

The Reactivity of Cyanogen towards Compounds Containing Active Hydrogens at Carbon Atoms. Part 4. The Cyanation of $[\text{Mn}(\text{acac})_2]$, $[\text{Mn}(\text{acac})_3]$ and $[\text{Zn}(\text{acac})_2]$

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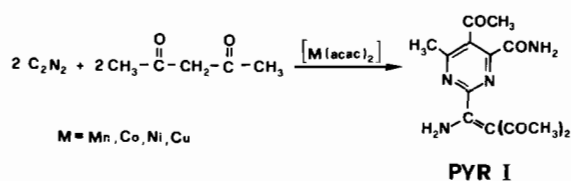
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The title compounds react with C_2N_2 in $\text{C}_2\text{H}_4\text{Cl}_2$ or CH_2Cl_2 under ambient conditions undergoing cyanation of the organometallic ring. The products are unstable and evolve with different rates to cyanide-containing coordination polymers.

$[\text{Zn}(\text{acac})_2]$ is a very effective catalyst for the addition of C_2N_2 to Hacac to give 3-(cyanoimino-methyl)pentane-2,4-dione under ambient conditions.

Introduction

We have recently found that the addition of C_2N_2 to pentane-2,4-dione (Hacac) and other β -dicarbonyl compounds in CH_2Cl_2 or $\text{C}_2\text{H}_4\text{Cl}_2$ at room temperature, catalyzed by $[\text{Ni}(\text{acac})_2]$ or $[\text{Cu}(\text{acac})_2]$, represents a new one-pot synthesis of highly functionalized pyrimidines [1, 2] (Scheme 1):

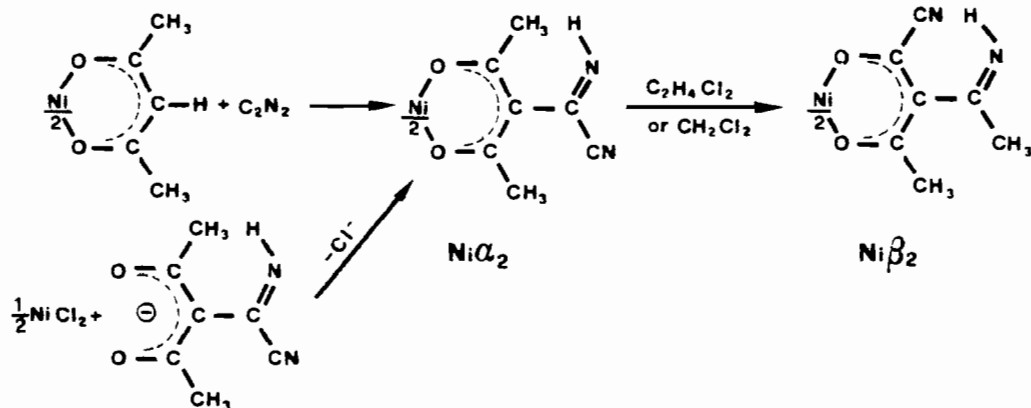


Scheme 1

When the β -dicarbonylic compound is acetylacetone, the corresponding pyrimidinic compound, hereafter referred to as PYR I, can be also obtained in the presence of catalytic amounts of $[\text{Mn}(\text{acac})_3]$ and $[\text{Mn}(\text{acac})_2]$ [1]. With these two catalysts the overall catalytic efficiency is, however, much more limited when compared with that exhibited by $[\text{Ni}(\text{acac})_2]$ and $[\text{Cu}(\text{acac})_2]$, even though the selectivity remains 100%.

It has been also found that $[\text{Ni}(\text{acac})_2]$ reacts with C_2N_2 in CH_2Cl_2 at ambient conditions to give bis[1-cyano-2-(1-iminoethyl)butane-1,3-dionato]nickel(II). The synthesis of this species is thought to proceed according to scheme 2 [3a], i.e. through the preliminary formation of bis[3-(cyanoimino-methyl)pentane-2,4-dionato]nickel(II), as the consequence of the insertion of C_2N_2 into the C-H methino bond.

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Scheme 2

The question whether the *isolated* species labelled as $[\text{Ni}\alpha_2]$ [3a] is a real isomer or a dimorphic form of $[\text{Ni}\beta_2]$ is still not satisfactorily solved and further investigation is in progress.

