3, J = 2 Hz, $\mathit{CH}_3C({=}O){=}C$), 3.64 (q, J = 6 Hz, $CH_3\mathit{CH}_2N$), 3.63 (q, J = 2, 1 Hz, $C{=}\mathit{CH}$), consistent with a very small yield of the product of reaction at the enol oxygen.

III. Ligand Displacements. (A). Ligand displacements were performed with gaseous H_2S in dichloromethane as previously described.[4] The physical properties are listed in Table I.

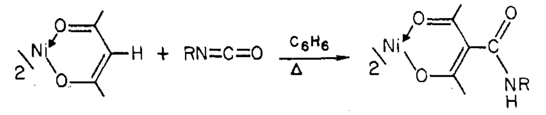
(B) H_2SO_4 in Benzene. To a solution containing 4.0 g (0.01 mol) of $Ni(acac)_2{\cdot}2C_2H_5NCO$ in 30 mL of benzene was added 3.2 mL (0.02 mol) of concentrated H_2SO_4 causing formation of a yellow $NiSO_4$ aqueous layer. The two-phase system was heated and stirred until the benzene layer was colorless, and the mixture then extracted with benzene overnight in a continuous extractor. The benzene layer was removed, treated with hexane, and cooled to −78 °C to yield white crystals which were filtered and washed with hexane. This product slowly melted at room temperature. Assuming that this product was *N*-ethylacetoacetamide (lit.[10] mp 30 °C), its 2,4-dinitrophenylhydrazone derivative was prepared[8] (mp 165 °C, lit.[11] mp 165 °C). *N*-Methylacetoacetamide was similarly prepared from $Ni(acac)_2{\cdot}2CH_3NCO$ (mp 47 °C, lit.[10] mp 47 °C) and its 2,4-dinitrophenylhydrazone derivative prepared (mp 184 °C, lit.[10] mp 184 °C). *N*-Isopropylacetoacetamide was similarly prepared, mp 44.5–45 °C. Anal. Calcd for $C_7H_{13}NO_2$: C, 58.7; H, 9.09; N, 9.79. Found: C, 58.55; H, 8.98; N, 9.90.

IV. Reactions of (Hacac + RNCO) Products. (A) Acid-Catalyzed Reaction of Hacac·PhNCO with Methanol. To a solution of 2.69 g of (Hacac·PhNCO) in 25 mL of dry benzene was added 0.5 mL of methanol and 2 drops of concentrated H_2SO_4. After refluxing the reaction mixture for 4 h, the solution was cooled (GC analyses showed the presence of methyl acetate) and hexane added to induce crystallization of a white product (mp 84–85 °C, lit.[4] 86 °C) whose IR and NMR spectra were identical with those of an authentic sample of acetoacetanilide.

(B) Reaction of Hacac·*p*-ClC_6H_4NCO with Benzylamine. To 3.5 g of Hacac·*p*-ClC_6H_4NCO in 50 mL of dry benzene was added 1.5 mL of benzylamine. After 3 h of reflux, the solution was reduced in volume on a rotary evaporator to furnish a yellow crystalline product whose NMR spectrum was consistent with a mixture of two substances. The crude mixture was dissolved in ether and extracted with dilute aqueous sodium hydroxide. The aqueous phase was acidified with concentrated HCl to yield white crystals of *p*-chloroacetoacetanilide, mp 130–132 °C, lit.[10] mp 131–133 °C. The ether layer was evaporated and the resulting solid recrystallized three times from dichloromethane/petroleum ether to furnish faintly yellow crystals of *N*-benzylacetamide, mp 58–60 °C, lit.[13] mp 61 °C.

