

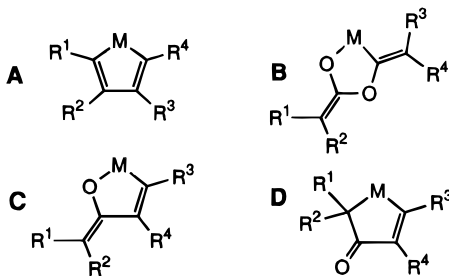
## Selective C–C Bond Formation on the First Ketene–Alkyne Complexes

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Metal  $\pi$ -complexes of alkynes<sup>1</sup> and of ketenes<sup>2</sup> are key intermediates in reactions capable of constructing synthetically challenging organic molecules.<sup>3,4</sup> Metal-mediated redox homocoupling of alkynes (to give metallacyclopentadienes **A**) is a reaction of wide scope at the heart of syntheses of dienes, arenes, heterocycles, and other organic products.<sup>3a,b</sup> Only two isolated reports of ketene homocoupling exist [**B**, M = Ti or Ni, R<sup>1</sup>–R<sup>4</sup> = Ph].<sup>5</sup> Even rarer is ketene–alkyne heterocoupling: the clearest example is limited to the parent compounds, giving **C** (M = Ti, R<sup>1</sup>–R<sup>4</sup> = H),<sup>6</sup> but organic products were not liberated from metallacycle **C**. Certain organic products from reactions of chromium carbene complexes and alkynes could be explained by invoking ketene–alkyne coupling as in **C**<sup>7a</sup> or as in **D**,<sup>7b</sup> although these metallacycles were not observed.



Here we report the chemo-, regio-, and stereoselective coupling of diphenylketene with internal alkynes on Ir(I) to give iridabenzopyrans **8** rather than **C** or **D**. In these reactions, the first ketene–alkyne complexes **3** are formed chemoselectively. Spectral features of **3** point to  $\eta^2$ -arene coordination, explaining

(1) Lewandos, G. S. In *The Chemistry of the Metal–Carbon Bond*; Hartley, F., Patai, S., Eds.; Wiley: New York, 1982; Vol. 1, Chapter 7, pp 287–323.

(2) (a) Geoffroy, G. L.; Bassler, S. L. *Adv. Organomet. Chem.* **1988**, *28*, 1. (b) Hofmann, P.; Perez-Moya, L. A.; Steigelmann, O.; Riede, J. *Organometallics* **1992**, *11*, 1167 and references therein.

(3) (a) Cyclotrimerization: Grotjahn, D. B. In *Comprehensive Organometallic Chemistry II*; Hegedus, L. S., Ed.; Pergamon, 1995; Vol. 12, Chapter 7.3, pp 741–770. (b) Reductive dimerization of alkynes: Broene, R. D. In *Comprehensive Organometallic Chemistry II*; Hegedus, L. S., Ed.; Pergamon; Oxford, 1995; Vol. 12, Chapter 3.7, pp 323–348. (c) Pauson–Khand cyclization: Schore, N. E. In *Comprehensive Organometallic Chemistry II*; Hegedus, L. S., Ed.; Pergamon; Oxford, 1995; Vol. 12, Chapter 7.2, pp 703–740.

(4) Ketene complexes from carbene complexes: (a) Wulff, W. D. In *Comprehensive Organometallic Chemistry II*; Hegedus, L. S., Ed.; Pergamon; Oxford, 1995; Vol. 12, Chapter 5.3, pp 469–548. (b) Hegedus, L. S. In *Comprehensive Organometallic Chemistry II*; Hegedus, L. S., Ed.; Pergamon; Oxford, 1995; Vol. 12, Chapter 5.4, pp 549–576. (c) Dötz, K.-H. In *Organometallics in Organic Synthesis*; de Meijere, A., tom Dieck, H., Eds.; Springer: Berlin, 1988. (d) Harvey, D.F.; Grenzer, E. M.; Gantzel, P. K. *J. Am. Chem. Soc.* **1994**, *116*, 6719. (e) Merlic, C. A.; Xu, D.; Gladstone, B. G. *J. Org. Chem.* **1993**, *58*, 538.

(5) (a) Fachinetti, G.; Biran, C.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1978**, *100*, 1921. (b) Hoberg, H.; Korff, J. *J. Organomet. Chem.* **1978**, *152*, C39.

(6) Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 5499. Vinylketene complexes of other metals can react with alkynes: Huffman, M. A.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1990**, *112*, 8617. Anderson, B. A.; Wulff, W. D.; Rheingold, A. L. *Ibid.*, **1990**, *112*, 8615.

