

Figure 2. Structures of complexes formed in the reactions of Figure 1, showing 50% probability ellipsoids and selected interatomic distances (Å) and angles (deg); primed and unprimed atoms are related by crystallographic symmetry: (top) $[\text{Fe}_3\text{S}_4(\text{SPh})_4]^{3-}$, mean distances under idealized D_{2d} symmetry are given, $\text{Fe}(1)\cdots\text{Fe}(2)$ 2.703 (2) Å, $\text{Fe}(1)\cdots\text{Fe}(3)$ 2.725 (2) Å; (middle) $[\text{Fe}_2(\text{SET})_6]^{2-}$, centrosymmetric; (bottom) $[\text{Fe}_3(\text{SPh})_3\text{Cl}_6]^{3-}$, C_2 axis along $\text{Fe}(1)\cdots\text{S}(2)$, $\text{Fe}(2)\cdots\text{S}(2)$ 2.365(2) Å, the Fe-Cl distance is the mean of three independent values. Estimated standard deviation values for individual Fe-S, Fe-Cl, and Fe \cdots Fe distances (excluding the latter distances in $[\text{Fe}_3(\text{SPh})_3\text{Cl}_6]^{3-}$) are typically ≤ 0.003 Å.

was cooled to 25 °C, the solid was collected, washed with 4:1 ether-acetonitrile, and recrystallized from acetonitrile to give green crystals of a material shown to be $(\text{Et}_4\text{N})_3[\text{Fe}_3(\text{SPh})_3\text{Cl}_6]$ (7, 39%, 260 nm (29 000), 330 (6900), 1850 (210) (ν_1); δ +41.1 (*o*-H), -12.3 (*m*-H), +32.8 (*p*-H); -30 °C). The structure of $[\text{Fe}_3(\text{SPh})_3\text{Cl}_6]^{3-}$ (Figure 2) contains a $\text{Fe}_3(\mu\text{-SPh})_3$ ring that, remarkably (and unlike the few structurally defined $\text{M}_3(\mu\text{-SR})_3$ cycles¹⁷), is planar. Further, the three phenyl groups are coplanar with this ring. The planar conformation occurs at the expense of very large Fe-S-Fe internal angles (140–142°) and produces Fe \cdots Fe separations of 4.4–4.5 Å. The latter values are substantially larger than those of 2–6,^{3,7,8} and some exchange coupling remains

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($\mu_{\text{Fe}} = 4.18 \mu_{\text{B}}$, CH_3CN , -30 °C). As in all species 1–6 the Fe atoms occupy tetrahedral sites in 7.

These and related^{5,8,16} results disclose an extensive chemistry of Fe(II)-thiolates, with respect to both the existence of a diverse set of discrete complexes with varying nuclearity and, owing to their reducing nature, reactions with sulfur to afford Fe-S-SR clusters. Neither the $[\text{Fe}_3\text{S}_4]^+$ core structure of 3 nor the $\text{Fe}_3(\text{SPh})_3$ ring of 7 has been previously encountered in individual molecules. Indeed, the only prior trinuclear Fe-(S)-SR species of known structure are $[\text{Fe}_3\text{S}(\text{S}_2\text{-}o\text{-xy})_3]^{2-18}$ and a ring-methylated variant¹⁹ and the cyclic nonplanar $(3\text{Fe}-3\text{S})^{3+}$ site in *A. vinelandii* ferredoxin I.²⁰ In the latter, deviations from the Fe_3S_3 least-squares plane are ≤ 0.31 Å and mean values of Fe \cdots Fe distances and Fe-S-Fe internal angles are 4.08 Å and 123°, respectively.²¹ $[\text{Fe}_3(\text{SPh})_3\text{Cl}_6]^{3-}$ reveals the feasibility by synthesis of a ring of comparable dimensions, but it is not a site analogue. The $(\text{Fe}_3\text{S}_4)^+$ core of 3, having an EPR signal at $g = 4.3$ and none near $g = 2.0$ in freshly prepared solutions, cannot represent structurally uncharacterized protein 3-Fe sites with the latter signal.²² However, complexes 3 and 7 may serve as precursors, in isomerization, redox, and other reactions, to new Fe-S-SR clusters including protein 3-Fe site representations. This possibility is under investigation.