In contrast with this behaviour $[\text{Mn}(\text{acac})_2]$, $[\text{Mn}(\text{acac})_3]$, $[\text{Co}(\text{acac})_2]$ and $[\text{Fe}(\text{acac})_2]$ did not give any stable $\text{M}\alpha_n$ or $\text{M}\beta_n$ species (Scheme 2) [1], but metal cyanides and unidentified organic products. As these cyanospecies should be the result of an unusual [4] metal-promoted heteropolar C–C bond fission of the cyanogen moiety, we have further investigated this reaction including Zn^{II} as a metal centre, which does not give rise to unpaired electrons.

Results

The Reaction of $[\text{Mn}(\text{acac})_3]$, $[\text{Mn}(\text{acac})_2]$ and $[\text{Zn}(\text{acac})_2]$ with C_2N_2 in 'Preparative Conditions'

The employed complexes (4 mmol) suspended (Mn^{II}) or dissolved (Mn^{III} , Zn^{II}) in anhydrous CH_2Cl_2 (typically 30 ml) react with C_2N_2 (~18 mmol, ~0.6 M) at room temperature to give intensively coloured precipitates. All products appear as brown (Mn^{III} and Mn^{II}) or red-orange (Zn^{II}) amorphous powders. These materials contain large amounts of chlorine (due to heavy incorporation of solvent as shown by the thermal behaviour) which can be reduced but not eliminated upon controlled heating, *under vacuo*.

Nevertheless, the elemental analyses obtained in the cases of Mn^{II} and Zn^{II} are not too far from a composition $\text{M}_2\text{C}_{22}\text{H}_{21}\text{N}_7\text{O}_6$, which corresponds to a coordination polymer in which the repeating unity is $[\text{M}_2^{\text{I}}\alpha_3(\mu\text{-CN})]$.

The IR data support this interpretation as they exhibit $\nu\text{C}\equiv\text{N}$ bands attributable to bridging cyanide ligands [5] around 2200 cm^{-1} , shoulders at 2220 (Zn^{II}) and 2230 (Mn^{II}) cm^{-1} , reasonably due to $\text{C}\equiv\text{N}$ groups bonded to an sp^2 hybridized carbon bound to a β -diketonato ring [1, 3], broad absorptions in the range $1800\text{--}1300$ and $1300\text{--}650\text{ cm}^{-1}$ due to β -diketonato skeletons, and broad absorptions in the range $3100\text{--}3700\text{ cm}^{-1}$, probably due to N–H stretching bands referring to heavily hydrogen-bonded $\text{N}\text{--}\text{H}\cdots\text{O}=\text{C}$ moieties.

Particularly interesting is the presence of CN^- ligands, which indicates that a heterolytic fission of the C–C bond of C_2N_2 has occurred, which is a completely new reaction occurring at a metal centre [4].

The Reaction of $[\text{Mn}(\text{acac})_3]$, $[\text{Mn}(\text{acac})_2]$ and $[\text{Zn}(\text{acac})_2]$ with C_2N_2 in 'Spectrophotometric Conditions'

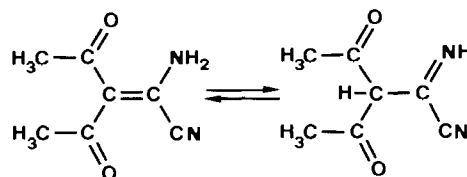
The $[\text{M}(\text{acac})_n]$ complexes (0.36 mmol) suspended (Mn^{II}) or dissolved (Mn^{III} , Zn^{II}) in anhydrous $\text{C}_2\text{H}_4\text{Cl}_2$ (typically 30 ml) react with C_2N_2 (12.6 mmol) at room temperature to give a visual pattern

quite similar to that observed in the 'preparative conditions'.

Since these conditions are comparable with those employed in the catalytic experiments mentioned in the introduction [1], they can provide useful information on the behaviour of the title compounds towards C_2N_2 in conditions which are similar to those strictly referring to the catalytic runs carried out so far for $\text{Mn}^{\text{III,II}}$ [1] and in this work for Zn^{II} .

The spectral changes observed in solutions for the employed metal complexes are reported in Fig. 1.

The family of strong bands appearing between 1500 and 1350 cm^{-1} for Mn^{II} and Zn^{II} can be safely attributed to the compound:



