[2 + 2 + 1] Alkyne Cyclotrimerizations: A Metallacyclopentadiene Route to Fulvenes

Joseph M. O'Connor,* Kristin Hiibner, Rich Merwin, Peter K. Gantzel, and Bella S. Fong

Department of Chemistry (0358), 9500 Gilman Drive
University of California, San Diego
La Jolla, California 92093-0358

Melanie Adams and Arnold L. Rheingold*

Department of Chemistry, University of Delaware
Newark, Delaware 19716

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Metal-mediated [2 + 2 + 2] cyclotrimerization of alkynes to produce aromatic six-membered rings is now established as an important route toward natural products and novel organic materials.[1] In sharp contrast, reports of [2 + 2 + 1] cyclotrimerization of alkynes to produce the thermodynamically less stable fulvene products are exceedingly rare (Scheme 1).[2,3] In principle, metallacyclopentadiene complexes may serve as intermediates for both types of cycloaddition reactions. Direct carbocycle formation from an η^2-alkyne-metallacyclopentadiene intermediate gives benzene product whereas an η^2-alkyne to vinylidene isomerization followed by carbocycle formation would lead to fulvene product.

Previously, we reported a number of reactions involving iridiacyclopentadienes and terminal alkynes (e.g., **1** to **2**, Scheme 2) that appear to proceed through vinylidene intermediates (**3**).[4] In no case was coupling observed between the vinylidene ligand and the butadiendiyl ligand. Intrigued by the possibility that a facial arrangement of the vinylidene and butadiendiyl ligands would prove to be a more favorable geometry for fulvene formation, we set out to prepare a metallacycle complex of the 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos) ligand and undertake reactivity studies with respect to terminal alkyne substrates. Herein we report the first examples of the desired metallacyclopentadiene to fulvene transformation.

When $(PPh_3)_2Ir[CR{=}CRCR{=}CR]Cl$ (R = CO_2CH_3)[5] (0.96 mmol) and 1,1,1-tris(diphenylphosphinomethyl)ethane (1.2 mmol)

Figure 1. ORTEP drawing of **5** showing selected atom labeling.

Scheme 1

Scheme 2

are heated at reflux for 24 h in toluene (20 mL), the triphos complex $(CH_3C(CH_2PPh_2)_3)Ir[CR{=}CRCR{=}CR]Cl$ (**4**, R = CO_2CH_3) precipitates as a white solid in 95% yield (Scheme 3). Addition of phenylacetylene (0.88 mmol) to a methylene chloride solution of **4** (200 mg, 0.18 mmol, 4.5 mM) and $AgBF_4$ (0.19 mmol) at room temperature (16 h) led to isolation of an orange-red solid (**6**)[6] which was dissolved in wet chloroform and stirred for 1 h to give fulvene complex **5** in 80% isolated yield.[7]

In the ^{1}H NMR spectrum ($CDCl_3$) of **5** a vinyl hydrogen resonance was observed as an apparent triplet at δ 6.28 ($^3J_{PH}$ = 7.0 Hz). A $^{13}C{-}^1H$ heteronuclear correlation 2D NMR experiment (HMQC)[8] established that the hydrogen giving rise to the δ 6.28 resonance in the ^{1}H NMR spectrum is attached to a carbon which resonates at 45.8 ppm ($^2J_{PC}$ = 51.2 Hz, $^1J_{CH}$ = 148 Hz) in the ^{13}C NMR spectrum.[9] The downfield chemical shift of the benzylic hydrogen (δ 6.28) and the 148 Hz carbon−hydrogen coupling constant argue against an agostic interac-

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(3) Cyclotrimerization of 3,3-dimethylbut-1-yne to a fulvene product has been observed with an early metal catalyst: Prof. I. P. Rothwell, personal communication.

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(5) Collman, J. P.; Kang, J. W.; Little, W. F.; Sullivan, M. F. *Inorg. Chem.* **1968**, *7*, 1298.
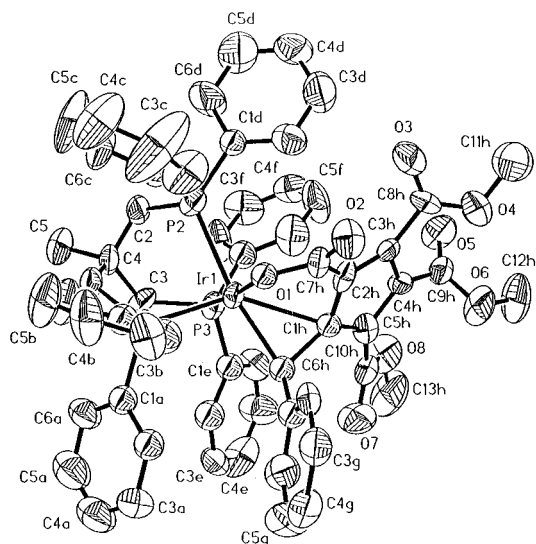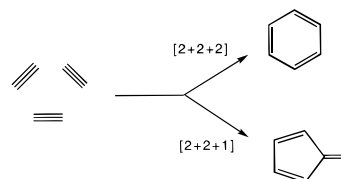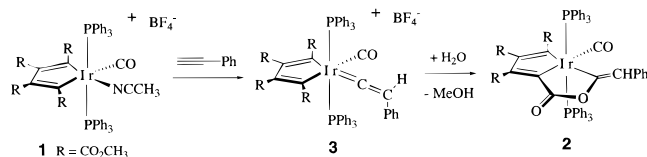
(6) In a ^{1}H NMR tube scale reaction ($CDCl_3$), **4** and phenylacetylene gave rise to a new complex (**6**) that exibits four carboxymethyl singlets at δ 4.03, 3.67, 3.38, and 2.85. Addition of water to the solution cleanly converted **6** to **5** and methanol. We tentatively assign a fulvene structure to **6** as indicated in Scheme 3.