Results and Discussion

Reaction of $[Ni(acac)_2]_3$[13] with 2 molar equiv of an isocyanate in dry benzene at reflux yields the $[Ni(acac)_2{\cdot}2RNCO]_3$ complexes (III) according to reaction 2 for R =



(2)

$[Ni (acac)_2]_3$ III, $[Ni(acac)_2{\cdot}2RNCO]_3$

CH_3, C_2H_5, *i*-C_3H_7, C_6H_5, *p*-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$, *p*-ClC_6H_4, and *p*-$CH_3C_6H_4SO_2$ (see Table I for physical properties). It should be noted that this reaction is formally analogous to the isocyanate reactions[4] with Cu[baen] (I) in which diamides are also the products (reaction 1). The products (III) are all pale green powders similar in appearance to the parent $[Ni(acac)_2]_3$. These products (III) possess room temperature magnetic moments, $\mu = 3.29–3.53\ \mu_B$, which are higher than that reported[14] for $[Ni(acac)_2]_3$, $\mu = 3.27\ \mu_B$, and in the range normally found[15] for tetrahedral nickel(II). Structural studies have confirmed that $[Ni(acac)_2]_3$ is a trimer in the solid state[13,14] and an equilibrium mixture of six-coordinate trimer and square-planar monomer in solution.[14,16] The electronic spectra of $Ni(acac)_2{\cdot}2PhNCO$ in $CHCl_3$ exhibit two transitions at 8734 cm^{-1} (ϵ = 14.2) and 15 220 cm^{-1} (ϵ = 9.2). A series of spectra taken over the concentration range of 0.05–0.005 M demonstrate that these solutions do not rigorously obey Beer's law though no isosbestic point[16] is evident. Nujol mull spectra of the solid state are identical with solution spectra. Thus, it seems clear that the predominant species in solution and in the solid state is six-coordinate and is likely trimeric.[16]

The infrared spectra of the $Ni(acac)_2{\cdot}2RNO$ complexes (Table II) serve as excellent confirmation of their structure. Each of the products possess medium to strong intensity bands in the 1640–1655 and 3260–3310-cm^{-1} regions which are not present in the infrared spectrum[17] of $Ni(acac)_2$. Consistent with the analogous reaction products[4] $[Cu(baen){\cdot}2RNCO]$ these bands are assigned to $\nu_{C=O}$(amide) and ν_{NH}(amide), respectively.

H_2S displacement from $[Ni(acac)_2{\cdot}2RNCO]_3$ or catalytic reactions (vide infra) furnish the free ligands. The melting points and IR, NMR, and mass spectra of these compounds are all consistent with the proposed structures. Reactions of the $[Ni(acac)_2{\cdot}2RNCO]_3$ complexes with H_2SO_4 (4 equiv) yielded *N*-alkylacetoacetamides. The identity of the products of these ligand displacement reactions coupled with the IR spectra and elemental analyses of the complexes definitely establishes that the structures are as depicted for III.

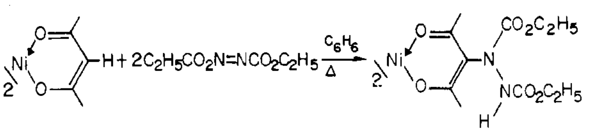
Table II. Infrared Data (cm^{-1}) for the Complexes [Ni(acac·RNCO)$_2$]$_3$ and Catalytically Prepared Ligands[a]

R	$\nu_{C=O}$(ketone)		$\nu_{C=O}$(amide)		ν_{N-H}	
	Complex	Ligand	Complex	Ligand	Complex	Ligand
CH_3	1592	1590	1652	1635	3300	3290
C_2H_5	1582	1590	1655	1640	3310	3290
i-C_3H_7	1590	1600	1650	1650	3305	3280
C_6H_5	1593	1590	1640	1645	3280	3280
p-$CH_3C_6H_4$	1590	1595	1650	1630	3275	3240
p-$CH_3OC_6H_4$	1594	1595	1648	1648	3295	3200
p-ClC_6H_4	1598	1595	1642	1650	3305	3285
p-$CH_3C_6H_4SO_2$	1588	1595	1658	1665	3260	3250

[a] The infrared spectra of the ligands displaced from the complexes with H_2S are identical with those of the catalytically prepared ligands.