(7) (a) Bao, J.; Wulff, W. D.; Dragisch, V.; Wenglowy, S.; Ball, R. S. *J. Am. Chem. Soc.* **1994**, *116*, 7616. (b) Xu, Y.-C.; Challener, C. A.; Dragisch, V.; Brandvold, T. A.; Peterson, G. A.; Wulff, W. D.; Willard, P. G. *J. Am. Chem. Soc.* **1989**, *111*, 7269. We thank a reviewer for bringing these examples to our attention.

facile regioselective C–H activation of the ketene phenyl substituent and ultimately, coupling of ketene and alkyne to give **8**.

Warming of either diphenylketene complex **1**<sup>8</sup> (Scheme 1) with alkyne **2** or of diphenylketene **4** with alkyne complex **5**<sup>9</sup> led to a mixture containing free P(*i*-Pr)<sub>3</sub> and the monophosphine complex **3** in a molar ratio of 1:1.<sup>10</sup> A series of NMR experiments implicate the formulation shown for **3**.<sup>11</sup> For example, by using 2D NMR, resonances for all 10 aryl protons of **3a** could be found between 6.98 and 8.25 ppm, showing that C–H activation (*vide infra*) had not yet occurred. Inequivalent alkyne CH<sub>3</sub> groups were revealed by sharp three-proton singlets at  $\delta$  1.95 and 2.33 ppm. HMBC (<sup>1</sup>H, <sup>13</sup>C) showed that the acetylenic carbons resonated at 164.79 (d, *J* = 9.1 Hz) and 144.07 (s) ppm.<sup>12</sup> These data and a second narrow <sup>13</sup>C{<sup>1</sup>H} doublet at 118.74 (d, *J* = 4.9 Hz) due to a ketene carbon verify the presence of one phosphine, *cis* to both ketene and alkyne.<sup>12</sup> The acetylenic carbons in **3a** appear far downfield from those in **5a** ( $\delta$  56.83), consistent with replacement of *trans*-Cl in **5a** with the  $\pi$ -acid ketene. Binding of the ketene to Ir in **3a** is implicated by a significant cross peak in the HMBC spectrum between the C=C=O carbon at 204.87 ppm and the alkyne protons at 1.95 ppm, and the chemical shifts of the C=C=O carbons are more consistent with coordination to the C=C bond.<sup>13</sup> Finally, and most significantly,  $\eta^2$ -binding of the metal to the ipso and ortho carbons of one ketene C<sub>6</sub>H<sub>5</sub> substituent is indicated by two sets of data: (1) the upfield shifts of the ortho proton resonances [ $\delta$  6.98 *vs* 8.25 ppm for those on the uncoordinated ring]; (2) the upfield shifts and splitting of the ipso and ortho carbon resonances [coordinated ring, ipso  $\delta$  118.42–118.60 (narrow unresolved m), ortho 118.74 (d, *J* = 4.9 Hz); uncoordinated ring, ipso 142.82 (s) and ortho 130.99 (s)]. The equivalence of the ortho and meta protons and carbons on the coordinated C<sub>6</sub>H<sub>5</sub> ring implies a rapid rotation of the ring, as documented in some other  $\eta^2$ -arene complexes.<sup>14</sup> Similar spectroscopic properties were seen for other ketene–alkyne complexes **3**. As alkyne displaces P(*i*-Pr)<sub>3</sub> from **1** to give **3**, the profound change in ketene binding, particularly  $\eta^2$ -arene coordination, presages regioselective C–H bond activation<sup>15</sup> of the ketene at an ortho position.

(8) Grotjahn, D. B.; Lo, H. C. *Organometallics* **1995**, *14*, 5463.

(9) Complexes of terminal alkynes to ClIr[P(*i*-Pr)<sub>3</sub>]<sub>2</sub>: Höhn, A.; Werner, H. *J. Organomet. Chem.* **1990**, *382*, 255.

(10) The combination of **4** and **5** produced **3** much more rapidly than when **1** and **2** were mixed. Isolation of **3** was not possible because of its further reactions.

(11) See Supporting Information.