i.e. 3-(cyanoiminomethyl)pentane-2,4-dione [1, 6], hereafter referred to as $\text{H}\alpha^*$, on the basis of a very accurate comparison of the observed bands with those seen at the end of the reactions (the IR spectrum of $\text{H}\alpha$ obeys Lambert–Beer's law in the range $0.5 \times 10^{-2}\text{--}2 \times 10^{-2}\text{ M}$). Also the observed $\nu_{\text{N-H}}$ band at 3440 cm^{-1} fits quite well with the spectrum of free $\text{H}\alpha$ in $\text{C}_2\text{H}_4\text{Cl}_2$. This last band appears slightly asymmetric in the case of Mn^{II} , owing to a shoulder around 3460 cm^{-1} , which suggests the presence of another N–H containing species in solution. A compound absorbing at 3460 cm^{-1} appears among the products of the reaction of $[\text{Mn}(\text{acac})_3]$ with cyanogen (see Fig. 1), in which case no $\text{H}\alpha$ is formed. A rough estimate of the concentration of the released $\text{H}\alpha$ gives $\sim 0.8 \times 10^{-2}\text{ M}$ (Mn^{II}) and $\sim 1.4 \times 10^{-2}\text{ M}$ (Zn^{II}). While $\text{H}\alpha$ clearly appears as a species, rapidly accumulating in solution upon cyanation of the Mn^{II} and Zn^{II} complexes (together with the concomitant precipitation of the CN^- -containing metal products), other species responsible for the weak bands at 3370 (Mn^{II}), 3350 (Zn^{II}), 3370 (Mn^{III}) accumulate for some time and then lose intensity within 24 h (Mn^{II} , Mn^{III}) or 30 min (Zn^{II}). The same trend is observed for the medium–strong bands at 1725 (Mn^{III}) and 1730 (Mn^{II}), whereas in the case of $[\text{Zn}(\text{acac})_2]$ only an ill-defined weak absorption hampered on the first band ($\sim 1750\text{ cm}^{-1}$) of the family of peaks due to free $\text{H}\alpha$ (Fig. 1) can be observed.

The metal-containing precipitates have the same color as those obtained in 'preparative' conditions and exhibit similar IR spectra. The major difference

*This compound exists in solution predominantly as a vinylogous amide [3a].