The reaction does not occur between [Ni(acac)$_2$]$_3$ and RNCO when R is t-C_4H_9 or $(CH_3)_3Si$. Similar steric effects obtain in the isocyanate–Cu[baen] system[4] and are consequently not surprising.

[Ni(acac)$_2$]$_3$ also reacts with diethyl azodicarboxylate according to reaction 3 to yield IV.

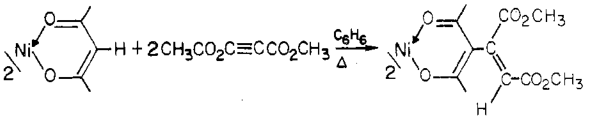


(3)

IV

The magnetic moment of IV is 3.70 μ_B at 294 K. As for Ni(acac)$_2$·2PhNCO, the electronic spectra of IV exhibit two transitions in $CHCl_3$ and in Nujol mulls at 8741 cm^{-1} (ϵ = 24) and 15 385 cm^{-1} (ϵ = 36) which do not obey Beer's law rigorously, and no isosbestic point is observed for spectra in solution as a function of concentration. Thus, the principal species is six-coordinate and likely a trimer.[16] Any explanation for the high paramagnetism can only be conjective. Complex IV, as drawn above, contains two structural moieties absent in [Ni(acac)$_2$]$_3$ which are readily identified in its infrared spectrum: ν_{N-H} (3300 cm^{-1}) and the additional carbonyl band arising from the four new ester functions ($\nu_{C=O}$ at 1720 cm^{-1}). Further support of the structure is provided by comparison of the H_2S displaced ligand with the catalytically prepared ligand; the NMR, IR, and mass spectra and melting points are identical.

Dimethyl acetylenedicarboxylate is an electron-deficient alkyne and additions to it yielding olefins occur readily.[18] This same basic reaction occurs between [Ni(acac)$_2$]$_3$ and $CH_3CO_2C{\equiv}CCO_2CH_3$ as shown in reaction 4 to yield V; μ = 3.35, electronic spectrum in $CDCl_3$, ν_1 8734 cm^{-1} (ϵ = 14) and ν_2 15 873 cm^{-1} (ϵ = 17.5). Nujol mull spectra are identical. The chloroform solution spectra do not rigorously obey Beers' law and no isosbestic point[16] is observed for solutions of varying concentrations. Hence, the predominant species is six-coordinate and likely a trimer.[19] The infrared spectrum of the product, V, possesses a carbonyl stretch $\nu_{C=O}$ at 1725 cm^{-1} due to the four ester functions. The product of H_2S ligand displacement is a liquid which is a viscous oil at room temperature. Its IR, NMR, and mass spectrum and boiling point are identical with those of the catalytically prepared product. An interesting structural question is the stereochemistry of the two olefin groups present in V.



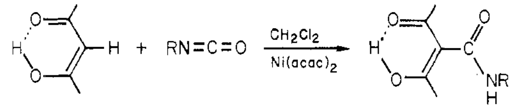
(4)

V

The olefins can be regarded as derivatives of dimethyl maleate (the cis configuration) or of dimethyl fumarate (the trans configuration). The chemical shift difference of the vinyl proton resonances for dimethyl maleate (δ 6.28) and dimethyl fumarate (δ 6.77) permits assignation of the stereochemistry in the ligand. The NMR spectrum of the H_2S-liberated ligand includes two vinyl resonances at δ 6.94 ppm and δ 6.03 ppm in the approximate integrated intensity ratio of 2:1, respectively. Therefore, both cis and trans configurations are present in the H_2S-liberated ligand in $CDCl_3$ with trans predominating. It is likely that a similar situation obtains for complex V, meaning that addition of dimethyl acetylenedicarboxylate is not stereospecific. Similar behavior has been noted[5] for the Ni[(baen)]·$2CH_3CO_2C{\equiv}CCO_2CH_3$ reaction product.