(7) Characterization details are provided as Supporting Information.

(8) Summers, M. F.; Marzilli, L. G.; Bax, A. *J. Am. Chem. Soc.* **1986**, *108*, 4285.

(9) The η^2-ethylene ligand in $(CH_3C(CH_2PPh_2)_3)Ir(\eta^2{-}CH_2{=}CH_2)Cl$ exhibits resonances at δ 1.23 and 2.37 ppm in the ^{1}H NMR spectrum (CD_2Cl_2) and at δ 26.2 ppm in the ^{13}C NMR spectrum (CD_2Cl_2): Barbaro, P.; Bianchini, C.; Meli, A.; Peruzzini, M.; Vacca, A.; Vizza, F. *Organometallics* **1991**, *10*, 2227.

Scheme 3[a]
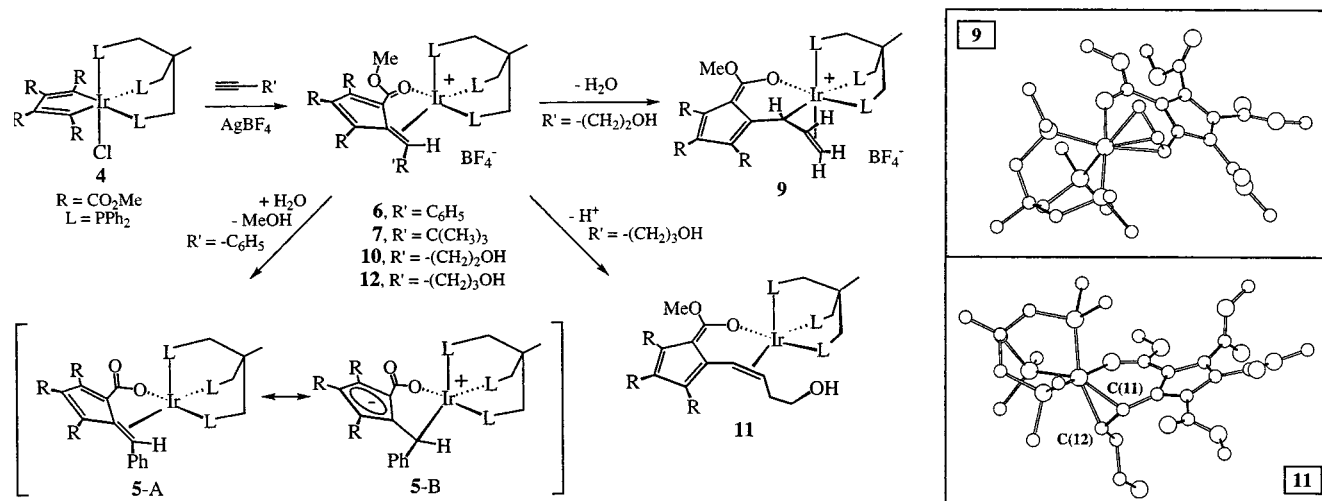
[a] Complexes **6**, **10**, and **12** are intermediates.

tion.[10] When phenyl acetylene-d_1 (PhC≡CD) is employed in a similar reaction with metallacycle **4** and AgBF$_4$, ^{1}H NMR spectroscopic analysis of the product, **5**-d_1, indicates complete (>95%) incorporation of deuterium into the hydrogen site, which gave rise to the δ 6.28 resonance. In the vinyl region of the ^{13}C{^{1}H} NMR spectrum (CDCl$_3$) of **5**, numerous signals are observed for the carbons of the seven nonequivalent phenyl groups and the fulvene ring carbons.

The ambiguous spectroscopic data led us to carry out a single-crystal X-ray diffraction study in order to elucidate the structure for **5** (Figure 1).[7] The complex adopts a distorted T-shaped trigonal bipyramid geometry with P(1), P(2), and the alkene ligand (C(1h), C(6h)) in the equatorial plane. The interplanar angle between the P(2)−Ir−P(1) and C(1h)−Ir−C(6h) planes is 5.7°. The five-membered carbon ring of the fulvene ligand is nearly planar with the largest deviation of the ring atoms from the mean plane at C(3h) (0.02 Å).[11] The Ir−C(1h) distance of 2.403(16) Å, the C(1h)−C(6h) distance of 1.577(25), and the Ir−C(1h)−C(6h) bond angle of 79.9(9)° all point to a major contribution to the ground state structure of **5** from charge-separated resonance structure **5-B**.

