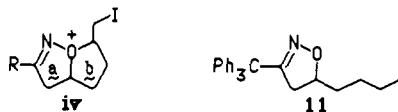


Bromine, like iodine, promotes electrophilic cyclization of isoxazoline **1**, whereas phenylselenenyl bromide does not (Table I). In contrast, isoxazoline **3** does undergo phenylselenenyl bromide promoted cyclization, again favoring the *cis* tetrahydrofuran product. Iodine promoted cyclizations of isoxazolines **9** (prepared from $\text{MeCH}(\text{OSiMe}_3)\text{CH}_2\text{NO}_2$ by dehydration with phenylisocyanate)¹⁴ and **10** (prepared from *i*-PrCH(OSiMe₃)CH₂NO₂ by dehydration with phenylisocyanate)¹⁴ also furnished tetrahydrofurans **4** and **5** but with disappointing diastereoselectivity.

While it is not clear how the R group in **ii** delegates stereoselectivity in the subsequent electrophilic cyclization, the observed chemistry is consistent with formation of isoxazolinium intermediate **iv**. Depending upon the R group, intermediate **iv** could then undergo a-ring fragmentation—either with loss (i.e., **iv** → **4** + **5**) or migration (i.e., **iv** → **6** or **8**) of R—to the observed iodocyclization products. The intermediacy of **iv** may also account

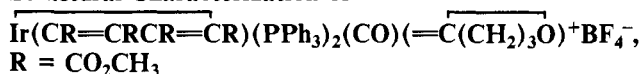


for the observed stereoselectivities: for example, the triphenylmethyl group may accommodate reversible addition of the isoxazoline moiety to an initially formed iodonium ion, whereas the (3-trimethylsilyl)isoxazoline may undergo nonreversible addition. As demonstrated with **11**, isoxazolines lacking the pendant C=C are stable to the iodocyclization conditions employed (I₂/CH₂Cl₂, 25 °C or 40 °C, 8 h) indicating that iodonium ion formation precedes a-ring fragmentation in these iodocyclizations. Current efforts are directed toward elucidating the relative importance of these and other effects in determining the stereochemical course of this novel transformation.

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The First Stable Metallacycle-Carbene Complexes: Structural Characterization of



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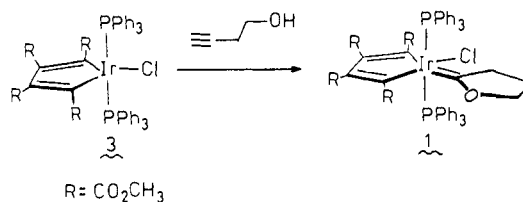
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Metallacyclopentadiene complexes are demonstrated or proposed intermediates in numerous metal-mediated cyclization reactions of acetylenes.¹ Although metallacycles have been extensively utilized as synthetic intermediates, surprisingly little is

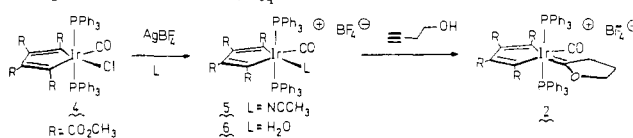
known about the structure and properties of metallacycles which contain an additional η^1 -bonded carbon ligand.² Such species have potential for the development of new modes of metallacycle reactivity.

We recently initiated a program designed to combine the metallacycle and carbene compound classes into a single mononuclear material in an effort to modify and/or couple their unique reactivities.³ Of particular interest in this regard is insertion of a carbene ligand into a metallacycle and subsequent reductive-elimination to give cyclopentadiene products. We report herein the synthesis and structural characterization of the first isolable metallacycle-carbene complexes: $\text{Ir}(\text{CR}=\text{CRCR}=\text{CR})\text{-(PPh}_3)_2(\text{Cl})(=\text{C}(\text{CH}_2)_3\text{O})$, **1** (R = CO₂CH₃)₄ and $\text{Ir}(\text{CR}=\text{CRCR}=\text{CR})(\text{PPh}_3)_2(\text{CO})(=\text{C}(\text{CH}_2)_3\text{O})^+\text{BF}_4^-$, **2** (R = CO₂CH₃).



When a chloroform solution of 3-butyn-1-ol (0.94 mmol) and the coordinatively unsaturated metallacycle $\text{Ir}(\text{CR}=\text{CRCR}=\text{CR})(\text{PPh}_3)_2(\text{Cl})$, **3** (R = CO₂CH₃)₄ [0.8 mmol, 0.02 M], is stirred at 23 °C for 15 h, the neutral metallacycle-carbene complex $\text{Ir}(\text{CR}=\text{CRCR}=\text{CR})(\text{PPh}_3)_2(\text{Cl})(=\text{C}(\text{CH}_2)_3\text{O})$, **1**, is formed in good yield (81% isolated).⁵ In the ¹³C{¹H} NMR spectrum of **1** a triplet at δ 286 (*J*_{PC} = 6 Hz) is assigned to the carbene carbon and two pseudo triplets at δ 152.4 (*J* = 7.0, 6.6 Hz) and 148.8 (*J* = 12.0, 12.6 Hz) are attributed to the metallacycle carbons bonded to iridium.⁶