Not all potential electrophiles undergo facile additions to Ni(acac)$_2$. No reaction takes place when Ni(acac)$_2$ is refluxed in benzene with diphenylacetylene, dimethyl maleate, dimethyl fumarate, 2-phenyl-3,3′-dimethylazirine, 3-amino-5,6-dimethyl-1,2,4-triazine, *sym*-diphenyltetrazine, or diphenylnitrilimine and only partial reaction occurs after 4 days at reflux in benzene with *N*-phenylmaleimide. A probable explanation for the observed failure of these species to add to Ni(acac)$_2$ stoichiometrically is that the unsaturation in these compounds does not possess substituents which are sufficiently electron withdrawing to render these compounds reactive under these reaction conditions.

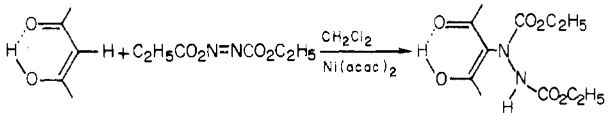
Uehara et al. recently reported[19] that certain divalent metal 2,4-pentanedionates act as catalysts for the reactions of the electrophiles trichloroacetonitrile, chloral, and phenyl isocyanate with 2,4-pentanedione. Ni(acac)$_2$ catalyzes the analogous reactions of the isocyanates and those other electrophiles which form addition products with it. These catalytic reactions can be represented as reactions 5, 6, and 7. (Spectral data are given in Tables II and III.) The maximum efficient turnover number for the catalyst Ni(acac)$_2$ in these systems is 10^2–10^3. When molar ratios of Ni(acac)$_2$:Hacac are 1:10^3 or less, reactions are very slow (although they do eventually yield the products VI–VIII), whereas molar ratios of 1:10^2 or



(5)

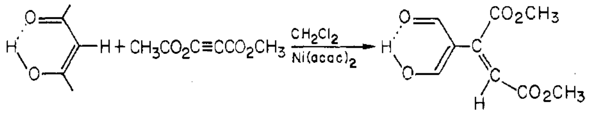
Hacac VI (Hacac·RNCO)

R = CH_3, C_2H_5, i-C_3H_7, C_6H_5, p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$, p-ClC_6H_4, and p-$CH_3C_6H_4SO_2$ but not t-C_4H_9 or $(CH_3)_3Si$



(6)

Hacac VII (Hacac·azo)



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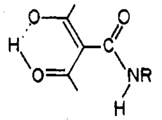
Hacac VIII (Hacac·alkyne)

Table III. Proton NMR Data for the Catalytically Prepared Ligands[a]



R	δ_{CH_3}	δ_{NH}[b]	δ_{OH}	δ_N Sub
CH_3	2.44 s, 2.16 s	15.88, 9.90	18.32 s	2.90 s, 2.82 s
C_2H_5	2.43 s, 2.14 s	15.87, 9.90	18.40 s	3.32 q (7), 1.18 t (7)
i-C_3H_7	2.41 s, 2.27 s	15.85, 9.92	18.36 s	4.08 dq (6), 1.20 d (6)
C_6H_5	2.52 s, 2.26 s	15.98, 11.65	18.08 s	7.40 m
p-$CH_3C_6H_4$	2.47 s, 2.13 s	15.97, 11.55	18.15 s	2.27 s, 7.20 ABq (8)
p-$CH_3OC_6H_4$	2.44 s, 2.16 s	15.99, 11.61	18.17 s	3.73 s, 7.04 ABq (9)
p-ClC_6H_4	2.52 s, 2.25 s	15.93, 11.59	17.83 s	7.37 ABq (5)
p-$CH_3C_6H_4SO_2$	2.43 s	16.09, 12.15	16.32 s	2.01 s, 7.57 ABq (8)

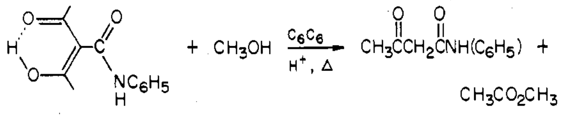
[a] Data presented as chemical shift (δ) multiplicity: s ≡ singlet, d ≡ doublet, t ≡ triplet, q ≡ quartet, ABq ≡ AB quartet, m ≡ multiplet (coupling constant); chloroform-*d* solutions, δ relative to internal Me_4Si. NMR data for the H_2S displaced ligands are identical. [b] See text for explanation.

slightly less cause rapid and essentially quantitative reaction.