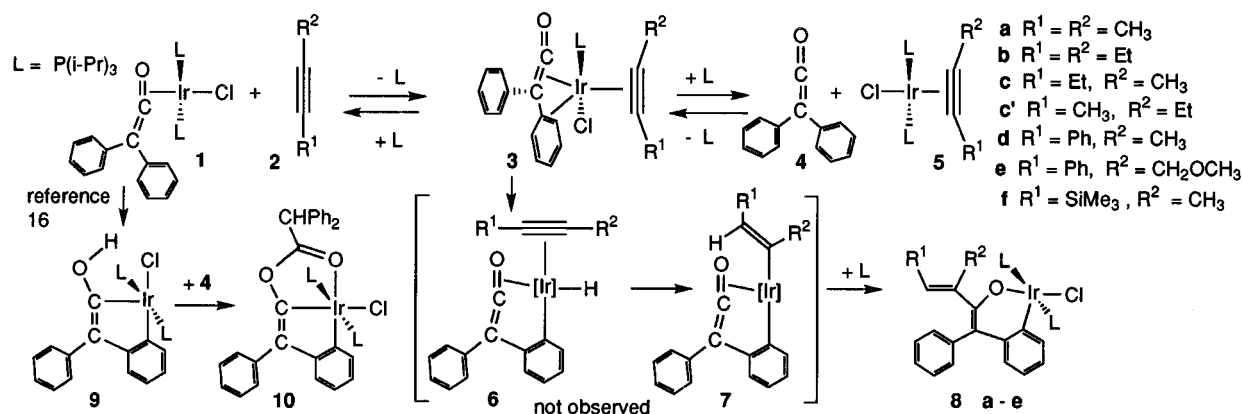
(12) (a) In ( $\eta^3$ -P,P,P-triphos)Ir(H)(PhCCH),<sup>12b</sup> the alkyne is clearly a two-electron donor and *trans* to one phosphine: <sup>13</sup>C NMR  $\delta$  155.0 [ddd, <sup>2</sup>*J*(CP<sub>trans</sub>) = 80.2 Hz, <sup>2</sup>*J*(CP<sub>cis</sub>) = 9.9, 6.3 Hz] and 153.3 [dt, <sup>2</sup>*J*(CP<sub>trans</sub>) = 82.7 Hz, <sup>2</sup>*J*(CP<sub>cis</sub>) = 6.3 Hz]. (b) Bianchini, C.; Barbaro, P.; Meli, A.; Peruzzini, M.; Vacca, A.; Vizza, F. *Organometallics* **1993**, *12*, 2505. Cf. Marinelli, G.; Streib, W. E.; Huffman, J. C.; Caulton, K. G.; Gagné, M. R.; Takats, J.; Dartiguenave, M. *Polyhedron* **1990**, *9*, 1867.

(13) Taken alone, the <sup>13</sup>C NMR data for the O=C=C unit of **3a** are consistent with coordination to either double bond or with none at all. Compare data for the O=C(1)=C(2) unit in **3a**, **4**,<sup>13c</sup> and **1**,<sup>8</sup> respectively: for C(1) =  $\delta$  204.87 (s), 201.2 (s), and 143.39 (t, *J* = 3.2 Hz); C(2) =  $\delta$  55.03 (s), 47.6 (s), and 74.26 (s); (C,C)-bound ketene complexes<sup>2a,8</sup> appear to have C(1) = 166.8–255.7 and C(2) = –33.0 to 74.7 ppm. (e) Tidwell, T. T. *Ketenes*; Wiley: New York, 1995; p 34.

(14) (a) Upfield carbon shifts and fluxionality in  $\eta^2$ -arene complexes: Li, C.-S.; Jou, D.-C.; Cheng, C.-H. *Organometallics* **1993**, *12*, 3945 and references therein. (b) NOE experiments<sup>11</sup> showed saturation transfer<sup>14c</sup> between ortho protons on the coordinated and noncoordinated C<sub>6</sub>H<sub>5</sub> rings, suggesting movement of the ketene ligand on Ir. Moreover, a negative NOE effect<sup>14d</sup> from protons of **3d** with those on **5d** suggests the equilibria shown at the top of Scheme 1. (c) Neuhaus, D.; Williamson, M. P. *The Nuclear Overhauser Effect in Structural and Conformational Analysis*; VCH: New York, 1989; Chapters 5, pp 141–148. (d) *The Nuclear Overhauser Effect in Structural and Conformational Analysis*; VCH: New York, 1989; Chapters 5, pp 175–180.

(15) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91.

## Scheme 1



Indeed, on further gentle warming **3** disappeared, giving alkyne–ketene coupling product **8** (41–55%).<sup>16a,b</sup> The iridabenzopyran core of **8** was implicated by spectral data.<sup>11</sup> The <sup>13</sup>C NMR spectrum of **8a**, for example, showed one downfield triplet ( $\delta$  113.83,  $J = 7.0$  Hz), suggesting bonding of only one carbon to Ir. HMBC and HMQC data pointed to connectivity of a diene unit and a vinylic proton, and NOE data<sup>11</sup> showed that exocyclic double bond substituents  $R^1 = R^2 = \text{CH}_3$  are cis to each other.<sup>18</sup> Identification of **8c** and its regioisomer **8c'** in an inseparable mixture (ratio 2:1) was secured by the multiplicities of the <sup>1</sup>H NMR resonances of the vinylic protons (**8c**, qt,  $J = 1.0$  and  $7.0$  Hz; **8c'**, q,  $J = 6.5$  Hz). In **8d** and **8e**, the vinylic proton resonance appears as a singlet. One consequence of coordinative unsaturation in complexes **8** is that CO adds within seconds at 1 atm, stereospecifically giving hexacoordinate adducts in which the CO ligand is trans to the aryl carbon.<sup>19</sup>