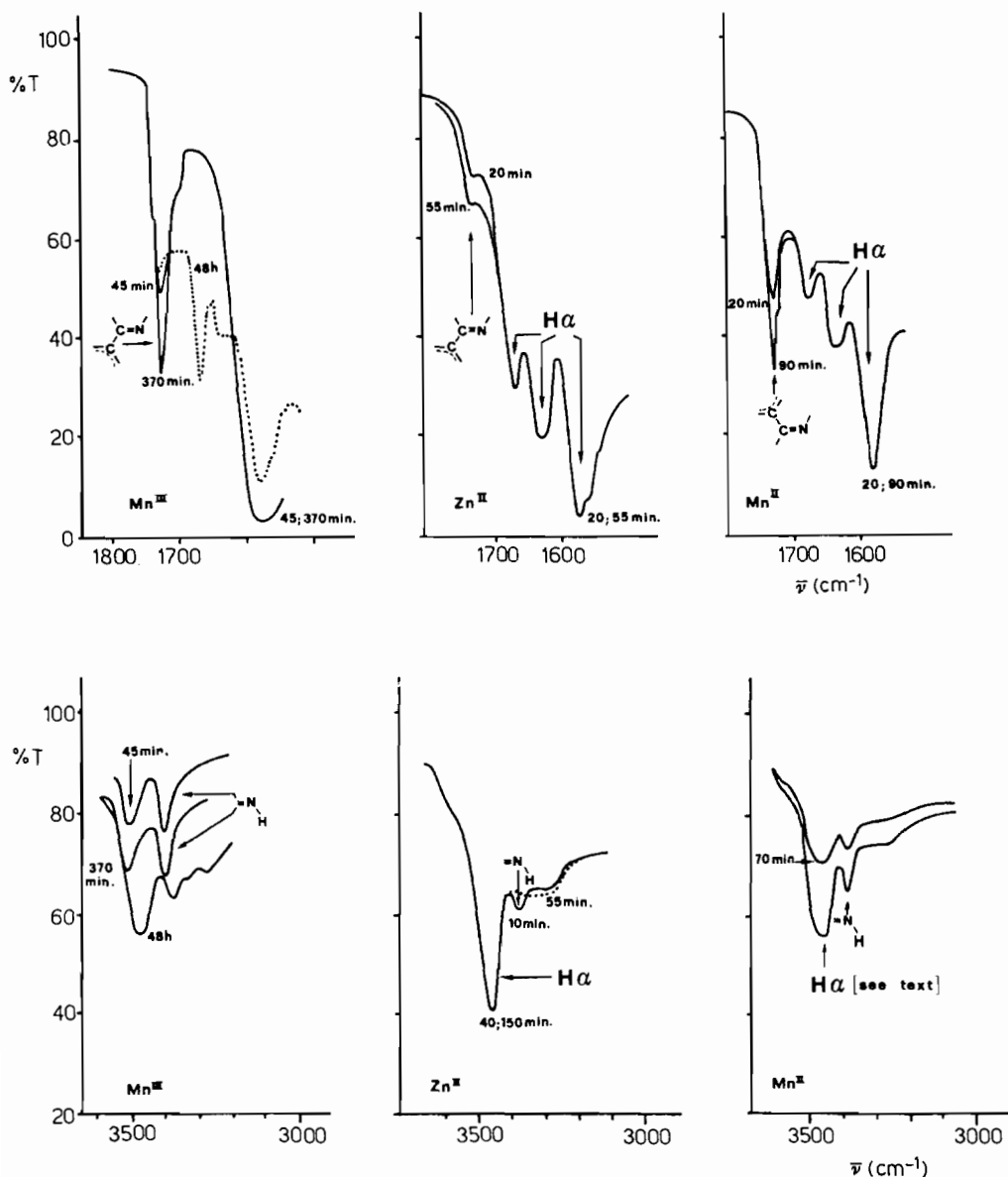


Fig. 1. Spectral IR changes observed in solution of $\text{C}_2\text{H}_4\text{Cl}_2$ during the reaction of $[M(\text{acac})_n]$ complexes with C_2N_2 .

between the IR spectra of the solid products under preparative and spectrophotometric conditions from $[\text{Zn}(\text{acac})_2]$ is that the 2220 band, which looks like a very merging doublet ('spectrophotometric' conditions), becomes a band centered at 2200 with a shoulder at 2220.

All these data indicate that cyanogen converts β -diketonate metal complexes *not* to stable species like $[\text{Ni}\alpha_2]$ or $[\text{Ni}\beta_2]$ (Scheme 1), but to compounds which could be formulated as oligomers (or polymers) of the moiety $[\text{M}_2^{\text{II}}\alpha_3(\mu\text{-CN})]$ (see above), the formation of which is accompanied by accumulation of free $\text{H}\alpha$, in the case of Mn^{II} and Zn^{II} . In the case of Mn^{III} the evolution of the $[\text{metal-}\alpha]$ species is obscure and no $\text{H}\alpha$ is formed.

In spite of the apparent inability of the title complexes to give stable $[\text{M}\alpha_2]$ or $[\text{M}\beta_2]$ (see Scheme 2) species, we could obtain clear spectrophotometric evidence of their presence, as reactive intermediates, in the solutions or suspensions, obtained upon reaction of $[\text{Mn}(\text{acac})_3]$, $[\text{Mn}(\text{acac})_2]$ and $[\text{Zn}(\text{acac})_2]$ in the 'early' stages of the reactions.

We have collected in Table I some data referring to IR spectra of known compounds containing the moiety:

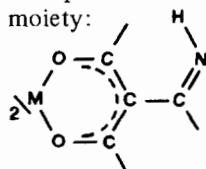
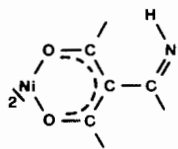
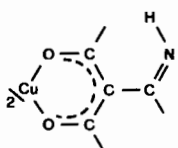
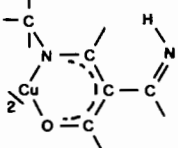
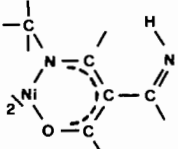


TABLE I. Spectrophotometric Features of Ring-bonded >C=N-H Group.

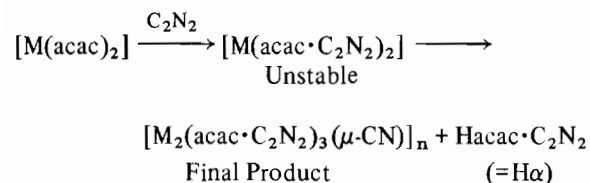
System	$\nu_{\text{C=N}}(\text{cm}^{-1})^{\text{a}}$	$\nu_{\text{N-H}}(\text{cm}^{-1})^{\text{a}}$	Ref.
	1670 ^b ~1640 ^c	3340 ^b 3200–3245 ^c	7 3
	1670 1630 ^c	3335 3260 ^c	7 1
	1650	3320	7
	1715	3350	7
[Mn(acac) ₃]/C ₂ N ₂	1725	3370	this work
[Mn(acac) ₂]/C ₂ N ₂	1730	3370	this work
[Zn(acac) ₂]/C ₂ N ₂	undetected	3350	this work

^aIn C₂H₄Cl₂ or stated. ^bIn CH₂Cl₂. ^cIn nujol mull.

