

Finally, a brief comment on the stereospecificity of cyanoketene/imidate cycloadditions is in order. As mentioned,⁴ a large variety of such cycloadditions have now been studied, and in all cases the reactions appear to be stereospecific, giving β -lactams having stereochemistry analogous to **3**. We suggest that such results from a conrotatory ring closure of the zwitterionic intermediates analogous to **2**. Thus, an endo preference for the cyano group and the iminium ion proton in these zwitterions must be invoked. Such structures are not completely obvious on steric grounds alone, particularly for chlorocyanoketene cycloadditions. However, an electrostatic attraction between the negative charge density on the cyano group in **2** and the positive charge of the iminium ion may dictate the suggested endo preference of the cyano group, while endo preference for the iminium ion proton can be made on the basis of steric arguments.

In conclusion we wish to summarize some significant points resulting from this investigation. (1) For the first time the zwitterion resulting from the interaction of a ketene with an imidate has been independently generated and shown to give the same products as the cycloadditions themselves. (2) The fact that a zwitterion is formed in the thermolysis of **1** establishes our earlier general proposal that such intermediates can result from appropriately substituted vinyl azides and thus a powerful predictive model is at hand.⁵ (3) The results here provide a precedent that suggests a general mechanistic probe for the cycloadditions of cyanoketenes. That is, from appropriately substituted cyclic β -azidoenones one can envisage the generation of zwitterions that could result from the cycloaddition of cyanoketenes to ketenes, alkenes, allenes, etc. (4) From a purely synthetic perspective, the construction of β -lactams from the readily available azidopyrrolinones⁵ may have clear advantages over simple cycloadditions of cyanoketenes to imines, particularly where the imines are difficult to prepare.

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- The rate of decomposition was followed by ¹H NMR analysis of the reaction solution as a function of time.
- It is, of course, possible that an intermediate in the thermolysis of **4** reacts with the imidate, **6**, to ultimately give **3**. However, we do not consider this to be a likely process.
- The equilibrium was also approached starting with equivalent amounts of **8** and **6**. Here, after 48 h in refluxing benzene, the respective concentrations of **8** and **3** were 89 and 11%.
- Such trapping experiments are analogous to the elegant work of R. Huisgen

and his co-workers concerning the cycloaddition of TCNE to enol ethers. See, for example, R. Huisgen, *Acc. Chem. Res.*, 10, 117 (1977); H. B. Kagan and J. L. Luche, *Tetrahedron Lett.*, 3093 (1968).

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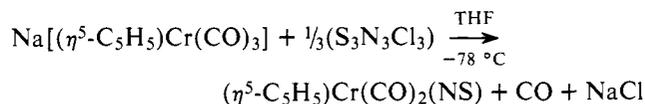
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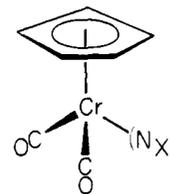
Preparation of (η^5 -C₅H₅)Cr(CO)₂(NS). The First Organometallic Thionitrosyl Complex¹

Sir:

At the present time there is a striking paucity of thionitrosyl complexes, and the few such coordination compounds that are known² result from the reaction of elemental sulfur, propylene sulfide, or disulfur dichloride with coordinated nitrido ligands in the precursors. We now wish to report that trithiazyl trichloride, S₃N₃Cl₃, can be used to directly introduce the thionitrosyl functionality into an organometallic complex by the reaction



Furthermore, a comparison of the physical properties of the new thionitrosyl product (**1**) with those exhibited by its nitrosyl analogue (**11**)³ enables us, for the first time, to contrast the bonding properties of NO and NS ligands.