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Registry No. 1, 82661-04-9; 2, 82661-06-1; 3, 82661-08-3; 4, 82665-06-3; 7, 82661-10-7; $(\text{Et}_4\text{N})_3[\text{Fe}_3\text{S}_4(\text{SPh})_4]$, 82661-12-9; FeCl_2 , 7758-94-3; $(\text{Et}_4\text{N})_2[\text{FeCl}_4]$, 15050-84-7.

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Synthesis and Structure of Tri-*s*-triazine

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From the time of Liebig¹ and Gmelin,² a group of related nitrogen compounds (melem, hydromelonic acid, cyameluric chloride, cyameluric acid, etc.) was known that possessed high heat stability, low solubility, and little chemical reactivity. However, these compounds remained structural puzzles for more than a century until Pauling and Sturdivant³ devised the correct formulation for their common nucleus, a coplanar arrangement of three fused *s*-triazine rings (1). We have now synthesized the unsubstituted nucleus, tri-*s*-triazine (1),⁴ for the first time and have determined its physical and spectroscopic properties and its structure by X-ray crystallography. This compound has been the subject of numerous theoretical calculations and predictions^{3,5} as

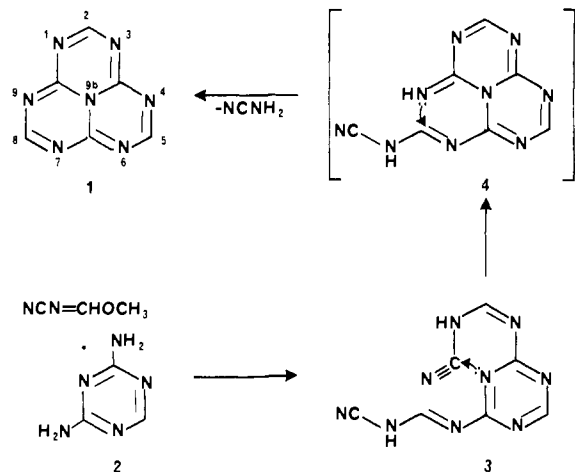
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a member of the cyclazine series,⁵⁻¹⁶ in which the term cyclazine denotes a fused conjugated ring system held planar by three covalent bonds to a fused conjugated ring system held planar by the three covalent bonds to an internal nitrogen atom.⁷ The properties of 1,3,4,6,7,9-hexaazacycl[3.3.3]azine (1), which is the ultimate member of the alternating C,N azacycl[3.3.3]azine series, are of considerable interest with respect to the 12- π electron periphery and the question of the involvement of the n electrons of the central N.

The mass spectrum of the product (3) resulting ($\geq 60\%$ yield) from the reaction of methyl *N*-cyanomethanimidate^{17,18} with 2,4-diamino-1,3,5-triazine (2) and NaOMe in Me₂SO/MeOH at room temperature showed a major m/e peak corresponding to the loss of cyanamide. Inlet conditions in the mass spectrometer, i.e., short residence time, high temperature, and very low pressure, suggested a favorable vacuum pyrolysis method for the conversion of 3 to 1, probably through the intermediacy of single ring closure and tautomerization (4), followed by second ring closure and elimination. A sublimation apparatus containing 2,4-bis(*N*-cyano-*N'*-formamidino)-1,3,5-triazine (3) maintained at < 0.025 mmHg was immersed in a Wood's metal bath at ~ 400 °C for ~ 2 min. Extraction of the sublimate and residual material with acetonitrile, filtration, and evaporation in vacuo yielded ($\geq 60\%$) tri-*s*-triazine, C₆H₃N₇ (1), which was obtained analytically pure by flash chromatography on Woelm silica gel with EtOAc/CHCl₃ (1:1) as the eluting solvent: ¹H NMR (all NMR in (CD₃)₂SO) δ 8.3; ¹³C NMR δ 171.6 (¹J_{CH} = 207.6 Hz, CH), 159.7 (junctional C); ¹⁵N NMR (downfield, DMF as internal standard) 133.8 (²J_{NCH} = 14.0 Hz, peripheral N's), 81.8 ppm (central N); mass spectrum, m/e (rel intensity, 10 eV) 173 (100, M⁺), 146 (2, M⁺ - HCN), 119 (12, M⁺ - 2HCN), 94 (13, C₃H₂N₄⁺); color, yellow;