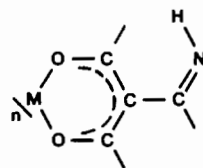
and the pertinent $\bar{\nu}$'s are compared with those of the bands observed in the 3400–1600 cm⁻¹ region during the cyanation of the title complexes in 'spectrophotometric' conditions.

From the data of Table I we conclude that unstable iminocarbonylenolate complexes are present as reactive intermediates in the solutions obtained from the title compounds and C₂N₂, and it seems quite likely that these species are the precursors of both H α and the [M₂ α ₃(μ -CN)] species (in the case of Mn^{II} and Zn^{II}). In the case of Mn^{III}, H α is not formed and another species strongly absorbing at 3490 cm⁻¹ appears to accumulate in parallel with the pertinent iminocarbonylenolate complex.

We think that an approximate description of the reaction sequence between C₂N₂ and [M(acac)₂] (M = Mn^{II}, Zn^{II}) can be the following:



The bulk of the data reported here offers a reasonable explanation of the catalytic data concerning Mn^{II} (and Mn^{III}) as catalysts in the synthesis of PYR I (see introduction), *i.e.* they offer precise spectrophotometric evidence of the formation of the catalytically crucial [3] moiety:



and they also outline their intrinsic thermal instability, which is the key reason for their limited catalytic efficiency [3a].

The Catalytic Cyanation of Hacac by C₂N₂ in the Presence of [Zn(acac)₂]

In spite of the limited thermal stability of the primary reaction product, [Zn(acac)₂] exhibits an outstanding catalytic power in the cyanation of Hacac but, in contrast with the behaviour of other

