

signals for methyl protons and that 12-type structure is predominant for 8⁸ also support the idea.

The function of biotin in enzymic carboxylation has long been associated with activation of carbon dioxide through bonding to a ring nitrogen.¹¹ Recently, however, Bruice and coworkers proposed that the "activated CO₂" is that which is bonded to the carbonyl oxygen.¹² The argument by the latter author is based mainly on the low reactivity of a ring nitrogen toward carbon dioxide.¹³ Thus, the facile transfer of an acyl group which we have described above may well be related to the reactivities of a ring nitrogen in biotin and the nitrogen-bonded carbon dioxide in question.

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(12) (a) R. F. Pratt and T. C. Bruice, *J. Amer. Chem. Soc.*, **94**, 2823 (1972); (b) T. C. Bruice and A. F. Hegarty, *Proc. Nat. Acad. Sci. U. S.*, **65**, 805 (1970).

(13) (a) M. Caplow, *J. Amer. Chem. Soc.*, **90**, 6795 (1968); (b) M. Caplow and M. Yager, *ibid.*, **89**, 4513 (1967); (c) M. Caplow, *ibid.*, **87**, 774 (1965).

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Synthesis and Luminescence of the Tris(2,2'-bipyridine)iridium(III) Ion

Sir:

Previous attempts to synthesize [Ir(bipy)₃]³⁺ (bipy = 2,2'-bipyridine) using halogen-iridium species (*e.g.*, K₃IrCl₆·3H₂O, IrCl₃·xH₂O) yielded only chloro complexes.¹ We speculated that an iridium (a "soft" metal) compound containing only "hard" ligands would react more readily with "softer" 2,2'-bipyridine to give [Ir(bipy)₃]³⁺ than do chloride (a "soft" ligand) containing species. Proceeding accordingly, we have obtained the long-sought [Ir(bipy)₃]³⁺. Luminescence results add to our knowledge of the lowest lying excited states of platinum metal-diimine complexes.

The best procedure started with boiling a mixture of 1.0 g (1.7 mmol) of K₃IrCl₆·3H₂O, 0.3 g of K₂S₂O₈, and 48 g of KHSO₄ in 17 ml of water to dryness, followed by fusion in air for up to 0.5 hr at 220–300°. The clear deep green melt² thus obtained was cooled to room temperature, treated with 3.1 g of 2,2'-bipyridine and 17 ml of water, and boiled to dryness (little color change). This mixture was fused in a CO₂ atmosphere; with agitation it became brown-yellow in 0.2 hr (two liquid phases). The mixture was kept at 220–240° for 6 hr (CO₂ atmosphere, occasional agitation). Then it was cooled, and further work was carried out in air. The solid was dissolved in 170 ml of water (heat) and neutralized with KHCO₃. Removal of K₂SO₄ was completed by adding 340 ml of methanol, cooling to 5–10° for 1–2 hr, and filtering. The filtrate was evaporated to about 35 ml, cooled (bipy precipitated), checked for neutrality, and treated with diethyl ether to extract the excess bipy. The solution was diluted with 500 ml of

(1) R. E. DeSimone and R. S. Drago, *Inorg. Chem.*, **8**, 2517 (1969).

(2) Similar reactions involving sulfuric acid produce apparently halogen-free sulfate complexes; see D. B. Brown, M. B. Robin, J. D. E. McIntyre, and W. F. Peck, *Inorg. Chem.*, **9**, 2315 (1970).

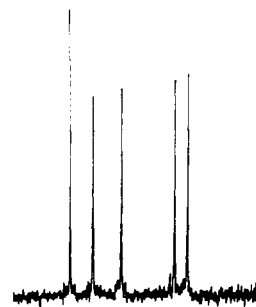


Figure 1. ¹³C nmr spectrum of [Ir(bipy)₃](NO₃)₃ in H₂O–D₂O. The chemical shifts starting at the left are –89.46, –83.77, –80.14, –76.69, and –60.04 ppm relative to internal dioxane standard. There were no additional peaks above the noise level from *ca.* –110 to +90 ppm. Areas or peak heights cannot be used to compare relative abundances.

0.2 *F* HNO₃ and evaporated at 90–100° to 10–20 ml, then carefully at 40–60° to dryness. The solid was dissolved in 10–20 ml of water, and the solution was neutralized with a little KHCO₃. It was chromatographed on Cellex-P cation resin (H⁺ form) with 0.05 *F* and then 0.1 *F* HNO₃. The highly luminescent 0.1 *F* HNO₃ fraction was evaporated to dryness and chromatographed (methanol) repeatedly on Sephadex LH-20. The weakly green-luminescing zone eluted from the column³ gave crystals of Ir(bipy)₃(NO₃)₃ on addition of 2-propanol and evaporation. These were recrystallized from methanol–2-propanol, giving pale yellow needles in nearly 50% yield based on the potassium hexachloroiridate. A light yellow perchlorate salt, obtained by metathesis with aqueous LiClO₄, was recrystallized from water. *Anal.* Calcd for [Ir(C₁₀H₈N₂)₃](ClO₄)₃·3H₂O: C, 35.57; H, 2.98; N, 8.30; Cl, 10.50. Found: C, 35.52; H, 3.01; N, 8.33; Cl, 10.35. Both salts were pure as shown by tlc (aqueous NaClO₄ on polyamide).