UV (CH₃CN) (CH₃N) λ_{\max} 443 nm (ϵ 268), 416 (199), 391 sh (95), 305 (22 700), 298 sh (18 900), 293 (20 600), 279 sh (13 580), 219 (9660); fluorescence (CH₃CN) $\lambda_{\max}^{\text{ex}}$ 307 or 445, $\lambda_{\max}^{\text{em}}$ 517 nm; Φ 0.014 (relative to fluorescein), τ 9.5 (by phase), 15.4 ns (by modulation).¹⁹

Crystals of tri-*s*-triazine (1) for single-crystal X-ray examination²⁰ were grown by slow evaporation of a solution of 1 in anhydrous acetonitrile in an atmosphere of dry xylene. The crystallographic data²¹ were collected on an Enraf-Nonius CAD4 computer-controlled κ axis diffractometer using ω - θ scan technique and Cu κ_{α} radiation (λ 1.541 84 Å). The intensities of 3342 reflections were collected, of which 2789 were unique and not systematically absent. The data were corrected for Lorentz and polarization factors. Only the 1436 reflections having intensities greater than 3.0 times their standard deviation were used in the refinements. Full-matrix least-squares refinement, including all hydrogens located and refined with isotropic temperature factors, converged with unweighted and weighted agreement factors of $R = 0.046$ and $R_w = 0.060$, respectively.

The molecular structure of 1 (cf. CA numbering), showing bond lengths and bond angles, is represented in Figure 1. The detailed dimensions are in the supplementary material. Of the two crystallographically independent molecules in the asymmetric unit, molecule B exhibits unusual thermal behavior, with some resultant anomalous dimensions. The dimensions for molecule A are, however, internally consistent. While corrections to the dimensions for thermal motion would provide a basis for detailed comparison with theory, the general aspects of the molecular structure are apparent from the results on molecule A, which shows only a slight departure, if any, from planarity. Specifically, the deviation of the central nitrogen from the weighted least-squares plane is -0.015 (2) Å as estimated by the thermal parameters.²² The peripheral C-N bond lengths were uniform, averaging 1.33 Å; the three central C-N bonds averaged 1.39 Å.²³ In each ring, the spread of the longer internal bonds, C-N-C, meeting at $\sim 120^\circ$ is compensated by a straightening, via average angles of 116, 129, and 116° of the opposite, apical site containing the shorter bonds, N-C-N (e.g., Figure 1A).

Which of the theoretical predictions are satisfied by the properties observed for tri-*s*-triazine (1), in addition to the planarity³ and the length of the peripheral C-N bonds?³ The compound is yellow, with a lowest energy transition close to that predicted by Leupin and Wirz,⁵ and it is also weakly fluorescent.⁵ The expectation that, in the cycl[3.3.3]azine series, delocalization and stabilization will result from the introduction of electronegative N atoms at the alternating peripheral locations 1,3,4, etc., in various azacycl[3.3.3]azines²⁴ is confirmed in 1 and in those members of this alternating series synthesized earlier that possess lower peripheral N content than 1.^{9,24-27} Similar chemical be-

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(21) Crystal data: C₆H₃N₇, mol wt 173.14; orthorhombic space group *Pbca*; peak width at half-height 0.20°; $a = 7.225$ (1) Å, $b = 27.193$ (6) Å, $c = 13.858$ (2) Å, $V = 2722.7$ Å³; $F(000) = 1408$, ρ_{calcd} ($Z = 16$) = 1.69 g cm⁻³; μ (Cu K α) = 10.4 cm⁻¹; temperature = 23 \pm 1 °C. The function minimized in the full-matrix least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, and the weight w is defined as $4F_o^2/\sigma^2(F_o^2)$. $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$.

(22) Thermal parameters are available upon request.

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(24) See ref 16c, especially p 347, Table III, and footnote 91 for calculated REPE (resonance energy per electron) values.

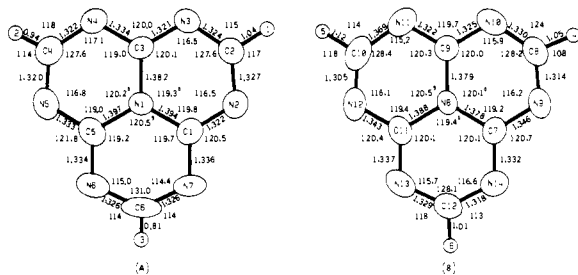


Figure 1. Bond lengths and bond angles for the two crystallographically independent molecules, A and B, of tri-*s*-triazine (**1**). The separate esd values are given in the supplementary material. For the bond lengths and angles not involving H, the esd values are in the range 0.003–0.005 Å and 0.2–0.3°, respectively.