Treatment of an acetonitrile solution of the coordinatively saturated metallacycle $\text{Ir}(\text{CR}=\text{CRCR}=\text{CR})(\text{PPh}_3)_2(\text{CO})(\text{Cl})$, **4** (R = CO₂CH₃)₄ with AgBF₄ leads to formation of the cationic metallacyclopentadiene complex $\text{Ir}(\text{CR}=\text{CRCR}=\text{CR})\text{-(PPh}_3)_2(\text{CO})(\text{CH}_3\text{CN})^+\text{BF}_4^-$, **5**, in 90% isolated yield.⁷ In a similar manner, reaction of **4** with AgBF₄ in THF (aqueous) gives the aquo complex $\text{Ir}(\text{CR}=\text{CRCR}=\text{CR})(\text{PPh}_3)_2(\text{CO})(\text{H}_2\text{O})^+\text{BF}_4^-$, **6**, in 70% isolated yield.⁷ In the presence of H₂O, **5** exists in equilibrium with **6** (*K*_{eq}^{23°C} = 4.2 × 10⁻³).



When a methylene chloride solution of **5** (0.5 mmol, ~0.02 M) and 3-butyn-1-ol (0.6 mmol) is refluxed for 12 h, a nearly quantitative yield (96%) of the cationic metallacycle-carbene

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(6) The relatively high field chemical shift of these latter two resonances rules out an alternative metallacyclopentatriene formulation as recently reported by Singleton for $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CPhCHCHCPh})(\text{Br})$. Albers, M. O.; de Waal, D. J. A.; Liles, D. C.; Robinson, D. J.; Singleton, E.; Wiege, M. B. *J. Chem. Soc., Chem. Commun.* **1986**, 1680.

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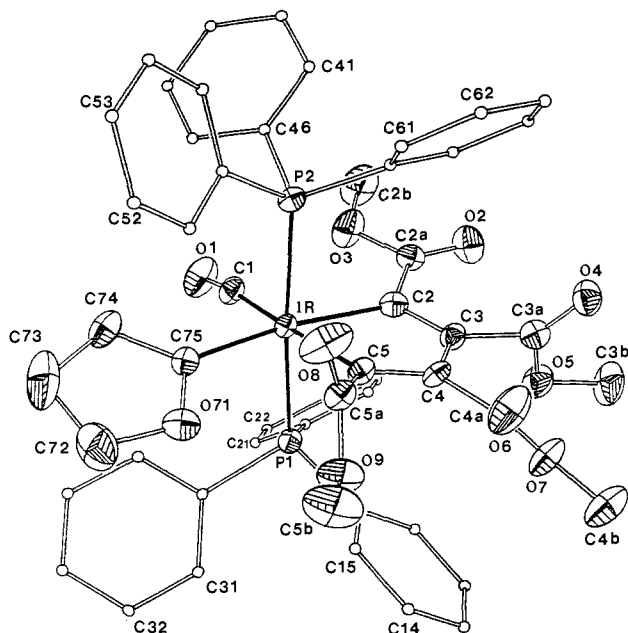


Figure 1. Molecular structure and labeling scheme for **2**: Ir-P(1), 2.445 (2); Ir-P(2), 2.403 (2); Ir-C(1), 1.925 (8); Ir-C(2), 2.108 (7); Ir-C(5), 2.101 (7); Ir-C(75), 2.025 (7); C(2)-C(3), 1.33 (1); C(3)-C(4), 1.48 (1); C(4)-C(5), 1.33 (1) Å; P(1)-Ir-P(2), 172.6 (1); P(1)-Ir-C(1), 84.7 (2); P(1)-Ir-C(2), 85.0 (2); P(1)-Ir-C(5), 91.5 (2); P(1)-Ir-C(75), 91.6 (2); P(2)-Ir-C(1), 92.8 (2); P(2)-Ir-C(2), 88.4 (2); P(2)-Ir-C(5), 90.3 (2); P(2)-Ir-C(75), 95.4 (2); C(1)-Ir-C(2), 96.1 (3); C(1)-Ir-C(5), 172.7 (3); C(1)-Ir-C(75), 91.5 (3); C(2)-Ir-C(5), 77.4 (3); C(2)-Ir-C(75), 171.3 (3); C(5)-Ir-C(75), 94.8 (3); Ir-C(2)-C(3), 114.9 (5); C(2)-C(3)-C(4), 115.3 (6); C(3)-C(4)-C(5), 115.9 (6); C(4)-C(5)-Ir, 115.2 (5)°.