That these reactions are catalyzed by $Ni(acac)_2$ is demonstrated by the fact that the products VI–VIII are not generated by mixing equimolar amounts of 2,4-pentanedione and the electrophile together in dichloromethane. Rather, with RNCO, the very slow addition which does occur leads to products derived primarily from reaction at the enol oxygen rather than from reaction at the methine carbon.

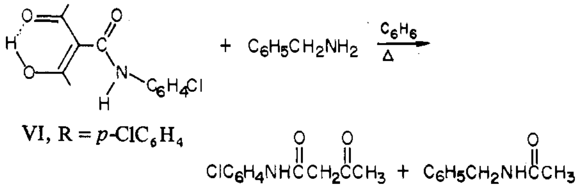
The structures of the catalytically prepared ligands can be assigned on the basis of their infrared and NMR spectra. As might be expected, their infrared spectra are very similar to the spectra recorded for the nickel complexes. Amide N—H and C═O stretches verify that the products are secondary amides. Very broad absorptions centered at about 3400 cm^{-1} are also present and are indicative of hydrogen-bound hydroxyl groups. ^1H NMR data indicate also that all of the compounds are present in $CDCl_3$ solution in the enol form, with very little evidence of tautomerism, as shown by the sharp OH resonances far downfield. Enolization is also apparent in the nonequivalence of the two methyl groups. These amides are further characterized by two widely separated broad N-H resonances characteristic of hindered rotation in amides.[20]

Not surprisingly, these diketo amides are quite reactive. Exposure to atmospheric moisture over a period of about a month causes decomposition with evolution of acetic acid. Compound VI, R = C_6H_5, undergoes facile acid-catalyzed reaction with methanol according to reaction 8. The diketo amides also react quickly and quantitatively with primary amines as shown by the reaction of VI (R = p-ClC_6H_4) with benzylamine, reaction 9, to furnish X and XI. As the scope of reactions 8 and 9 does not appear limited by functional groups, the reactions appear to be good synthetic routes to a variety of acetoacetamides avoiding the necessity of preparing and handling diketene.[11]



(8)

VI, R = C_6H_5



VI, R = p-ClC_6H_4

(9)

XI, p-chloroaceto-acetanilide

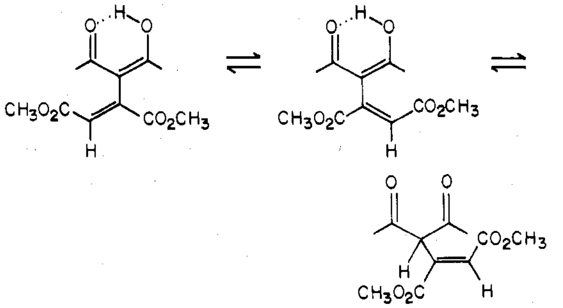
X, N-benzyl-acetamide

The $Ni(acac)_2$-catalyzed reaction of 2,4-pentanedione with diethyl azodicarboxylate proceeds quickly and exothermically to produce compound VII in near quantitative yield (reaction 8). The structure is supported by infrared and NMR spectroscopy. The infrared spectrum of VII includes a sharp, strong N–H band at 3280 cm^{-1} and an ester carbonyl stretch at 1760 cm^{-1}. The NMR spectrum is quite diagnostic of the structure and includes the following resonances: δ 15.64 (s, 1, OH), 7.60 (s, b, 1, NH), 2.30 (s, 3, $CH_3C{=}O$), 2.42 (s, 3, CH_3COH), 4.24 (d of q, 4, J = 7 Hz, CH_3CH_2O), 1.30 (t, 6, J = 7 Hz, CH_3CH_2O). The splitting pattern of the *O*-methylene protons is the result of a very slight nonequivalence in their immediate environments which is not observed for the methyl resonances of the *O*-ethyl groups.

