under Contract No. DE-AC03-76SF00098. The crystal structure analysis was performed by Dr. F. J. Hollander, staff crystallographer at the UC Berkeley X-ray crystallographic facility (CHEXRAY).

Supplementary Material Available: Spectroscopic and analytical data for complexes **1**, **1-d_4**, **3**, **4**, **5**, **7**, **9**, and **10** and details of the structure determination for complex **1**, including experimental description, ORTEP drawings showing full atomic numbering and packing in the crystal, and tables of crystal and data collection parameters, general temperature factor expressions (B's), positional parameters and their estimated standard deviations, root-mean-square amplitudes of anisotropic displacements, intramolecular distances and angles, and least-squares planes (18 pages); tables of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

Synthesis, Structure, and Reactivity of a Monomeric Pentamethylcyclopentadienyliridium(III)-Imido Complex

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We wish to report a simple, direct synthesis of Cp*IrNBu^t (Cp* = η^5-C_5Me_5). Despite its low formal oxidation state and coordination number, this Ir(III) compound is a monomer, as demonstrated by the first X-ray diffraction study on a group 9–11 terminal imido complex. It also exhibits unique reactivity at the MN linkage.[1,2]

Treatment of $[Cp^*IrCl_2]_2$[3] with 4 equiv of LiNHBu^t in tetrahydrofuran affords the complex Cp*IrNBu^t, **1**, as yellow crystals in 80–90% yield. The reaction can be run on a 1 g scale; formation of the byproduct Bu^{t}NH$_2$ was confirmed by gas chromatography. In the ^{1}H NMR spectrum, the signal due to the *tert*-butyl methyl protons of **1** appears as a triplet (J = 1.6 Hz) as a result of coupling to ^{14}N. This coupling is characteristic of axially symmetric electron density at the nitrogen nucleus, as has been observed previously in imido complexes and in alkyl isonitriles, and suggests a linear M–N–C linkage.[4] Complex **1** also displays an IR stretching absorption characteristic of the imido ligand at 1258 cm^{-1} (the exact assignment must await ^{15}N labeling studies[5]) and was further characterized by ^{13}C NMR spectrometry and elemental analysis. The mass spectrum shows molecular ions at m/e 399 and 397 for the two iridium-containing isotopomers.

The monomeric nature of **1** suggested by the ^{1}H NMR and mass spectra was confirmed by an X-ray diffraction study performed on a single yellow, blocky crystal obtained by crystallization from pentane at −30 °C.[6] As shown in the ORTEP diagram included in Scheme I, complex **1** adopts a "one-legged piano stool" or "pogo-stick" geometry. The nearly linear Ir–N–C angle (177.2 (5)°) is consistent with Ir–N multiple bonding; the short Ir–N bond length (1.712 (7) Å) is similar to the value (1.68 Å) predicted by Nugent and Haymore for an Ir–N triple bond.[7] We therefore suggest that the strong π-donor imido ligand functions formally as a four-electron donor, making **1** an 18-electron complex.

Complex **1** undergoes a number of unprecedented reactions. In contrast to the behavior of the transient iridium–imido complex[8] $[Ir(NH_3)_5NH]^{3+}$, **1** is nucleophilic at nitrogen: it reacts with an excess of methyl iodide to form $[Cp^*IrI_2]_2$[9] and $[Me_3NBu^t]^+I^-$.[10] The imido complex interacts with 2 equiv of *tert*-butyl isocyanide to form $Cp^*Ir(CNBu^t)(C(NBu^t)_2)$, **2**, in which one isocyanide has added across the Ir–N multiple bond to form a carbodiimide,[11] and the resulting 16-electron complex has been trapped by another isocyanide. Addition of 1 equiv of isocyanide affords a 1:1 mixture of **1** and **2**. Similarly, compound **1** undergoes a coupling-trapping reaction with 2 equiv of CO to form the carbonyl isocyanate complex **3** [ν_{CO} = 1956 and 1801 cm^{-1}; ^{13}C NMR δ 174.68 and 143.46 ppm].

