$[Zn(acac)_2]$ Catalyzed Addition of Cyanogen to Dipivaloylmethane: Facile Synthesis of 2,2,6,6-Tetramethyl-4(1-amino-1-cyano)methyliden-3,5-heptanedione

B. CORAIN, M. BASATO, E. MORI

Centro di Studio sulla Stabilità e Reattività dei Composti di Coordinazione, C.N.R., Istituto di Chimica Analitica, 35100 Padua, Italy

and G. VALLE

Centro di Studio dei Biopolimeri, C.N.R., Istituto di Chimica Organica, 35100 Padua, Italy

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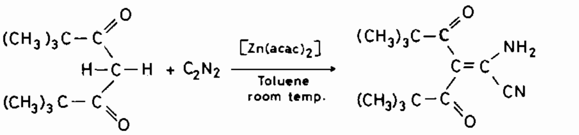
In the course of our studies on the metal-promoted activation of cyanogen [1–4] we have found that C_2N_2 can be very effectively added to dipivaloylmethane (Hdpm; *1*) in toluene at ambient conditions in the presence of catalytic amounts of $[Zn(acac)_2]$ ($[Zn^{2+}] = 1 \times 10^{-3}$ *M*; [Hdpm] = 0.2 *M*; $[C_2N_2]$ = 0.4 *M*) to give the title compound (*2*) (in yields of *ca.* 50%; selectivity 70% after 150 h; scheme 1) as white, extremely pure crystals upon simple slow evaporation of the solvent at room temperature.



Scheme 1

2 is soluble in n-hexane, diethyl ether and the common organic solvents and it exists predominantly as the vinylogous amide both in d_6-DMSO and $CDCl_3$. The two $C(O)C(CH_3)_3$ groups are free to rotate around the C–C bonds in DMSO at room temperature, while a strong C=O···H–N bond prevents completely the rotation of one of these groups in $CDCl_3$ (Table I). *2* was characterized by IR and mass spectra as well as by thermal analysis. *2* melts at 89 °C and appears to be thermally stable in the range 50–200 °C. The conformation is depicted in Fig. 1.

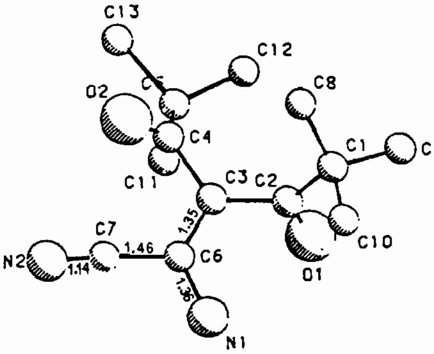
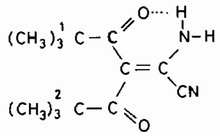


Fig. 1. Molecular structure of *2* (some bond distances in Å are given in the figure).

Crystal data. From single crystal diffractometry, MoKα radiation, the crystals are monoclinic, space group $P2_1/n$; $a = 16.856(6)$, $b = 11.764(5)$, $c = 6.898(4)$ Å, $\beta = 90.0(8)^\circ$, $D_c = 1.14$, $D_o = 1.13$ g cm^{-3}; $Z = 4$. Intensity data were collected on a Philips diffractometer PW1100 to a $\theta = 25^\circ$. 1344 reflections with $I > 3\sigma(I)$, among 2416 unique ones, were considered. Structure factors were phased by Multan program and non-hydrogen atoms were refined anisotropically by block-diagonal least squares ($w = 3.25/(\sigma^2(F) + 0.00056 F^2)$). Hydrogen atoms were obtained from a Fourier difference synthesis and isotropically refined. The final conventional R factor was 0.060. Apparently *2* exists as vinylogous amide in the solid state, but this circumstance should not of course prevent *2* from existing also as 1,3-ketoenolic species in convenient solvents, thus being able to give metal ketoenolate complexes under suitable conditions [5].

TABLE I. ^1H NMR Data for $[Hdpm{\cdot}C_2N_2]$ in Various Media.

Medium	Resonance (ppm)	Group	Structure in solution
d_6-DMSO	0.99	$^{1,2}C(O)C(CH_3)_3$	
	6.68	NH_2	
d_6-DMSO/$CDCl_3$ (1:1)	1.13	$^1C(O)C(CH_3)_3$	
	1.10	$^2C(O)C(CH_3)_3$	
	6.90	NH_2	
$CDCl_3$	1.19	$^1C(O)C(CH_3)_3$	
	1.13	$^2C(O)C(CH_3)_3$	
	5.33	NH_2	

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The bonding ability of *2* was tested towards nickel(II) according to reaction 1:

$$[\mathrm{Ni(acac)_2}] + 2\mathrm{Hdpm{\cdot}C_2N_2} \overset{K}{\rightleftharpoons} [\mathrm{Ni(dpm{\cdot}C_2N_2)_2}] + 2\mathrm{Hacac} \qquad (1)$$

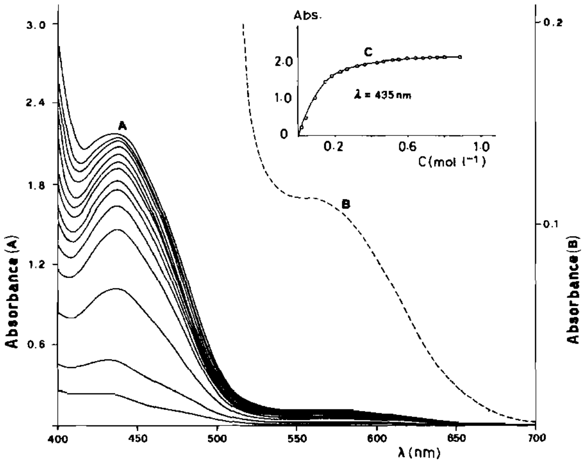

Fig. 2. Spectral and thermodynamic data for the reaction of $[\mathrm{Ni(acac)_2}]$ with $[\mathrm{Hdpm{\cdot}C_2N_2}]$; $[\mathrm{Ni^{2+}}] = 1 \times 10^{-2}$ *M*. A) Representative spectral changes for a $[\mathrm{Ni(acac)_2}]_2$ solution ($= 1 \times 10^{-2}$ *M*) containing increasing amounts of $[\mathrm{Hdpm{\cdot}C_2N_2}]$ ($C = 1.86 \times 10^{-2} \div 8.8 \times 10^{-2}$ *M*). B) Spectrum at $[\mathrm{Hdpm{\cdot}C_2N_2}] = 8.8 \times 10^{-1}$ *M*, expanded scale. C) Absorbance of the peak at $\lambda = 435$ nm *vs.* $[\mathrm{Hdpm{\cdot}C_2N_2}]$ concentration.

The relevant data are collected in Fig. 2. It is seen that addition of *2* produces the gradual development of a species absorbing at 555 nm, $\epsilon = 120$ (535 nm for $[\mathrm{Ni(dpm)_2}]$, $\epsilon = 80$) in $\mathrm{CH_2Cl_2}$. These figures are identical to those exhibited by an authentic sample of $[\mathrm{Ni(dpm{\cdot}C_2N_2)_2}]$ obtained upon cyanogen addition to $[\mathrm{Ni(dpm)_2}]$ in n-hexane, by cooling at −30 °C [6].

The liposolubility of the metal complexes derived from *2*, coupled with the circumstance that in these complexes each organometallic ring possesses a considerable coordination ability towards metal centers [7] and, conceivably, good binding possibility towards electrophilic centers present in organic substrates, make *2* a promising ligand-progener Hdpm-like but in principle more chemically versatile for nmr applications [8].

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