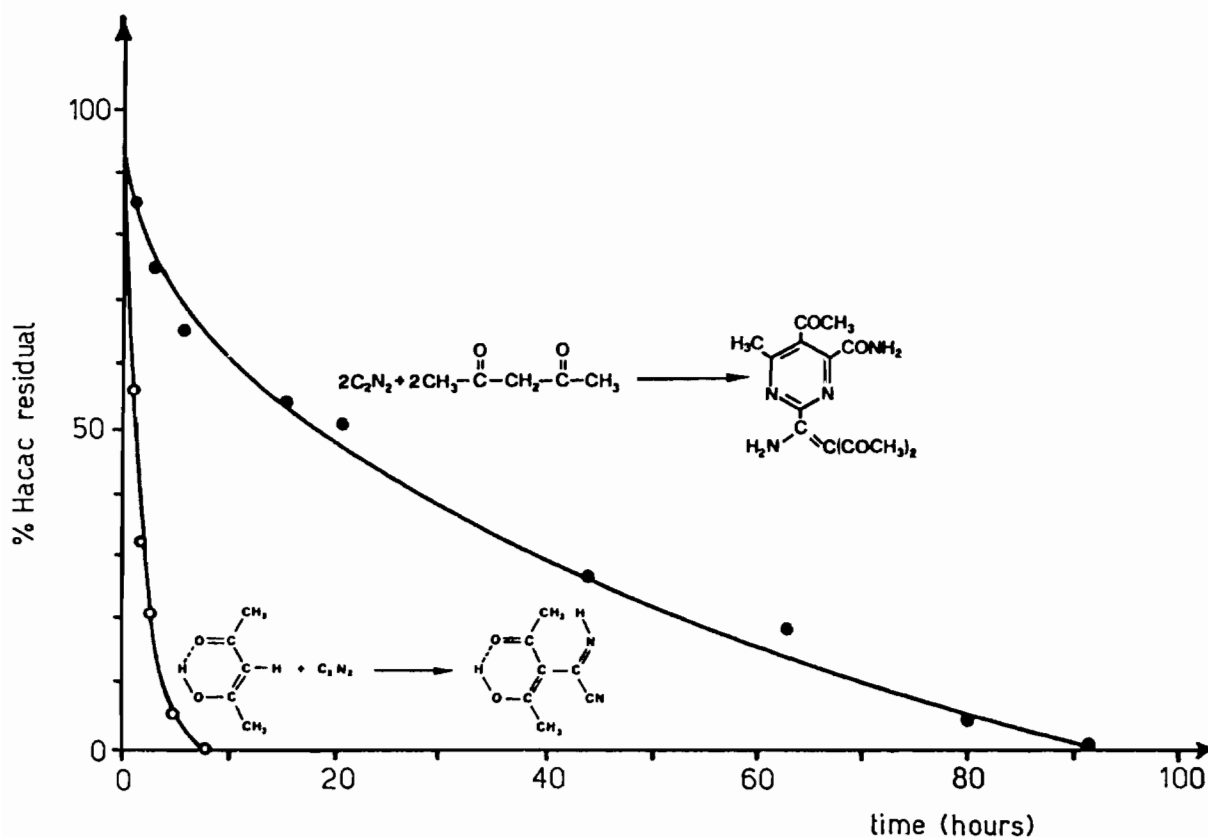


Fig. 2. The cyanation of Hacac catalyzed by $[\text{Zn}(\text{acac})_2]$ and $[\text{Cu}(\text{acac})_2]$. —●—●—●—, $[\text{Cu}(\text{acac})_2]$; —○—○—○—, $[\text{Zn}(\text{acac})_2]$. In both cases $[\text{cat.}] = 1.2 \times 10^{-3} \text{ M}$, $[\text{Hacac}] = 0.35 \text{ M}$, $[\text{C}_2\text{N}_2] = 0.42 \text{ M}$.

good catalysts such as $[\text{Ni}(\text{acac})_2]$ and $[\text{Cu}(\text{acac})_2]$, the metal-catalyzed synthesis does not readily give PYR I (at least after a reaction time of 24 h) but H α in 100% yield.

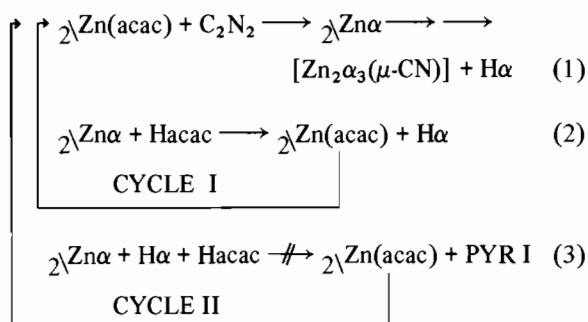
Figure 2 depicts a typical catalytic test carried out with $[\text{Zn}(\text{acac})_2]$ and, on the same scale, also a test carried out with $[\text{Cu}(\text{acac})_2]$ is drawn for comparison. Both putative catalysts appear to be efficient but, if compared in terms of TN's/min for Hacac consumption, $[\text{Zn}(\text{acac})_2]$ is about 10 times more effective than $[\text{Cu}(\text{acac})_2]$, the corresponding selectivity for their respective syntheses being 100% in both cases.

The good quality of these catalytic systems is demonstrated by the fact that the final solutions (*i.e.* those obtained at t_∞ for both tests) maintain high catalytic efficiency, if recycled with fresh C_2N_2 and Hacac: 100% to H α (Zn^{II}) and 60% to PYR I (Cu^{II}).

No further recycling tests have been made in this work, but the obtained data seem very promising in this respect.

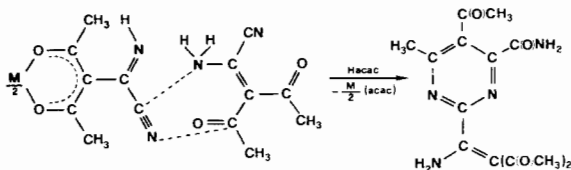
In connection with a complete mechanistic work carried out by us in these laboratories [8] on the $[\text{Cu}(\text{acac})_2]$ -catalyzed synthesis of PYR I, the 100% selectivity for the synthesis of H α catalyzed by

$[\text{Zn}(\text{acac})_2]$ can be explained on the basis of the following cycle:



We have seen in the present study that the cyanation of $[\text{Zn}(\text{acac})_2]$ proceeds largely to $[\text{Zn}_2\alpha_3(\mu\text{-CN})]$ and H α , giving barely detectable amounts of cyanoiminomethylacetone metal species (*e.g.* $[\text{Zn}\alpha]$). However, the occurrence of CYCLE I is conditioned by the survival in solution of a very limited concentration of $[\text{Zn}\alpha_2]$, which, upon protonation with substitution of the coordinated α^- ligand, can renew the putative catalyst $[\text{Zn}(\text{acac})_2]$ thus making it possible for the catalysis to occur. The occurrence of CYCLE II, on the contrary, is expected

to require a higher concentration of the species $[_2\text{Zn}\alpha]$ in that the stereochemistry, the stoichiometry and the kinetics of CYCLE II (eqn. 3) are far more demanding (Scheme 3).



Scheme 3. Proposed scheme for the interaction of free $\text{H}\alpha$ with metal-coordinated α^- .