Metal carbenes are known to undergo [2 + 2] cycloadditions with unsaturated substrates to form metallacycles.[12] Despite the isoelectronic nature of the imido and carbene ligands, this is a novel type of reaction for metal–imido complexes.[13] Reaction of **1** with carbon dioxide in pentane solution yields red crystals of **4**. This material exhibits spectral properties consistent with the structure illustrated in Scheme I [IR ν_{CO} = 1708 cm^{-1} (C_6H_6 solution); ^{13}C NMR δ 170.92 for the CO_2 carbon; MS parent ion at m/e 443/441]. Crystals of **4** suitable for X-ray analysis were obtained by vapor diffusion of hexamethyldisiloxane into toluene at −30 °C.[14] The structure demonstrates that formal [2 + 2]

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(2) For examples of imido compounds of the late (groups 9–11) transition metals see: monomeric complexes with terminal imido ligands: (a) Ashley-Smith, J.; Green, M.; Mayne, N.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1969**, 409. (b) McGlinchey, M. J.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1970**, 1265. (c) Ashley-Smith, J.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1972**, 1805. Dimeric μ_2 bridging complexes: (d) Meij, R.; Stufkens, D. J.; Vrieze, K.; Brouwers, A. M. F.; Overbeek, A. R. *J. Organomet. Chem.* **1978**, *155*, 123. (e) Sharp, P. R.; Ge, Y.-W. *J. Am. Chem. Soc.* **1987**, *109*, 3796. μ^3-Bridging trimeric clusters: (f) Otsuka, S.; Nakamura, A.; Yoshida, T. *Inorg. Chem.* **1968**, *7*, 261. (g) Muller, J.; Dorner, H.; Kohler, F. H. *Chem. Ber.* **1973**, *106*, 1122. (h) Abel, E. W.; Blackmore, T.; Whitley, R. S. *Inorg. Nucl. Chem. Lett* **1974**, *10*, 941. (i) Gall, R. S.; Connelly, N. G.; Dahl, L. F. *J. Am. Chem. Soc.* **1974**, *96*, 4017. (j) Bedard, R. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1986**, *108*, 5942. (k) Wakatsuki, Y.; Okada, T.; Yamazaki, H.; Cheng, C. *Inorg. Chem.* **1988**, *27*, 2958.

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(5) Osborne, J. H.; Trogler, W. C. *Inorg. Chem.* **1985**, *24*, 3098.

(6) The X-ray diffraction study was carried out at the University of California, Berkeley, X-ray diffraction facility (CHEXRAY). Crystal data: *Pbcm*, V = 1528.2 (7) Å^3, Mo Kα λ = 0.71073 Å, μ_{calcd} = 86.8 cm^{-1}, d_{calcd} = 1.73 g cm^{-3}, a = 9.3284 (16) Å, b = 13.2916 (19) Å, c = 12.3250 (19) Å, T = 25 °C, Z = 4; the final residuals for 83 variables refined against the 873 data for which $F^2 > 3\sigma(F^2)$ were R = 2.06%, wR = 2.60%, and GOF = 1.168. The R value for all 1053 data was 3.32%. Details of the structure determination are provided as Supplementary Material.

(7) Reference 1c, p 134. This number was estimated using Pauling's relative metallic sizes and the typical Re$\equiv$NR bond length of 1.69 Å.