havior of tri-*s*-triazine (**1**) to *s*-triazine^{3,28} is exemplified by the decomposition of both in water. The chemical shift value of 8.3 for the protons in tri-*s*-triazine is greater than any previously observed for unsubstituted azacycl[3.3.3]azines,^{16c} greater also than that, δ 7.3, for N—CH=N—Ar model, *N,N*-dimethyl-*N'*-phenylformamide,²⁹ and smaller than the δ 9.2 value for ¹H in "aromatic" *s*-triazine.³⁰ The ¹⁵N NMR chemical shift of the peripheral nitrogens in **1**, ~237 ppm downfield from ammonia,³¹ is less than that for (¹⁵N)-*s*-triazine, 282.9.³² The central C—N bonds are shortened from the usual 1.47-Å single-bond distance to an observed 1.39-Å average value. The deshielded central ¹⁵N resonance at ~186 ppm downfield from NH₃ prompts examination of the ring-current effect on the central N in other representative azacycl[3.3.3]azines. Application of the abbreviated synthesis to such cyclazines is in progress.

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Registry No. 1, 204-34-2; 2, 504-08-5; 3, 82679-23-0; methyl *N*-cyanomethanimidate, 51688-22-3.

Supplementary Material Available: Complete crystallographic data, including tables listing atomic positional and thermal parameters, bond angles, torsional angles, intermolecular contact distances, weighted least-squares planes, and observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

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Preparation and Reaction of Metal Ketene Complexes of Zr and Ti

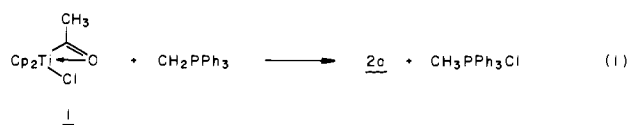
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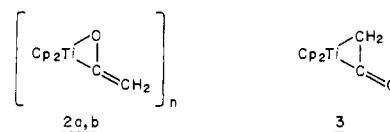
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Transition-metal ketene complexes have been proposed as intermediates in catalytic^{1a} and stoichiometric^{1b} reductions of carbon monoxide and as models for the isoelectronic ligand, carbon dioxide.² Complexes that contain highly stabilized ketene fragments, especially diphenylketene, have generally (but see ref 3) been prepared by direct reaction of the ketene with a coordinately unsaturated metal complex^{2,4} or by carbonylation of metal alkylidenes.⁵

We have found a general route to unsubstituted and alkyl-substituted ketene complexes of titanium and zirconium.⁶ In an attempt to prepare titanocene enolate complexes, the η^2 -acetyl **1**^{7a} was treated with CH₂PPh₃ in dichloromethane-ether at -50 °C (eq 1). Yellow **1** reacted instantly to give a red solution from



which red microcrystalline **2a** soon precipitated. Methyltriphenylphosphonium chloride was isolated from the supernatant. Reaction of **1** with NaN(SiMe₃)₂ in ether also gives **2a**. The



product is a moderately air-sensitive solid that is stable at room temperature for several days under an inert atmosphere and is sparingly soluble in a variety of solvents but decomposes rapidly in methylene chloride. In benzene, red **2a** isomerizes to yellow **2b**, reaching equilibrium in a matter of minutes at room temperature. The ratio of **2a**:**2b** at equilibrium is ca. 1:10. The yellow isomer crystallizes from benzene solution. Several lines of evidence suggest that **2a** and **2b** have the basic η^2 (C,O) ketene structure shown. The ¹H NMR spectra exhibit inequivalent methylene protons for each isomer with chemical shifts and coupling constants in the range typical of terminal olefins.⁸ An η^2 (C,C) ketene, **3**, should show a single methylene resonance. The proposed structure is similar to that observed for diphenylketene complexes of Ti,

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(8) ¹H NMR (C₆D₆): **2a** δ 3.36 (s, 1 H), 4.19 (s, 1 H), 5.99 (s, 10 H); **2b** δ 3.88 (d, *J* = 1.5 Hz, 1 H), 4.85 (d, *J* = 1.5 Hz, 1 H), 5.66 (s, 10 H). IR (KBr) **2a** 1610 cm⁻¹; **2b** 1610 cm⁻¹.