2. Adducts containing a terminal CFClI group undergo further stepwise telomerization with tetrafluoro- and trifluorochloroethylene.

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# SYNTHESIS, MOLECULAR AND CRYSTAL STRUCTURE OF 3-[(N-BENZOYL) DIAMINOMETHYLENE]PENTANE-2,4-DIONE, A NOVEL CHELATING LIGAND

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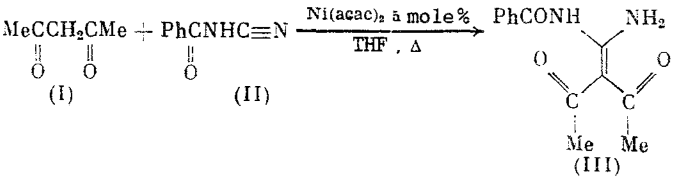
We have recently reported that β-dicarbonyl compounds with a reactive methylene group add to cyanamide and monosubstituted cyanamides in the presence of $Ni^{2+}$ complexes to give the ketene aminals [1, 2].

We have now examined the reaction of acetylacetone (I) with benzoylcyanamide (II), and investigated the structure of the product, 3-[(N-benzoyl) diaminomethylene]pentane-2,4-dione (III). In a preliminary communication [3], it was reported that heating (II) with an excess of (I) at 140°C in the presence of 10 mole% of $Ni(acac)_2$ gave (III), the structure of which was confirmed by spectral methods. Further work has shown that (III) is obtained readily in 90% yield by boiling equimolar amounts of (I) and (II) in THF in the presence of 5 mole % of $Ni(acac)_2$. No (III) was formed in the absence of this catalyst, or in the presence of acidic ($BF_3 \cdot Et_2O$) or basic (NaOEt) catalysts.



(1)

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N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1134-1138, May, 1989. Original article submitted March 3, 1988.

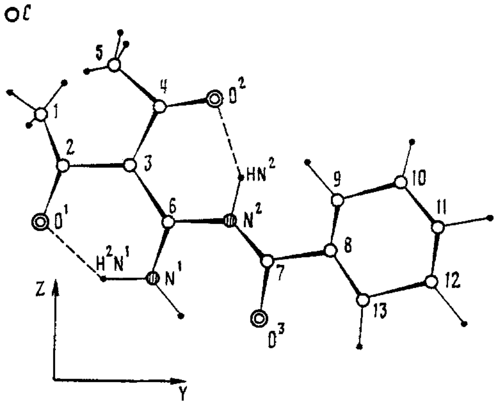
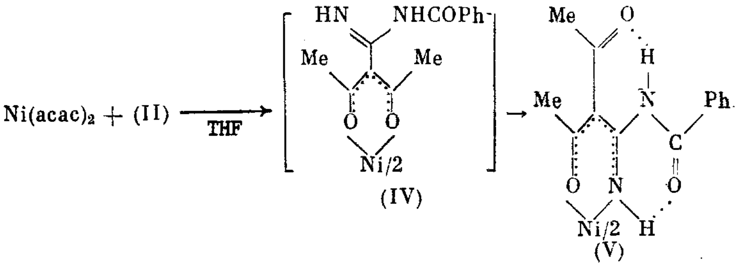


Fig. 1. Structure of the (III) molecule projected on to the coordinate plane Y.

In order to establish the part played by $Ni(acac)_2$ in reaction (1), its behavior with (II) in the absence of free (I) was examined. On stirring a mixture of (II) and $Ni(acac)_2$ in THF at 20°C for four days, or boiling the mixture for 4 h, a brick-red solid complex separated, which from spectral examination was (V) (it was assumed that the β-diketonate complex (IV) was first formed, but this could be detected, since it apparently readily isomerizes to (V))



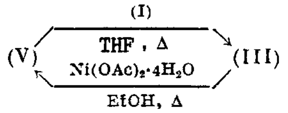
(2)

The mass spectrum of (V) showed a strong molecular ion peak with m/z 548, and a peak for the ion $[M-COMe]^+$ with m/z 505.