I, X = S; II, X = O

In a typical experiment 4.50 g (20.1 mmol) of Na[(η^5 -C₅H₅)Cr(CO)₃]³ were dissolved in 100 mL of THF under N₂ and the resulting yellow solution was cooled to -78 °C. To this rapidly stirred solution was added dropwise a bright green THF solution (40 mL) containing 1.55 g (6.34 mmol) of S₃N₃Cl₃.⁴ Gas evolution occurred, a precipitate formed, and the reaction mixture developed a dark red-brown coloration. After the addition of the S₃N₃Cl₃ solution was complete, the mixture was stirred for 1 h at -78 °C and then was allowed to warm slowly to room temperature. Solvent was removed in vacuo and the residue was extracted with hexane (250 mL) and filtered. The filtrate was taken to dryness in vacuo and sublimation of the dried residue at 35 °C (5 × 10⁻³ mm) onto a water-cooled probe produced 0.93 g (4.25 mmol, 21% yield) of crystalline (η^5 -C₅H₅)Cr(CO)₂(NS). Anal. Calcd for C₇H₅CrO₂NS: C, 38.36; H, 2.30; N, 6.39. Found:⁵ C, 38.64; H, 2.20; N, 6.37.

Dicarbonyl (η^5 -cyclopentadienyl)thionitrosylchromium (I) is a dark red-violet, diamagnetic solid which dissolves in common organic solvents to give blood-red solutions that eventually deposit some decomposed matter when exposed to air for several hours; I itself is reasonably stable in air, but is best stored under N₂. Its IR spectrum in hexane (Table I) exhibits the expected three strong bands attributable to terminal CO and NS groups. The ν (NS) band occurs in the frequency range found² for other thionitrosyl complexes. The ν (CO) bands of **1** appear at slightly higher frequencies than

Table I. Physical Properties of (η^5 -C₅H₅)Cr(CO)₂(NX) Complexes

	I, X = S	II, X = O
Color	Red-violet	Orange-red
Mp, °C	68.0-69.0	69.5-70.5
ν (CO), cm ⁻¹ (in hexane) ^a	2033 (s), 1962 (s)	2028 (s), 1955 (s)
ν (NX), cm ⁻¹ (in hexane) ^a	1180 (s)	1713 (s)
¹ H NMR, δ (ppm) (in CDCl ₃) ^b	5.08	5.03
¹³ C NMR, δ (ppm) (in CDCl ₃) ^b	92.75 (C ₅ H ₅)	90.76 (C ₅ H ₅)
	239.43 (CO)	237.63 (CO)

^a Recorded on a Perkin-Elmer 457 spectrophotometer and calibrated with the 1601-cm⁻¹ band of polystyrene film. ^b ¹H and ¹³C NMR spectra were recorded on Varian Associates T60 and CFT20 spectrometers, respectively, with Me₄Si being employed as an internal standard. The indicated chemical shifts are downfield from Me₄Si.

Table II. Low-Resolution Mass Spectral Data for (η^5 -C₅H₅)Cr(CO)₂(NX) Complexes^a

I, X = S			II, X = O		
<i>m/e</i>	Rel abundance	Assignment ^b	Rel abundance	<i>m/e</i>	
219	36	C ₅ H ₅ Cr(CO) ₂ (NX) ⁺	26	203	
191	8	C ₅ H ₅ Cr(CO)(NX) ⁺	21	175	
163	74	C ₅ H ₅ Cr(NX) ⁺	13	147	
117	100	C ₅ H ₅ Cr ⁺	100	117	
52	63	Cr ⁺	37	52	

^a Obtained at 70 eV on an Atlas CH4B spectrometer using the direct-insertion method at room temperature. ^b The assignments involve the most abundant naturally occurring isotopes in each fragment.

those of II, thereby suggesting that the NS ligand is more effective in removing electron density from the central metal than is the NO ligand.⁶ The Cr-(NS) bond in I also appears to be somewhat stronger than the Cr-(NO) bond in II, as evidenced by the mass spectral data displayed in Table II. While both complexes exhibit fragmentation patterns corresponding to the sequential loss of ligands and the common base peak can be assigned to the C₅H₅Cr⁺ ion, the C₅H₅Cr(NS)⁺ ion is markedly more abundant in the mass spectrum of I than is the C₅H₅Cr(NO)⁺ ion in the spectrum of II.