The white crystalline product VII is more hydrolytically stable than the amides VI; exposure to ambient atmospheric moisture over a period of several weeks does not result in any lowering of the melting point.[21]

$Ni(acac)_2$ catalysis of the addition of dimethyl acetylenedicarboxylate leads to VIII (reaction 9). The infrared spectrum of VIII includes ν_{CO} 1730 (ester) and ν_{CH} 3010 cm^{-1} (vinyl hydrogen).[22] The NMR spectrum includes the following resonances: δ 16.05 (s, 1, OH), 6.98 (s, 1, $C{=}CH$), 3.80 (s, 3, OCH_3), 3.72 (s, 3, OCH_3), 1.95 (s, 6, CH_3) plus five singlets of slight intensity between δ 2.40 and δ 2.00 ppm. This compound exhibits a tendency for keto-enol tautomerism as evidenced by a weak resonance at δ 5.50 ppm (methine CH) with integrated intensity corresponding to less than one proton.

Since only one resonance is observed for the olefinic proton at δ 6.98 ppm, the stereochemistry about the olefin appears to be exclusively trans based upon the argument developed previously establishing stereochemistry of the H_2S displaced ligand. It appears then that the catalytic reaction is stereoselective in the anticipated direction. The plethora of methyl signals is evidence that, along with some keto-enol tautomerism, both the cisoid and transoid configurations of the diene are extant in $CDCl_3$ solution as shown in eq 10.

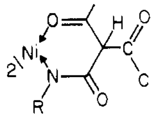


(10)

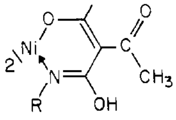
Catalysis of electrophilic additions to 2,4-pentanediene is not limited to $[Ni(acac)_2]_3$. The reaction between phenyl isocyanate and 2,4-pentanedione in benzene is catalyzed by several other anhydrous metal 2,4-pentanedionates. The relative catalytic efficiency of the catalysts was assessed by reacting 0.46 mol of catalyst with 5 mL of PhNCO and 4.72 mL of Hacac in 15 mL of dry benzene for 20 h at ambient temperature and determining the yield of product. In this way the catalysts were ranked as follows in decreasing order of efficiency: $Ni(acac)_2 > Mg(acac)_2 > Cd(acac)_2 > Zn(acac)_2 > Co(acac)_2 > Li(acac) > Mn(acac)_3 > Cu(acac)_2 > Fe(acac)_3$. $Al(acac)_3$, $Pd(acac)_2$, and $Cr(acac)_3$ did not catalyze the reaction. Work is in progress to explain this ordering and to determine specific rate constants.

An observation which appears to connect all of the reactions herein described is the following: catalysis of electrophilic addition to 2,4-pentanedione by $[Ni(acac)_2]_3$ is limited to those compounds which will form stoichiometric adducts with $[Ni(acac)_2]_3$. Stated in alternate fashion, if an electrophile "E" does not react with $[Ni(acac)_2]_3$ to form $[Ni(acac)_2{\cdot}2E]_3$, then $[Ni(acac)_2]_3$ will not catalyze the parallel (Hacac + E) reaction. This fact suggests that the $[Ni(acac)_2{\cdot}2E]_3$ complex adducts must be formed as necessary intermediates in the catalytic reactions. Consequently, catalysis occurs by reaction of a coordinated ligand. This is consistent with the observations that the rate is dependent upon the catalyst concentration, that the reaction does not occur or is much slower in the absence of the catalyst, and that the stoichiometric adducts $[Ni(acac)_2{\cdot}2E]_3$ are efficient catalysts themselves.

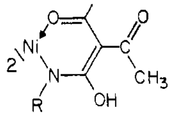
The compounds VI can themselves be reacted with nickel salts to furnish $[Ni(acac)_2{\cdot}2E]_3$ which are identical with those prepared by stoichiometric addition of the electrophile to $[Ni(acac)_2]_3$. No linkage isomerization products of the types XII–XIV are observed. Further no linkage isomerization was observed in the Ni[baen]·2PhNCO system.[4] Therefore, the linkage isomerization type catalysis mechanism for $M^{II}(acac)_2$-catalyzed electrophilic addition to 2,4-pentanedione suggested by Uehara[19] et al. is probably not occurring. Instead, reaction 11 more likely accounts for the catalysis mechanism.