The PMR spectral findings show that the complex is paramagnetic, and consequently has the square planar structure. The nonequivalence of the two methyl groups in the spectrum of this compound in $CDCl_3$ (δ 2.46 and 2.31 ppm) supports the structure (V).

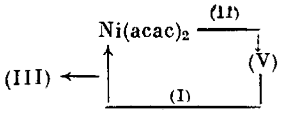
Examination of the IR spectra of chloroform solutions of the complex showed that both NH groups are involved in intramolecular hydrogen bonding (IHB) N–H ... O=C. Even when the solutions are highly dilute, no absorption for free NH is seen. This is in accordance with the structure (V), since in the alternative product (IV) at least one of the NH groups would be free in dilute solution.

On treatment with an excess of (I), the chelate (V) is readily converted into the ketene aminal (III), In turn, (III) reacts with $Ni(OAc)_2 \cdot 4H_2O$ in ethanol to give (V)



(3)

The role of $Ni(acac)_2$ as a catalyst in reaction (1) may therefore be shown as follows (4):



(4)

TABLE 1. Atom Coordinates in (III) (nonhydrogen atoms ×$10^4$, hydrogen atoms ×$10^3$)

| Atom | $x$ | $y$ | $z$ | Atom | $x$ | $y$ | $z$ |
|---|---|---|---|---|---|---|---|
| $C^1$ | −0750(5) | 1998(2) | 4195(2) | $H^1(C^1)$ | 24(5) | 192(2) | 481(2) |
| $C^2$ | 0520(5) | 2434(2) | 3315(2) | $H^2(C^2)$ | −182(5) | 240(2) | 445(2) |
| $C^3$ | 2757(4) | 3002(2) | 3379(2) | $H^3(C^1)$ | −133(6) | 140(2) | 399(2) |
| $C^4$ | 3610(5) | 3422(2) | 4281(2) | $H^1(C^5)$ | 217(5) | 315(2) | 564(2) |
| $C^5$ | 2028(6) | 3575(2) | 5127(2) | $H^2(C^5)$ | 14(5) | 352(2) | 492(2) |
| $C^6$ | 4097(5) | 3180(2) | 2505(2) | $H^3(C^5)$ | 252(6) | 421(3) | 532(3) |
| $C^7$ | 7725(5) | 4012(2) | 1771(2) | $H^1(N^1)$ | 441(5) | 299(2) | 106(2) |
| $C^8$ | 9878(5) | 4619(2) | 2037(2) | $H^2(N^1)$ | 149(6) | 254(2) | 163(3) |
| $C^9$ | 10406(5) | 4929(2) | 2979(2) | $H(N^2)$ | 679(5) | 385(2) | 327(2) |
| $C^{10}$ | 12499(6) | 5496(2) | 3174(2) | $H(C^9)$ | 909(5) | 470(2) | 356(2) |
| $C^{11}$ | 14066(5) | 5748(2) | 2417(2) | $H(C^{10})$ | 1296(5) | 575(2) | 393(2) |
| $C^{12}$ | 13543(5) | 5447(2) | 1470(2) | $H(C^{11})$ | 1562(6) | 621(2) | 252(2) |
| $C^{13}$ | 11466(5) | 4879(2) | 1279(2) | $H(C^{12})$ | 1480(5) | 568(2) | 90(2) |
| $O^1$ | −0444(4) | 2223(1) | 2507(2) | $H(C^{13})$ | 1108(5) | 461(2) | 56(2) |
| $O^2$ | 5738(4) | 3764(1) | 4401(1) | | | | |
| $O^3$ | 7252(4) | 3790(1) | 0918(1) | | | | |
| $N^1$ | 3319(4) | 2878(2) | 1632(2) | | | | |
| $N^2$ | 6258(4) | 3699(1) | 2544(2) | | | | |

It is also possible that the electrophilicity of the C≡N group in (II) is enhanced by coordination with Ni(acac)$_2$. A similar mechanism has been proposed for the Ni(acac)$_2$-catalyzed reaction of β-dicarbonyl compounds with cyanogen and trichloroacetonitrile [5].