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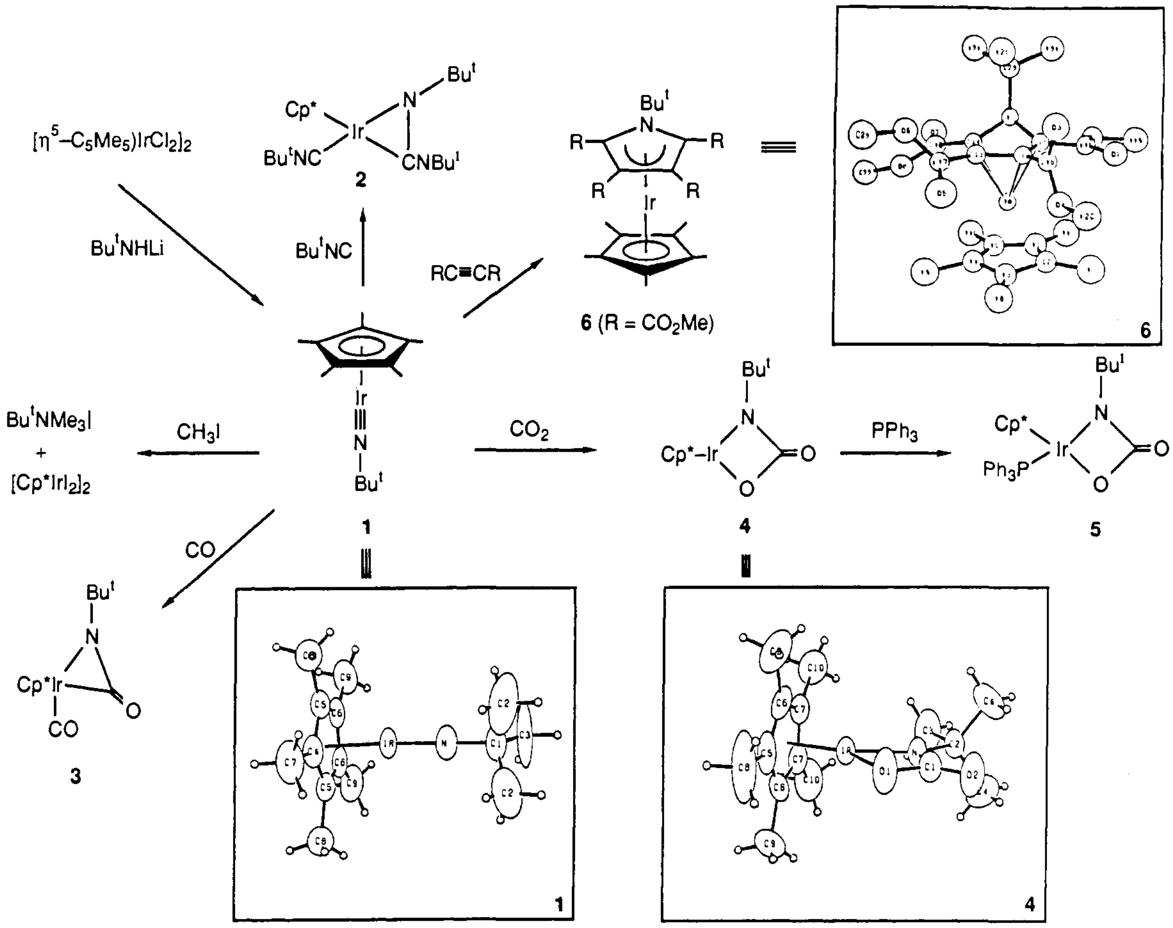
Scheme I



cycloaddition has occurred to give a four-membered metallacycle; an ORTEP diagram is included in Scheme I. As expected, the Ir–N bond has lengthened (to 1.943 (6) Å), and the Ir–N–C angle has decreased (to 141.6 (5)°) upon cycloaddition with CO_2. The N–C bond length increases (from 1.447 (11) to 1.488 (9) Å). All of these observations are consistent with a decrease in Ir–N bond order and a change in hybridization at nitrogen from sp to sp^2. Metallacycle **4** is formally a 16-electron species, but donation of the N lone pair electrons to the Ir center may provide some Ir–N double bond character. The coordinatively unsaturated nature of **4** is demonstrated by its reaction with PPh_3 to give the 18-electron adduct **5**.[15]

