Rhodium Cross-Stitching Sews Up Dibenzofulvalenes

**Significance:** Extended conjugated aromatic molecules possess unique optoelectronic properties that have proven critical for the development of functional materials. Conventional methods for the construction of such polycyclic structures are often linear, iterative processes that hinder scale-up and further development. This method provides hitherto unreported carbonyl-bridged dibenzofulvalenes in a single step by an alkyne insertion cascade.

**Comment:** Zinc methoxide uniquely enables boronic ester 1 and ketone 2 to undergo coupling and cyclization via rhodium(I) catalysis, affording a modest variety of products. Compound 3a can be efficiently transformed into dibromide 4, and the latter compound is easily diversified into a variety of substituted compounds possessing a range of optical and electronic properties. Finally, this method proved able to furnish C-, Si-, Ge-, S-, and P-bridged structures.

**Selected examples of product diversification:**

1. **Alternate bridging groups:**
   - 3a $\rightarrow$ 4
     - $\text{Br}_2$ (4 equiv)
     - CH$_2$Cl$_2$, r.t., 2 h
     - 86% yield

2. **Alternate bridging groups:**
   - 3a $\rightarrow$ 5
     - BnSH, K$_2$CO$_3$, DMF
     - 80 °C, 86% yield

3. **Alternate bridging groups:**
   - 3a $\rightarrow$ 6
     - PhB(OH)$_2$, Pd$_2$⋅DBA$_3$, Pt-Bu$_3$⋅HBF$_4$, KF
     - H$_2$O, THF, 82% yield

4. **Alternate bridging groups:**
   - 3a $\rightarrow$ 7
     - EtOH, K$_2$CO$_3$, DMF
     - 60 °C, 90% yield

5. **Alternate bridging groups:**
   - 3a $\rightarrow$ 8
     - Et$_3$N, THF, 86% yield

6. **Alternate bridging groups:**
   - 3a $\rightarrow$ 9
     - N-methylaniline, K$_2$CO$_3$, DMF
     - 100 °C, 90% yield

7. **Alternate bridging groups:**
   - 3a $\rightarrow$ 10
     - Et$_2$N, THF, 86% yield

8. **Alternate bridging groups:**
   - 3a $\rightarrow$ 11
     - Ph$_2$, Pd$_2$⋅DBA$_3$, Pt-Bu$_3$⋅HBF$_4$, KF
     - H$_2$O, THF, 82% yield

9. **Alternate bridging groups:**
   - 3a $\rightarrow$ 12
     - Me$_3$Si
     - PhB(OH)$_2$, Pd$_2$⋅DBA$_3$, Pt-Bu$_3$⋅HBF$_4$, KF
     - H$_2$O, THF, 82% yield

10. **Alternate bridging groups:**
    - 3a $\rightarrow$ 13
        - N-methylaniline, K$_2$CO$_3$, DMF
        - 100 °C, 90% yield

11. **Alternate bridging groups:**
    - 3a $\rightarrow$ 14
        - Ph$_2$, Pd$_2$⋅DBA$_3$, Pt-Bu$_3$⋅HBF$_4$, KF
        - H$_2$O, THF, 82% yield