The ¹³C nmr spectrum (Figure 1) coupled with the elemental analysis proved the product to be [Ir(bipy)₃]³⁺. The five lines correspond to the five distinct carbon atoms of a D₃-symmetry tris complex. The simplest *cis*-[Ir(bipy)₂X₂]ⁿ⁺ contains ten kinds of carbon atoms. The complex ¹H nmr spectrum in D₂O strongly resembles the spectra^{1,4} of [Os(bipy)₃]²⁺ and [Fe(bipy)₃]²⁺, while it is distinctly different from the characteristic spectra^{1,5} of *cis*-[Ir(bipy)₂Cl₂]⁺ and *cis*-[Si(bipy)₂(OCH₃)₂]²⁺. A *trans*-[Ir(bipy)₂XY]ⁿ⁺ structure is rejected on the basis of the elemental analyses, the ¹H nmr spectrum and the failure to observe such species in many systems, although *cis*-bis(2,2'-bipyridine) complexes are common.^{6,7}

The absorption (~22°) and luminescence spectra (77°K) of [Ir(bipy)₃]³⁺ are given in Figure 2. The 77°K mean lifetime (τ) of ~80 μsec establishes the emission as a phosphorescence.

The emission spectra of [Ir(bipy)₃]³⁺ and [Rh-

(3) This zone was preceded and followed by brightly yellow or green-yellow luminescent products which are under investigation.

(4) S. Castellano, H. Gunther, and S. Ebersole, *J. Phys. Chem.*, **69**, 4166 (1965).

(5) D. Kummer and K. Köster, *Z. Anorg. Allg. Chem.*, **398**, 279 (1973).

(6) L. H. Berka, R. R. Gagne, G. E. Philippon, and C. E. Wheeler, *Inorg. Chem.*, **9**, 2705 (1970).

(7) P. Andersen and J. Josephsen, *Acta Chem. Scand.*, **25**, 3255 (1971).

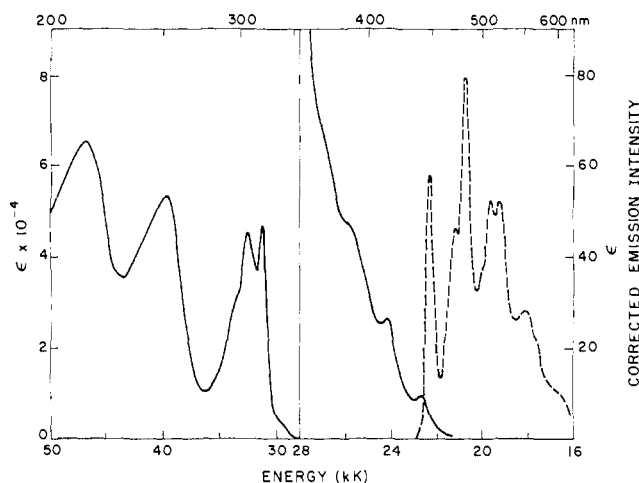


Figure 2. Absorption (22° in methanol or water) and luminescence (77°K in methanol-ethanol glass) spectra of $[\text{Ir}(\text{bipy})_3]^{3+}$. The emission spectrum is corrected by use of the published spectrum of $[\text{Ir}(\text{bipy})_2\text{Cl}_2]^+$.^{8b}

$(\text{bipy})_3]^{3+}$ ⁸ are virtually identical in band shapes and energies. The highest energy emission band of $[\text{Ir}(\text{bipy})_3]^{3+}$ is at 22.3 kK while that of $[\text{Rh}(\text{bipy})_3]^{3+}$ is at 22.4 kK. The $[\text{Rh}(\text{bipy})_3]^{3+}$ emission ($\tau = 2.2$ msec) is a ligand $\pi-\pi^*$ phosphorescence.⁸ In striking contrast, the charge transfer (CT) emission of $[\text{Ir}(\text{bipy})_2\text{Cl}_2]^+$ falls at 21.5 kK ($\tau = 11.4$ μsec).⁹ τ 's for "pure" CT emissions of Ir(III)-diimine type complexes are ~ 10 – 20 μsec .⁹ Thus, we assign the emission of $[\text{Ir}(\text{bipy})_3]^{3+}$ to a predominantly $\pi-\pi^*$ ligand phosphorescence. It seems unlikely that the emitting state contains a large component (>20 – 30%) of CT parentage on the basis of decay time and the failure to observe low-lying CT-excited singlet states in absorption, but a definitive answer on state parentage awaits determination of the absolute quantum yield.