Ir(CR=CR=CR)(PPh₃)₂(CO)(=C(CH₂)₃O)⁺BF₄⁻, **2**, is obtained following workup. Similar reaction with **6** at 23 °C also generates **2**. In the ¹³C{¹H} NMR spectrum (CDCl₃) of **2**, pseudo triplets are observed at δ 171 (*J* = 6, 8 Hz), 161 (*J* = 9, 12 Hz), and 140 (*J* = 8, 11 Hz). The analogous ¹³CO-labeled complex allows assignment of the δ 171 resonance to the carbon atom of the CO ligand. In the ³¹P{¹H} NMR spectrum of **2**, a singlet is observed at δ 11.0 which requires either a plane of symmetry containing the 2-oxacyclopentylidene ligand or rapid rotation about the iridium-carbene bond. We were unable to observe line broadening in the ¹H NMR resonances of the 2-oxacyclopentylidene ligand between -80 °C and +80 °C.

In order to structurally characterize this new class of metallacycle complex, a single-crystal X-ray diffraction study was performed on **2** (Figure 1).⁸ The complex deviates from ideal octahedral geometry with the C(2)-Ir-C(5) angle constrained by the metallacycle ring to 77.4 (3)° and the trans PPh₃ ligands bent away from the carbene ligand toward C(2) of the metallacycle. The Ir-C(2) and Ir-C(5) bond distances of 2.108 (7) and 2.101 (7) Å are significantly longer than the 2.054 (4) Å Ir-C distance reported by Bergman for (η⁵-C₅Me₅)Ir(PMe₃)(H)(CH=CH₂).⁹ In **2**, the plane of the 2-oxacyclopentylidene ligand bisects the plane

(8) Crystal data for **2** (293 K): C₂₃H₄₈IrO₁₀P₂BF₄, monoclinic, *Cc*, *a* = 12.723 (2) Å, *b* = 21.195 (4) Å, *c* = 18.432 (3) Å, β = 90.37 (1)°, *V* = 4970 (1) Å³, *Z* = 4, *D*_{calc} = 1.585 g cm⁻³, μ = 29.8 cm⁻¹. A pale pink specimen (0.30 × 0.31 × 0.34 mm) was used for data collection (Nicolet R3m/μ, 4° ≤ 2θ ≤ 52°, Mo Kα). Of 5178 reflections collected, 5041 were independent (*R*_{int} = 1.8%), and 4748 with *F*_o ≥ 3σ(*F*_o) were considered observed and empirically corrected for absorption (*T*_{max}/*T*_{min} = 0.370/0.324). The Ir atom was located by heavy atom methods. During the final refinement the BF₄⁻ ion was constrained to a tetrahedral geometry with a common, refined B-F distance (1.222 (7) Å, ~0.13 Å shorter than normal), and the phenyl rings were constrained to rigid hexagonal rings. With all non-hydrogen atoms anisotropically refined and hydrogen atoms treated as idealized isotropic contributions: *R*(*F*) = 3.11%, *R*(w*F*) = 3.76%, all data *R*(*F*) = 3.47%, *GOF* = 1.018, Δ/*σ* = 0.08, Δ(ρ) = 1.8 eÅ⁻³ (0.90 Å from Ir), and *N*_o/*N*_v = 8.34. All computer programs and sources of scattering factors are contained in the SHELXTL program library (Nicolet Corp., Madison, WI).

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of the metallacycle at an angle of 24°.¹⁰

Further reactivity of these unprecedented metallacycle-carbene complexes is currently under exploration with an emphasis on methods for inducing formation of cyclopentadiene products.

Acknowledgment. Partial support from the Monsanto Company and the Academic Senate at the University of California, San Diego is gratefully acknowledged.

Supplementary Material Available: Tables of analytical, NMR, and IR spectroscopic data for all new compounds, listings of fractional coordinates, bond distances, bond angles, hydrogen atom coordinates, and thermal parameters (8 pages); table of observed and calculated structure factors (30 pages). Ordering information is given on any current masthead page.

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Measurement of High-Resolution NMR Spectra in an Inhomogeneous Magnetic Field

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Low homogeneity of the static magnetic field results in a broadening of the nuclear magnetic resonance (NMR) spectral transitions; this precludes NMR spectral analyses based upon the interpretation of the familiar NMR parameters, chemical shifts, and scalar coupling constants. Possible solutions to this problem can involve use of either zero-quantum coherence¹⁻⁴ (ZQC), or, alternatively, the *N*-type peaks produced by the SECSY experiment,^{5,6} for which the line widths are independent of magnetic field inhomogeneity. However, neither technique produces the conventional spectrum of a spin system. A third alternative, which has been demonstrated for partially orientated liquids, uses total spin coherence transfer echoes^{7,8} to produce the conventional spectrum of a spin system. Unfortunately, this elegant technique has two disadvantages which limit its application in isotropic liquids: at least one spin must be coupled to *all* the other spins in a given spin system to create the total spin coherence upon which the technique depends; furthermore, the more spins there are active in a coherence, the lower is the intensity with which it will be excited. Together these two considerations usually impose a practical upper limit of four to the number of spins active in any one coherence in an isotropic liquid. All three of the above options involve two-dimensional experiments,⁹ and in each case only the F1 dimension is independent of magnetic field inhomogeneity.

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