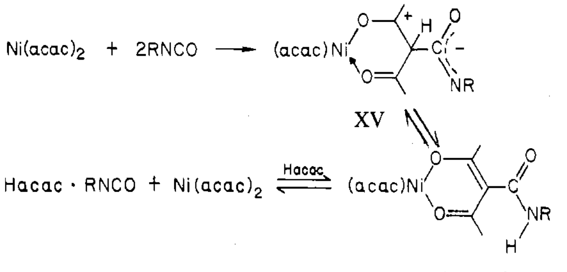
XII



XIII



XIV



(11)

A dipolar intermediate similar to XV has been demonstrated in the addition of tosyl isocyanate to active methylene compounds by others.[23] The postulated final step of the reaction sequence, ligand exchange, is facile as the reaction of equimolar amounts of 2,4-pentanedione and III in dichloromethane rapidly yields VI and $Ni(acac)_2$ at room temperature. Similar mechanisms presumably obtain for the catalyzed additions of diethyl azodicarboxylate and dimethyl acetylenedicarboxylate to 2,4-pentanedione. Work is in progress to definitively establish the catalysis mechanism.

Concurrent investigations of other systems involving catalysis of electrophilic addition to β-diketone-type ligands indicates that these types of catalytic reactions are not confined to 2,4-pentanedione catalyzed by metal 2,4-pentanedionates but extend to keto amides and Schiff bases as well.[24] Potentially new and useful synthetic routes to a wide variety of heretofore unknown and unusual compounds will become available as the scope of this new class of catalytic electrophilic additions is expanded.

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Registry No. III (R = CH_3), 64103-44-2; III (R = C_2H_5), 64103-47-5; III (R = i-C_3H_7), 64103-48-6; III (R = C_6H_5), 64103-49-7; III (R = p-$CH_3C_6H_4$), 64103-50-0; III (R = p-$CH_3OC_6H_4$), 64103-51-1; III (R = p-ClC_6H_4), 64114-06-3; III (R = p-$CH_3C_6H_4SO_2$), 64103-43-1; IV, 64103-46-4; V, 64103-45-3; VI (R = CH_3), 64091-93-6; VI (R = C_2H_5), 64091-92-5; VI (R = i-C_3H_7), 64092-05-3; VI (R = C_6H_5), 64092-04-2; VI (R = p-$CH_3C_6H_4$), 64092-03-1; VI (R = p-$CH_3OC_6H_4$), 64092-02-0; VI (R = p-ClC_6H_4), 64092-01-9; VI (R = p-$CH_3C_6H_4SO_2$), 64092-00-8; VII, 64091-99-2; VIII, 64113-62-8; $Ni(acac)_2$, 3264-82-2; $Mg(acac)_2$, 14024-56-7; $Cd(acac)_2$, 14689-45-3; $Zn(acac)_2$, 14024-63-6; $Co(acac)_2$, 14024-48-7; Li(acac), 19185-99-0; $Mn(acac)_3$, 14284-89-0; $Cu(acac)_2$, 13395-16-9; $Fe(acac)_3$, 14024-18-1; CH_3NCO, 624-83-9; C_2H_5NCO, 109-90-0; i-C_3H_7NCO, 1795-48-8; C_6H_5NCO, 103-71-9; p-$CH_3C_6H_4NCO$, 622-58-2; p-$CH_3OC_6H_4NCO$, 5416-93-3; p-ClC_6H_4NCO, 104-12-1; p-$CH_3C_6H_4SO_2NCO$, 4083-64-1; $C_2H_5CO_2N{=}NCO_2C_2H_5$, 1972-28-7; $CH_3CO_2C{\equiv}CCO_2CH_3$, 762-42-5; benzylamine, 100-46-9.

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