The ketene animal (III) is a "push-pull" ethylene, in which one of the carbon atoms forming the double bond bears an electrophilic substituent, and the other an electron-acceptor group [6]. The clearly apparent conjugation between the donor and acceptor moieties in these molecules has a marked effect on their reactivity and physicochemical properties. For this reason, such ethylenes have attracted attention as subjects for x-ray examination. For example, in a series of S,N- and N,N-ketene acetals [7], and aminocarbonyl compounds related thereto (Me$_2$NCH=C(COOMe)$_2$ [8, 9] and Me$_2$NCH=CH—CH=C(COR)$_2$ (R = Me, OMe) [10], the influence of p—π conjugation on the geometric parameters of the molecule, especially the length of the C=C bond, has been well demonstrated.

We have carried out an x-ray structural examination of the ketene aminal (III) to establish its crystal and molecular structure (Fig. 1 and Table 1).

An interesting feature of the molecule of (III) is the involvement of all the nitrogen and oxygen atoms in the formation of three IHB: (N$^1$)H$^2$...O$^1$ (1.63(3) Å), (N$^2$)H...O$^2$ (1.65 (3) Å) and (N$^1$)H$^1$...O$^3$ (1.89(3) Å).

The central region of the molecule, including the ethylene group with its surrounding atoms (C$^2$, C$^3$, C$^4$, C$^6$, N$^1$, and N$^2$), together with the atoms of the amide group (C$^7$ and O$^3$) are virtually planar, the departures of the atoms from this plane (P) not exceeding 0.03 Å. The rotation of the fragments C$^2$C$^3$C$^4$ and N$^1$C$^6$N$^2$ around the C$^3$—C$^6$ double bond is 4.1°. It is noteworthy that in 2,2-diacetylketene aminals, in which the N atoms are substituted and IHB are not formed, this angle reaches 60-70° [7].

The acetyl groups C$^1$C$^2$O$^1$ and C$^5$C$^4$O$^2$ are rotated relative to P by 16.7 and 20.6° respectively on opposite sides, forming an angle of 33.9° with each other. As a result of IHB, each of the C=O groups and the C=C fragment are in the s-cis-configuration, whereas in the ketene aminals mentioned above which are substituted at nitrogen, the C=O groups are situated differently relative to the C=C bond.

The bond length distribution in the fragment C$^4$C$^3$C$^2$C$^6$N$^1$N$^2$ is largely dependent on p—π conjugation. The length of the ethylenic bond C$^3$—C$^6$ (1.418(3) Å) is closer to the C$_{sp^2}$—C$_{sp^2}$ single bond value than to that for the double bond. On the other hand, the single bonds C$^3$—C$^4$ and C$^2$—C$^3$ (1.435(3) and 1.443(3) Å) are somewhat shortened. The C$^6$—N$^1$ bond (1.325(3) Å) is close to the double bond value, and C$^6$—N$^2$ is lengthened to 1.371(3) Å, probably as a result of p—π interactions in the amide group N$^2$C$^7$O$^3$. The length of the C=O bond is greater than normal, possibly owing both to its involvement in conjugation and in IHB.

The colorless crystals of (III) were readily soluble in acetone and chloroform, moderately so in THF and ethanol, and sparingly in hexane. The IR spectra of (III) obtained in KBr disks, the melt, and in solution in cabron tetrachloride and chloroform, were similar, and even at high dilutions in carbon tetrachloride the spectrum showed no absorption for free NH groups, but absorption for NH groups involved in IHB persisted. Comparison of the IR spectrum of (III) with that of the N-unsubstituted 3-(diaminomethylene)pentan-2,4-dione [2] enables the highest-frequency absorption (3330 cm$^{-1}$) to be assigned to the weakest IHB, N—H...O=C (Ph), and that at 1680 cm$^{-1}$ to the amide group. The very broad, smeared out absorption of low intensity with a maximum in the 3100-2800 cm$^{-1}$ region is characteristic of the remaining NH groups bonded to the acetyl groups.

In the PMR spectrum of (III) in CDCl$_3$, three signals for NH are seen at low field, their chemical shifts (14.98, 11.16, and 9.88 ppm) remaining unchanged on dilution.