Formation of **8** can be viewed as a consequence of  $\eta^2$ -arene complexation in **3**, leading to C–H activation product **6**, in which the number of ligands on Ir is undetermined, hence the

(16) (a) Better yields (41–55%) of **8** were obtained by adding **4** (0.6 equiv) to **5**, heating at 60 °C for 2–3 h, adding a second portion of **4** (0.6 equiv), and heating until **5** was consumed; total time, 14–26 h.<sup>11</sup> A minor byproduct was **10**<sup>17</sup> (ca. 5%). From reactions of **1** and **2**, isolation of **5** shows ketene–alkyne substitution occurs. (b) Spectral data suggest that a chromatographically unstable component, perhaps related to **C** or **D**, is derived from metal, alkyne, and ketene.<sup>11</sup> Its amount is negligible for  $R^1$  and  $R^2 = \text{alkyl}$  but rivals that of **8** when  $R^1 = \text{Ph}$ . Efforts continue to convert the compound to an isolable product. (c) Homocoupling of ketene or alkyne on Ir(I) is excluded by control experiments: (i) **5d** does not react with **2d** (60 °C, 2 d), excluding formation of **A**; (ii) warming of **1** in the presence of **4** gives **10**, not **B** (as reported earlier, **9** and **4** give **10**);<sup>17</sup> (iii) free ligands **2d** and **4** do not give [2 + 2] cycloadducts<sup>16d</sup> after 40 h at 60 °C. (d) Reference 13e, pp 514–518 and *Houben-Weyl Methoden der Organischen Chemie*, Vol. E15, Part 2, pp 2472–2474.

(17) C–H activation on **1** leads to **9**; **9** and **4** give **10**. At no point in these studies did we find evidence for  $\eta^2$ -arene complexation as in **3**: Grotjahn, D. B.; Lo, H. C. *J. Am. Chem. Soc.* **1996**, *118*, 2097.

(18) Both cis- and trans-products from alkyne insertion into Ni–C bonds: Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 4410. See also Alexander, J. J. In *The Chemistry of the Metal–Carbon Bond*, Vol. 2; Hartley, F., Patai, S., Eds.; Wiley: New York, 1985; pp 339–400.

symbol [Ir] is used.<sup>20</sup> Subsequent alkyne insertion<sup>18</sup> could give **7**, and insertion of the ketene C=O bond into the Ir–vinyl bond would give **8**.<sup>21</sup> Notable features of the overall process from **3** to **8** are the regio- and stereoselective functionalizations of both the ketene and the alkyne. On the basis of exclusive formation of regioisomers **8d,e** and the 2:1 ratio of regioisomers **8c** and **8c'**, we note that the larger group tends to emerge as the terminal diene substituent  $R^1$ .<sup>18,22</sup> Successful production of **8e** shows that the reaction tolerates an ether functionality at an activated position.

The unique structure and reactivity of ketene–alkyne complex **3** gives rise to polycyclic organometallic products unobtainable either from ketene–alkyne cycloadditions<sup>16d</sup> or from other metal-mediated processes. Studies of stereospecific elaborations of the extensive  $\pi$ -system in **8** and demetalations are underway and will be reported in due course.

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**Supporting Information Available:** Preparations, spectral data, spectra, and combustion analyses of 16 compounds (33 pages). See any current masthead page for ordering information and Internet access instructions.

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(19) The stereochemistry of CO addition was secured in part by use of <sup>13</sup>CO on **8d** and observation of <sup>2</sup>J<sub>C–C</sub> = 33.7 Hz between the CO and aryl C across the metal in the resulting adduct.<sup>11,17</sup>

(20) Compound **6** is drawn with (C,O)-coordinated ketene because this explains the course of subsequent insertions leading to **8**, but Ir could be coordinated to the C,C bond or not at all. However, we favor an 18-electron species with [Ir] = IrCl[P(*i*-Pr)<sub>3</sub>] bound to ketene.

(21) Diphenylketene insertion into a Ni–CH<sub>3</sub> bond shows the same regiochemical sense as transformation of **7** to **8**: Jeffery, E. A.; Meisters, A. *J. Organomet. Chem.* **1974**, *82*, 315.

(22) Under the conditions used to form **8a–e**, **5f** rearranged to *trans*-[P(*i*-Pr)<sub>3</sub>]<sub>2</sub>Ir[C=C(CH<sub>3</sub>)(SiMe<sub>3</sub>)]Cl,<sup>11</sup> a reaction known on Rh: Werner, H.; Baum, M.; Schneider, D.; Windmüller, B. *Organometallics* **1994**, *13*, 1089. Terminal alkynes also give vinylidenes or products thereof.