The NMR data of compounds I and II (Table I) provide an interesting contrast. The ¹H NMR spectrum of I consists of a single sharp peak which occurs at a slightly lower field than the corresponding absorption due to the cyclopentadienyl protons of II. Similarly, the ¹³C NMR chemical shifts of the cyclopentadienyl and carbonyl carbons are further downfield from Me₄Si for complex I. A comparable downfield shift for δ (¹³C₅H₅) has previously been observed⁷ when a CO group in (η^5 -C₅H₅)Mn(CO)₃ (isoelectronic with II) has been replaced by a CS group to give (η^5 -C₅H₅)Mn(CO)₂(CS) (isoelectronic with I). However, such a substitution also results in an upfield shift of δ (¹³CO) which is exactly opposite to the effect that we observe in going from II to I. Rather than speculate on the factors responsible for this apparent anomaly, we have initiated single-crystal x-ray diffraction studies of I and II to ascertain the mode of linkage of the NO and NS groups in the two complexes. This information is essential for any future theoretical interpretation of the different electron-donating and electron-accepting abilities of the two ligands.

The reaction employed to prepare I resembles a procedure that we have previously used⁸ to synthesize various organometallic nitrosyl complexes, namely the treatment of organometallic carbonyl anions with nitrosyl chloride, ClNO. Indeed, we believe that an important feature of our preparation of I is

that in THF the trithiazyl trichloride reagent probably exists as a solvated monomer, NSCl(THF)_x. However, our attempts to prepare other organometallic thionitrosyl complexes by this route have not succeeded as yet because S₃N₃Cl₃ appears to be a stronger oxidizing agent than ClNO. For instance, treatment of the more nucleophilic anions⁹ [(η^5 -C₅H₅)M(CO)₃]⁻ (M = Mo or W) with S₃N₃Cl₃ in THF at -78 °C results in the formation of [(η^5 -C₅H₅)M(CO)₃]₂ (III) and (η^5 -C₅H₅)M(CO)₃Cl (IV) as the only isolable organometallic products in yields of ~25 and ~15% (based on M), respectively. III is probably formed by the oxidation of the anionic reactant and IV could result from the reaction of II with NSCl(THF)_x in a manner somewhat analogous to that reported¹ for ClNO. Consistent with this interpretation is the fact that [Mn(CO)₅]⁻ is simply oxidized to Mn₂(CO)₁₀ by S₃N₃Cl₃ in THF.

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An Intramolecular Model of 1,3-Dipolar Cycloaddition to the 5,6 Double Bond of a Pyrimidine Nucleoside. A New Route to the Regiospecific Synthesis of 4-Substituted Triazole Reversed Nucleosides

Sir:

[2 π + 2 π] photodimerization^{1,2} and photocycloaddition of pyrimidines to electron-rich monoolefins³ have been extensively studied in terms of photochemical transformation of natural nucleic acid and preparative chemistry aiming at effective carbon-carbon bond formation and functionalization. However, there has been no example of the thermally induced cycloaddition of pyrimidine bases as nucleic acid components except a few 1,3-dipolar cycloaddition reactions of an azide with pyrimidine nuclei activated with 5-nitro or 5-bromo substituents.^{4,5} Indeed, synthetic exploitation of pyrimidine bases as dipolarophiles or dienophiles is an important open field to be explored in view of the great variability of expected products and the direct use of natural nucleosides or their derivatives with a given stereochemistry involving, among others, that of the anomeric position. From this point of view, 1-(5'-azido-5'-deoxy-2',3'-O-isopropylidene- β -D-ribofuranosyl)-uracil (I),⁶ which was originally synthesized as the precursor of 5'-amino-5'-deoxyuridine, is a readily accessible, simple model compound for roughly evaluating the reactivity of the "naked" 5,6 double bond of uracil base with 1,3 dipoles. This