All these observations show that the conformation of (III) is the same in solution as in the crystal.

These features of the structure of (III) enable it to be regarded as a potential chelating ligand capable of forming both mono- and binuclear complexes.

## EXPERIMENTAL

PMR spectra were obtained on a Bruker WM-250 instrument, and $^{13}$C NMR spectra on a Bruker AM-300 spectrometer. IR spectra were recorded on a UR-20 instrument, and mass spectra (m/z) on a Varian MAT CH-6 mass spectrometer.

*3-[(N-Benzoyl)diaminomethylene]pentane-2,4-dione (III).* A mixture of 1.46 g of (II), 1.00 g of (I), and 0.13 g of Ni(acac)$_2$ in 15 ml of THF was boiled for 4 h under dry argon. The solvent was then removed, and the residue crystallized from ethanol to give 2.21 g (90%) of (III), mp 127-128°C. Found: C 63.27; H 5.84; N 11.26%. $C_{13}H_{14}N_2O_3$. Calculated: C 63.40; H 5.73; N 11.38%. Mass spectrum, m/z: 246 [M$^+$], 231 [M—Me]$^+$, 203 [M—COMe]$^+$. IR spectrum (ν, cm$^{-1}$, $CCl_4$): 3330 (NH), 3100-2800 (NH, CH), 1680 (COPh), 1631 (CO), 1603, 1585 (C=C). PMR spectrum (δ, ppm, $CDCl_3$): 14.98 s (NH), 11.16 s (NH), 9.88 s (NH), 7.99-7.40 m (Ph), 2.41 s (Me), 2.39 s (Me). $^{13}$C NMR spectrum (δ, ppm, $CDCl_3$): 119.23 ($\underline{C}$OMe), 169.59 ($\underline{C}$OPh), 162.08 (NCN), 133.42, 132.48, 129.01, 127.96 (Ph), 102.62 ($>C=$), 32.50 (2 Me).

*Chelate Complex of (III) with Ni$^{2+}$(V). a) Synthesis from Ni(acac)$_2$ and (II).* A mixture of 0.257 g of Ni(acac)$_2$ and 0.292 g of (II) in 5 ml of THF was boiled for 4 h under dry argon. The brick-red precipitate was filtered off and recrystallized from toluene to give 0.489 g (80%) of (V), mp 219-220°C (decomp.). Found: C 56.98; H 4.57; N 10.20; Ni 10.59%. $C_{26}H_{26}N_4NiO_6$. Calculated: C 56.86; H 4.11; N 10.33; Ni 10.69%. Mass spectrum, m/z: 548 [M]$^+$. IR spectrum (ν, cm$^{-1}$ in KBr): 3260 (NH), 3200-2700 (NH, CH), 1670 (COPh), 1630 (CO), 1600, 1580 (CO, C=C). PMR spectrum (δ, ppm, $CDCl_3$): 13.70 s (NH), 8.85 br. s (NH), 8.04-7.48 m (Ph), 2.46 s (Me), 2.31 s (Me).

*b). Synthesis from Ni(OAc)$_2$·4H$_2$O and (III).* A mixture of 0.249 g of Ni(OAc)$_2$·4H$_2$O and 0.492 g of (III) in 10 ml of ethanol was boiled for 20 min. The brick-red solid which separated was filtered off and crystallized from toluene to give 0.400 g (73%) of the chelate (V), mp 219-220°C (decomp.). The IR and PMR spectra of the material were identical with those of the compound obtained from Ni(acac)$_2$ and (II).

*Reaction of Chelate (V) with Acetylacetone (I).* A mixture of 0.549 g of (V) and 0.400 g of (I) in 10 ml of THF was boiled under dry argon for 1.5 h (until all the (V) had dissolved to give a green solution). The solvent was distilled off, chloroform added to the residue, and filtered through silica (L 40 × 100 μ, eluent chloroform). The chloroform was removed to give 0.453 g (92%) of (III), mp 127-128°C (from ethanol).