The imido compound **1** does not react with 1-phenylpropyne or 2-butyne even at 85 °C, but it does readily add 2 equiv of dimethyl acetylenedicarboxylate at room temperature. The stoichiometry of this reaction was determined by integration of the carboxylate methyl signals in the ^1H NMR spectrum and confirmed by elemental analysis and mass spectrometry. The ^1H NMR spectrum of this 1:2 adduct from 20 to −70 °C shows two signals for the carboxylate methyl protons. The ^{13}C NMR spectrum contains signals due to the pairs of inequivalent carbonyl, carboxylate, and acetylenic carbons. The IR spectrum is not well resolved in the carbonyl region, but a strong peak at 1723 cm^{-1} with a shoulder at 1703 cm^{-1} is observed. A single-crystal X-ray diffraction study, performed on a yellow platelike crystal of the complex obtained from diffusion of hexamethyldisiloxane into toluene at −30 °C, demonstrated that it is compound **6** (Scheme I) in which the two molecules of alkyne have combined with the NBu^t group to form a complexed pyrrole to which the Cp*Ir fragment is bound in an η^4 fashion; the Ir and N are no longer within bonding distance.[16] The net result of this reaction, then, is the formation of a C–C bond and two C–N bonds, with the cleavage of an Ir–N triple bond.[17]

The fact that imido complex **1** is monomeric and shows no tendency to dimerize requires reevaluation of previous ideas about the stability of complexes formed by binding reactive organic fragments to the Cp*Ir center. These results provide further encouragement that related species, such as iridium oxo or phosphinidene[18] complexes may be detectable or even isolable with the appropriate ancillary ligands attached to the metal. Efforts to explore these possibilities as well as further studies of **1** and related late transition metal imido complexes are continuing.

Acknowledgment. We are grateful for financial support of this work from the National Institutes of Health (Grant No.

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(15) For another recent example of "bifunctional" CO_2 activation, see: Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1985**, *107*, 2985. For other references, see: (a) Darensbourg, D. J.; Kudaroski, R. A. *Adv. Organomet. Chem.* **1983**, *22*, 129. (b) Ziessel, R. *Nouv. J. Chim.* **1983**, *7*, 613. (c) Behr, A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 661.

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GM25459) and for a loan of $IrCl_3·3H_2O$ from the Johnson Matthey Co.

Supplementary Material Available: Spectroscopic and analytical data for complexes **1–6**, details of the structure determination for complexes **1** and **4**, including experimental description and ORTEP drawings showing full atomic numbering and packing in the crystal, and tables of crystal and data collection parameters, general temperature factor expressions (*B*'s), positional parameters and their estimated standard deviations, and intramolecular distances and angles (29 pages); tables of observed and calculated structure factors for **1** and **4** (14 pages). Ordering information is given on any current masthead page.

Total Synthesis of (−)-Eudistomin L and (−)-Debromoeudistomin L

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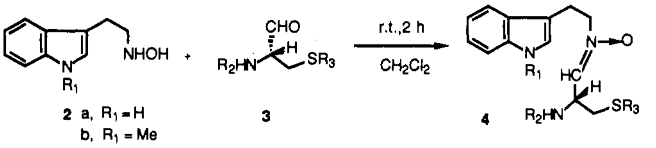
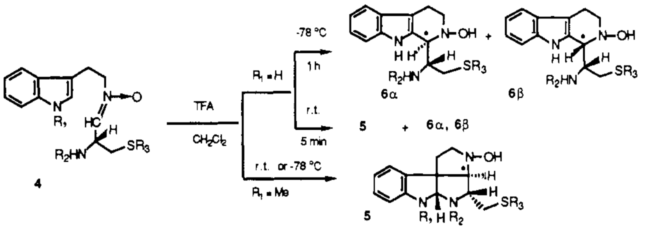
In 1984, Rinehart and Kobayashi reported the isolation of the first naturally occurring tetrahydro-β-carbolines incorporating an oxathiazepine ring, the eudistomins **1a–d** (Scheme III) from the colonial tunicate *Eudistoma olivaceum*.[1] More recently, the sulfoxide of eudistomin K[2] and the unsubstituted eudistomin **1e**[3] were isolated from *Ritterella sigillinoids*. These compounds display potent activity against *Herpes simplex* virus, type 1 (HSV-1). This fact, coupled with the unusual structural features, has attracted interest in **1** as a synthetic target and several groups have reported preliminary results.[4]

We wish to report the first total synthesis of (−)-eudistomin L (**1a**) and (−)-debromoeudistomin L (**1e**) in an optically pure form possessing the natural configuration. We have recently reported preliminary results on the Pictet–Spengler (PS) reaction of N_b-hydroxytryptamines **2** with the cysteinals **3**.[4e] Further investigations disclosed that the optically active nitrones **4**[5] can be isolated as the first intermediates of the PS reaction when **2** is reacted with L-cysteinal **3** (CH_2Cl_2, room temperature) (Scheme I, Table I).