The result of the reasoning developed so far is that the 100% selectivity of $[\text{Zn}(\text{acac})_2]$ as catalyst is the result of two, at first sight contradictory, features of the $\text{Zn}/\text{C}_2\text{N}_2/\text{Hacac}$ system, *i*) the thermal instability of $[_2\text{Zn}\alpha]$ (eqn. 1) and *ii*) the exceedingly high reactivity of $[_2\text{Zn}\alpha]$ towards Hacac to give $[_2\text{Zn}(\text{acac})]$ (eqn. 2).

Experimental

The $[\text{Mn}(\text{acac})_3]$ (Merck) used was recrystallized from toluene/*n*-pentane. $[\text{Zn}(\text{acac})_2]$ from the same source was recrystallized from anhydrous $\text{C}_2\text{H}_4\text{Cl}_2$, by leaving the solution for 24 h over 4 Å molecular sieves, solvent removal, and addition of anhydrous diethyl ether. Filtration under air exclusion gave a white microcrystalline compound, which gave satisfactory elemental analysis. $[\text{Mn}(\text{acac})_2]$ (Merck) was used as received.

$\text{C}_2\text{H}_4\text{Cl}_2$ and CH_2Cl_2 were dried by classical procedures. C_2N_2 (Matheson) was declared to be 'technical' and was directly taken from the cylinder. Conveniently concentrated solutions of C_2N_2 were prepared by aspirating directly suitable amounts of gas from the cylinder into the desired volume of solvent. The C_2N_2 concentration was determined as previously described [9]. All experiments were run in closed cylindrical glass vessels equipped with special gas-tight glass stopcocks. The reactions were monitored by removing 0.5 ml aliquot amounts of the solution (or suspension) with a syringe and analyzing by IR (1 mm Path length cell) or GLC (the solid, if any, was removed by a Millipore equipment to be attached to the syringe). GLC measurements were made on a Carbowax 20M on Chromosorb, 10%; column, 2 m, 1/8"; the internal standard was *n*-pentadecane.

Instruments

Routine spectra were recorded on a Perkin-Elmer 257. Elemental analyses were carried out by Mr. Barth and Miss Graf in the microanalysis laboratory of the Anorganisch-Chemisches Institut, Technische Universität, München. Thermoanalyses were per-

formed on a Perkin-Elmer TGS-2 apparatus. GLC measurements were carried out on a Perkin-Elmer 900.

The Cyanation in 'Preparative Conditions'

$[\text{Mn}(\text{acac})_3]$

1.44 g of the complex were dissolved in 30 ml of anhydrous CH_2Cl_2 containing C_2N_2 , $\sim 0.6 M$ ($\text{C}_2\text{N}_2/\text{Mn}^{\text{III}}$ molar ratio ~ 4.5). After 24 hours the dark-brown suspension was filtered off under air exclusion, washed with CH_2Cl_2 (50 + 10 ml), and dried for 15 min *in vacuo*. The resulting dark-brown material (1.70 g) appears as an homogeneous amorphous powder under the microscope (40 magnifications), slowly losing weight at ambient conditions. A thermal analysis under Ar shows a 'fast' weight-loss of 15% in 8 min in the range 30–110 °C followed by a slow decomposition up to 1000 °C. The crude compound, analyzed after *ca.* 24 hours storage in a desiccator, gave C = 39.71; H = 3.89; N = 12.59; Cl = 21.07. After 24 h pumping at 0.1 tor at *ca.* 20 °C, a 100 mg sample gave C = 44.33; H = 3.96; N = 16.50; Cl = 2.21. The product is insoluble in the common organic media; it is slightly soluble in CH_3OH and H_2O , with decomposition. The IR spectrum in nujol mull (which does not change remarkably upon CH_2Cl_2 removal) exhibits bands at 3300 (s, broad), 2190 (m), 2230 (w, shoulder), four merged bands of medium intensity centered at 1590 (in the range 1800–1500), and at 1020 (w) cm^{-1} .

$[\text{Mn}(\text{acac})_2]$

The procedure is identical to that described above, but the suspension of $[\text{Mn}(\text{acac})_2]$ was kept under vigorous stirring. 1.02 g of $[\text{Mn}(\text{acac})_2]$ gave 1.74 g of brown product, found amorphous and homogeneous under 40 magnifications. In the range 30–120 °C it loses 16% of weight in 9 min. The thermogravimetric behaviour is then consistent with a continuous decomposition process up to 700 °C. The crude compounds, stored as described for $[\text{Mn}(\text{acac})_3]$, gave C = 39.94, H = 3.72; N = 13.22; Cl = 21.01 (*i.e.* a composition very similar to that observed for the product from Mn^{III}) and after 24 h pumping at 0.1 tor at 60 °C it gave C = 41.02; H = 3.92; N = 16.64; Cl = 5.38 ($\text{C}_{20,1}$, $\text{H}_{23,2}$, $\text{N}_{7,0}$). Solubility and IR spectra are very similar to those of the compound obtained from Mn^{III} .