*X-ray Structural Examination of (III).* Recrystallization from ethanol gave acicular, monoclinic monocrystals of (III): $a = 5.763$ (1), $b = 15.562$ (1), $c = 13.569$ (1) Å, $\gamma = 99.38$ (1)°, $V = 1200.73$ Å$^3$, $Z = 4$, space group P21/b. The elementary cell parameters and a full set of intensities with $I \geq 3\sigma$ were obtained on a RÉD-4 four-circle autodiffractometer ($\lambda CuK_\alpha$, graphite monochromator, θ/2θ scanning, $\theta < 60°$, 1690 reflections. Primary treatment of the data (format conversion, calculation of the Lp factor, assembly of the data file for calculation) was carried out on an EC-1022 computer using the DÉM program, compiled by us from the PLDS amd WPC subprograms of the SAD-4 suite (Institute of Crystallography of the Academy of Sciences of the USSR). The model was obtained by the direct method, and all 18 hydrogen atoms were located by the best E-synthesis. Structure refinement was carried out by two successive Fourier syntheses, then by least squares in full-matrix version with anisotropic approximation. All the hydrogen atoms were located from the difference synthesis, and refined isotropically. The final value of the R factor was 0.053. Calculations of the structure were carried out on a BÉSM-6 computer using the "Pentgen-75" program. The atom coordinates in (III) are shown in Table 1. The interatomic distances and valence angles, and the temperature factors, may be obtained from the authors.

## CONCLUSIONS

1. Acetylacetone reacts with benzoylcyanamide in the presence of 5 mole% of Ni(acac)$_2$ to give a novel chelating ligand, 3-[(N-benzoyl)diaminomethylene] pentane-2,4-dione (III). The key step in the reaction is addition of Ni(acac)$_2$ to the C≡N group in benzoylcyanamide to give the chelate.

2. X-ray structural examination has shown that a characteristic feature of the molecule (III) is the involvement of all the O and N atoms in the formation of three intramolecular N—H ...O=C hydrogen bonds.

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# INVESTIGATION OF THE INTERACTION OF METAL-CENTERED FREE RADICALS WITH α-DIKETONES, CONTAINING PERFLUORO-TERT-BUTYL AND 1-METHYL-o,m-CARBORANYL GROUPS USING THE EPR METHOD

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UDC 543.422.27:542.91:541.515:
661.668:547.442.2'127

It was shown earlier that when metal-centered free radicals (MCR, Mn, Re, Mo, and W) interact with perfluoro-α-diketones, paramagnetic chelate complexes (PCC) are formed [1]. The formation of trans- or cis-spin adducts (SA) could not be detected in EPR spectra in this case, while they were detected in the case of some α-diketones and MCR of group IVB metals [2]. This may have been related with a high rate of trans-cis isomerization of the SA or with the formation of chelates. To assess the effect of the volume of substituents in α-diketones on these transformations, we investigated in the present work the interaction of MCR with $CF_3COCOR$, where R = $(CF_3)_3C$ (I); 1-Me-o- (II), and 1-Me-m-carboranyl (III). As the source of free radicals, we used the dimers $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, $Fe_2(C_5H_5)_2(CO)_4$, $Mo_2(C_5H_5)_2(CO)_6$, $W_2(C_5H_5)_2(CO)_6$, as well as $Bu_3SiH$.

It was established that depending on the conditions (the temperature, the nature of the α-diketone and of the MCR), two different types of spectra can be registered. At relatively low temperatures, the spectra are characterized by relatively low HFI constants with the nuclei of the metal and high HFI constants with the fluorine atoms of the $CF_3$ group (type A). At higher temperatures the spectra are characterized by higher HFI constants with the nuclei of the metal and by somewhat lower HFI constants (in comparison the those of the low-temeprature spectra) with the fluorine nuclei (type B).

Figure 1 shows the typical EPR spectra for the radicals of both types, and Tables 1 and 2 show their spectral data. The characteristics of the type B spectra are similar to those investigated earlier [1]. This allows us to classify the radicals of this type as PCC. The radicals with type A spectra are spin adducts, and the fact that only one SA type was registered shows that it is in the trans form.

When the temperature was increased above the values indicated in Table 1 (in the absence of UV irradiation), we were able to observe, in some cases, the transformation of type A

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