Scheme I



Scheme II



Scheme III

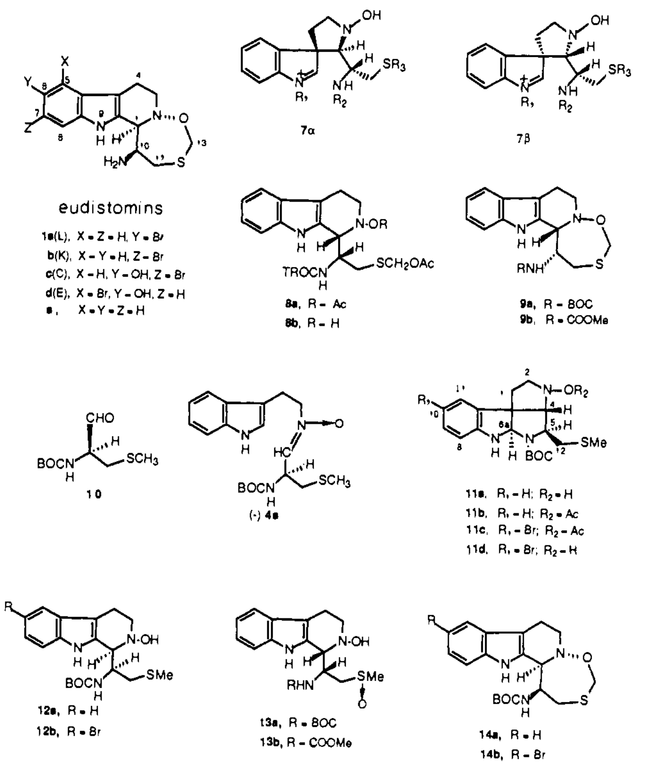


Table I. Isolation of the Optically Active Nitrones **4**

entry	**4**	R_1	R_2	R_3	yield (%)	$[\alpha]_D{}^a$ (deg)	mp (°C)
1	a	H	COOMe	Me	97.0	+56.9	
2	b	H	TROC	CBZ	77.6	+21.1	
3	c	H	BOC	TROC	96.7	+35.5	
4	d	H	TROC	Me	92.0	+41.0	
5	e	H	BOC	Me	92.8	+67.3	135.5–136.5
6	f	Me	COOMe	TROC	95.4	+30.0	96–97

[a] In MeOH.

When **4** (R_1 = H) was treated with trifluoroacetic acid (TFA, room temperature), the corresponding tetracyclic compounds **5** were obtained together with the normal PS reaction product, tetrahydro-β-carbolines **6** (Scheme II, Table II, entries 8–11), whereas at low temperature, **6** were the only products isolated, and, none of 5 was detected (Table II, entries 1–7). The compounds **5** were obtained as a single isomers, while **6** were obtained as a mixture of two diastereoisomers **6α** and **6β** with high diastereoselectivity for **6β**. On the other hand, **4** (R_1 = Me) gave **5** regardless of the reaction temperature (Table II, entries 12–15). Subsequent treatment of **5** (R_1 = H) with TFA in CH_2Cl_2 afforded **6α** and **6β**. The stereochemistry of *C position is reversed in the major carboline **6β** in contrast to that of **5**.[4e] Unlike **5** (R_1 = H), **5** (R_1 = Me) does not rearrange to **6**, and the nitrone **4** (R_1 = Me, R_2 = COOMe, R_3 = MEM) was isolated (30%) when **5** (R_1 = Me, R_2 = COOMe, R_3 = MEM) was treated with $ZnBr_2$. We believe that the mechanism of this PS reaction is qualitatively similar to the known mechanism[6] which proceeds through the

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