When 3,3-dimethylbut-1-yne is employed as the alkyne substrate in reaction with **4** and AgBF$_4$, the cationic fulvene complex **7** is isolated as a bright-orange solid in 77% yield.[7] In the ^{1}H NMR spectrum of **7** (CDCl$_3$) a vinyl hydrogen resonance is observed as an apparent triplet at δ 6.36 (dd, $^3J_{PH}$ = 8.0, 5.5 Hz), and four methyl singlets are observed at δ 4.0, 3.77, 3.37, and 3.21. As was observed for **5**, an HMQC ([13]C−[1]H) NMR experiment established that the hydrogen giving rise to the δ 6.36 resonance in the ^{1}H NMR spectrum is attached to a carbon that resonates upfield at 57.7 ppm ($^2J_{CP}$ = 53.8 Hz, $^1J_{CH}$ = 143 Hz) in the ^{13}C NMR spectrum. We assign a fulvene structure to **7** based on the similarity of the spectroscopic properties to those for **5**.

A reasonable mechanism for the formation of **5** and **7** from **4** involves initial coordination of the alkyne to the metal, rearrangement to a vinylidene ligand, and reductive cyclization to the carbocycle product. In an effort to trap the vinylidene ligand in this system we examined the reactions of 3-butyn-1-ol and 4-pentyn-1-ol with **4**. Previously, we observed the reaction of **1** with 3-butyn-1-ol to give a quantitative yield of the oxacyclopentylidene complex, (PPh$_3$)$_2$(CO)-

Ir[CR=CRCR=CR][=C(CH$_2$)$_3$O]$^+$BF$_4^-$ (**8**, R = CO$_2$CH$_3$).[4] The carbene ligand in **8** is formed by intramolecular trapping of a vinylidene intermediate by the pendent hydroxyl group. Remarkably, when 3-butyn-1-ol is added to a methylene chloride solution of AgBF$_4$ and **4**, the π-allyl complex **9** is formed and isolated as a yellow powder in 48% yield (Scheme 3).[7] The formation of **9** is more complicated than in the case of **5** and **7** due to dehydration of the primary alcohol. In order to circumvent the dehydration we employed 4-pentyn-1-ol in a reaction with **4**/AgBF$_4$ and observed formation of alkene complex **11**,[7] which was isolated in 36% yield. Complex **11** is presumably derived from a fulvene intermediate such as **12**, which undergoes loss of an allylic proton to generate the cis η^2-alkene ligand. The structures of both **9** and **11** were established by X-ray crystallographic analysis (Scheme 3).[12]

The butadiendiyl ligand of **4** was originally derived from 2 equiv of dimethyl acetylenedicarboxylate, thus the net transformations reported here represent [2 + 2 + 1] cyclotrimerization of alkynes to give fulvenoid product, in preference to the aromatic compounds normally formed in alkyne cyclotrimerizations. Preliminary results indicate that the terminal alkyne substituents exert a remarkable influence on the partitioning between [2 + 2 + 1] and [2 + 2 + 2] cycloaddition pathways in the reactions of **4**/AgBF$_4$. Thus, acetylene, propargyl alcohol, and ethyl ethynyl ether all give high yields of [2 + 2 + 2]-derived products from reaction with **4** and AgBF$_4$.[13] Efforts are currently underway to determine the scope and mechanism of these new cyclotrimerization reactions in order to define the parameters that control partitioning between [2 + 2 + 1] and [2 + 2 + 2] cycloaddition pathways.

Supporting Information Available: Characterization data for **4**, **5**, **7**, **9**, and **11** and details of crystal structure determinations, diagrams, listings of fractional coordinates, bond distances, bond angles, hydrogen atom coordinates, and thermal parameters for **5**, **9**, and **11** (41 pages). See any current masthead page for ordering and Internet access instructions.

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(11) Deviations from the C(1h)−C(5h) plane: C(1h) 0.001, C(2h) −0.014, C(3h) 0.022, C(4h) −0.021, C(5h) 0.011, C(6h) −0.054, C(7h) −0.215.

(12) The alkene−iridium bonding in **11** is much more symmetric than that observed for **5**. For **11**: Ir−C(11) 2.166(11) Å, Ir−C(12) 2.123(10) Å, Ir−C(11)−C(12) 68.8(6)°, and Ir−C(12)−C(11) 72.1(6)°.

(13) (a) O'Connor, Hübner, unpublished results. (b) See also: Bianchini, C.; Caulton, K. G.; Chardon, C.; Eisenstein, O.; Folting, K.; Johnson, T. J.; Meli, A.; Peruzzini, M.; Rauscher, D. J.; Streib, W. E.; Vizza, F. *J. Am. Chem. Soc.* **1991**, *113*, 5127.