Of particular interest is the weak absorption progression in the 22–26 kK range which is the mirror image of the emission (~ 1.3 – 1.5 kK vibrational progression). The luminescence ($\sim 22^\circ$) is the same for excitation at 23.0, 24.5, or 27.4 kK and also mirror images the absorption. Thus, we assign these weak absorption bands to an $S_0 \rightarrow {}^3\pi-\pi^*$ transition, the inverse of the luminescence. The unusually high intensity of these transitions for a $S_0 \rightarrow T_1$ process probably arises from a large internal heavy-atom effect ($Z = 77$ for Ir) and possibly to some admixing of T_1 with upper CT states. The apparent absence of $S_0 \rightarrow T$ absorptions in $[\text{Rh}(\text{bipy})_3]^{3+}$ is probably due to the lower Z of Rh and the very high energy of the CT states.

Our current work indicates that the previously unknown tris(1,10-phenanthroline)iridium(III) and possibly the bis(2,2',2''-terpyridine)iridium(III) cations can be prepared by analogous procedures. The highly luminescent species are being tested as photosensitizers.

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(8) (a) D. H. W. Carstens and G. A. Crosby, *J. Mol. Spectrosc.*, **34**, 113 (1970). (b) D. H. W. Carstens, Ph.D. Dissertation, University of New Mexico, 1969.

(9) R. J. Watts, G. A. Crosby, and J. L. Sansregret, *Inorg. Chem.*, **11**, 1474 (1972).

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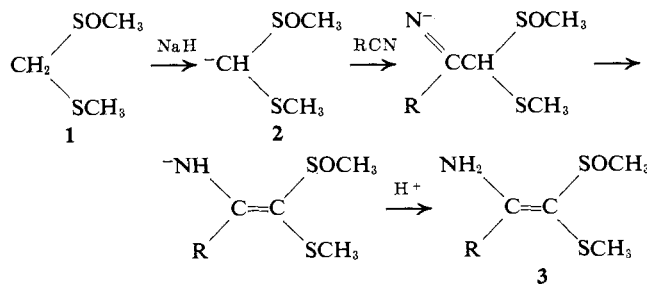
New Synthesis of α -Amino Acids from Nitriles

Sir:

We would like to describe an entirely new route to α -amino acids from nitriles¹ and its application to the synthesis of 5-hydroxytryptophan, a biologically important compound in the metabolic cycle of the tryptophan-serotonin system.²

We have found that the carbanion (**2**) derived from methyl methylthiomethyl sulfoxide (**1**)³ adds to nitriles to form a new type of enamine, *i.e.*, an enamino-sulfoxide (**3**).⁴ The formation of an enamino-sulfoxide may be rationalized by assuming addition of the carbanion (**2**) to the C–N triple bond, followed by proton migration (Scheme I).⁵

Scheme I



The synthesis of methyl esters of *N*-acetyl- α -amino acids was accomplished by sequential treatment of **3** with acetic anhydride to give the unusual rearrangement product **4**,⁶ base-catalyzed ester exchange to **5**, and reductive desulfurization with Raney nickel⁷ (Scheme II).

(1) For the general synthesis of nitriles, see K. Friedrich and K. Wallenfels in "The Chemistry of the Cyano Group," Z. Rappoport Ed., Interscience, New York, N. Y., 1970, Chapter 2.

(2) V. Erspamer, *Progr. Drug Res.*, **3**, 151 (1961).

(3) We have reported new synthetic methods for labile aldehydes, α -hydroxyaldehydes, and phenylacetic acid derivatives by using this reagent. See K. Ogura and G. Tsuchihashi, *Tetrahedron Lett.*, 3151 (1971); 1383, 2681 (1972).

(4) The enamino-sulfoxide **3** is a mixture of geometric isomers (*Z*- and *E*-forms; the ratio being *ca.* 9:1). See ref 11.

(5) A similar mechanism is proposed for the Thorpe-Ziegler cyclization of dicyanides to form enamino-nitriles by E. C. Taylor and A. McKillop, *Advan. Org. Chem.*, **7**, 1 (1969).

(6) The transformation of **3** to **4** may be accounted for by a mechanism involving acetylation of the amino group and the Pummerer-type rearrangement of the sulfinyl group, with the concomitant migration of the methylthio group. Details of the mechanism are now being studied.

(7) Reduction of **4** with deactivated Raney nickel in acetone afforded methanethiol esters of *N*-acetyl- α -amino acids in 75–82% yields [Raney nickel (W-II activity) was deactivated prior to use by refluxing in acetone for several minutes].