$\text{Zn}(\text{acac})_2]$

The concentrations of the reagents were analogous to those employed for Mn^{II} . The initially obtained solution was stirred only for thirty seconds and then left undisturbed for 24 hours. The precipitation of the red orange product (1.50 g from 0.90 g initial $[\text{Zn}(\text{acac})_2]$) occurred within a few minutes. The crude compound loses about 7% of its weight between 20 and 100 °C. Above this temperature a

thermal decomposition occurs. After treatment *in vacuo* a 0.1 tor at 20 °C for 64 h and at 60 °C for two hours, the product exhibited the analysis: C = 42.69; H = 3.76; N = 15.33; Cl = 3.36 (C_{22,7}, H_{24,1}, N_{7,0}). The IR spectrum in nujol (it does not change remarkably after vacuum treatment) exhibited bands at 3300 (s, broad), 2200 (m), 2220 (m, shoulder), in the range 1800–1500 (four merged bands of medium intensity centered at 1620), and at 1150 (w) cm⁻¹. The solubility behaviour is similar to that of the other two materials, but the compound is slightly more soluble in ethanol than in methanol, in which solvents it partially decomposes.

The Cyanation in Spectrophotometric Conditions

Typically, 0.40 mmol of the reacting complexes were dissolved or suspended (Mn^{II}) in 30 ml of anhydrous C₂H₄Cl₂, 0.4 M in C₂N₂, and the solution was kept under vigorous stirring for 24 hours.

The progress of the cyanation reaction was concomitant with the precipitation of brown powders (Mn^{III}, Mn^{II}) and of a red-orange one (Zn^{II}). The IR spectra of these compounds are very similar (and similarly rather featureless) to those described in the previous section. Remarkable again is the presence of ν_{CN} bands indicating the presence of bridging metal-coordinated cyanide (2180, Mn^{III}; 2190, Mn^{II}; 2220, Zn^{II}).

Catalytic Experiments with [Zn(acac)₂]

[Zn(acac)₂] (0.024 mmol) was added to a C₂H₄Cl₂ solution (20 ml) of C₂N₂ 0.42 M and Hacac 0.35 M. The solution was left under vigorous stirring and the precipitation of white crystals of H α could be observed after a few minutes. The disappearance of Hacac was monitored by GLC upon removing aliquot amounts of the suspension (~0.5 ml) and filtration by a Millipore equipment. The yield after 8 hours was 0.874 g (81%) of very pure 3-(cyanoiminomethyl)pentane-2,4-dione (IR control). The IR of the solution was identical to that of a saturated solution of the product (solubility is *ca.* 2×10^{-2} M) and the total observed yield therefore ~88%*. No trace of PYR I could be observed in solution. 0.5 ml of Hacac and 20 ml of 0.4 M C₂N₂ solution were added to the solution obtained after filtration of the product and the system was left under stirring for three days. Further 0.760 g of H α could be obtained upon spontaneous precipitation.

*An estimate of overall 100% yield is based on the 100% consumption of Hacac and 100% selectivity (absence of by-products).

Catalytic Experiment with [Cu(acac)₂]

Under identical experimental conditions a yellow product begins, after 4 hours, to precipitate. Filtration after 72 hours gave 0.785 g of pure PYR I (IR control). The observed yield was 74% and the selectivity was 100% (the IR spectrum of the final solution is identical to that of a saturated solution of PYR I). Addition of fresh 0.5 ml of Hacac and 8 mmol of C₂N₂ to the filtered solution gave a further 450 mg of PYR I after 3 days (60% yield).

Conclusions

Although the reactions of [Mn(acac)₃], [Mn(acac)₂] and [Zn(acac)₂] with C₂N₂ in chlorinated solvents are not fully understood, we think that the quite different observed catalytic behaviour of [Ni(acac)₂], [Cu(acac)₂], [Mn(acac)₂], [Mn(acac)₂], [Co(acac)₂] on the one hand, and of [Zn(acac)₂] on the other is a remarkable and promising finding in the general aim of metal-catalyzed functionalization, by C₂N₂, of various organic substrates. The possibility of selectively synthesizing mono cyanogen-addition products (*i.e.* H α like) and bis-ones (*i.e.* pyrimidines) seems clearly at hand. It also seems conceivable to obtain a catalytic system suitable to prepare pyrimidinic compounds derived from two C₂N₂ molecules and two different β -dicarbonyl compounds.

Acknowledgement

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