

A Novel Synthesis of 4,5-Didehydrotropone–Co₂(CO)₄•dppm Complexes

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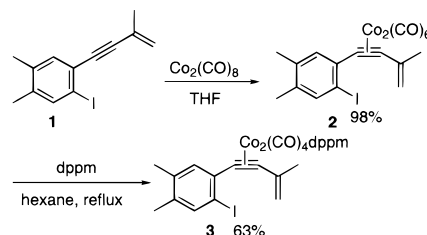
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Cycloalkyne–Co₂(CO)₆ complexes have recently attracted attention as useful intermediates for the synthesis of natural products.¹ Most of the known cycloalkyne–Co₂(CO)₆ complexes have been prepared utilizing the ability of the alkyne–Co₂(CO)₆ complex itself to stabilize a propargylic cation.² We have become interested in the preparation of Co₂(CO)₆ complexes of aromatic molecules such as benzyne or didehydrotropone as they possess both interesting structures and potential utility as synthetic reagents.³ We have chosen a palladium-catalyzed Heck-type coupling of appropriate iodo olefin precursors as a method to synthesize these highly unsaturated cyclic molecules.⁴ In this paper is described the preparation of the first class of this type of complex, 4,5-didehydrotropone–Co₂(CO)₄•dppm complexes, employing a palladium-catalyzed carbonylative cyclization.

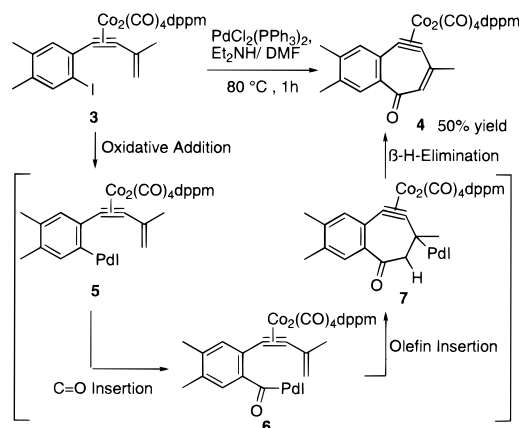
We have chosen 1-iodo-4,5-dimethyl-2-(3-methyl-3-buten-1-ynyl)benzene **1** as a precursor for use in the Heck-type cyclization forming benzyne- or 4,5-didehydrotropone–Co₂(CO)₆ complexes. Complexation of **1** with Co₂(CO)₈ in THF gave the alkyne–Co₂(CO)₆ complex **2** in high yield. As alkyne–Co₂(CO)₆ complexes are in general not stable, we also prepared by heating **2** with diphenylphosphinomethane (dppm) in hexane, the corresponding dppm-substituted complex **3**,⁵ which is expected to be more thermally stable than **2** (Scheme 1).

When the alkyne–Co₂(CO)₆ complex **2** was treated with PdCl₂(PPh₃)₂ in DMF in the presence of Et₂NH under argon followed by warming the mixture slowly to 80 °C, only decomposition of the complex occurred. However, the same reaction employing the dppm-substituted complex **3** gave a new complex, whose structure was confirmed by X-ray analysis to be the 4,5-didehydrotropone derivative **4**. This compound was produced by

Scheme 1



Scheme 2



oxidative addition of the carbon–iodine bond to palladium(0) to give **5**, insertion of carbon monoxide to give acylpalladium intermediate **6**,⁴ and then intramolecular insertion of the olefin to this acylpalladium followed by β -hydride elimination as shown in Scheme 2.

As the carbonyl group of the product was thought to be derived from a ligand of the cobalt complex of the starting material **3**, or the produced 4,5-didehydrotropone-cobalt complex **4**, and this would lead to a decrease in the product yield, we examined the cyclization reaction in the presence of various alternative CO sources. The reaction under a CO atmosphere gave the product in nearly the same yield as that under argon. Next the use of Co₂(CO)₈ or an alkyne–Co₂(CO)₆ complex as a source of CO was examined, in the expectation that such complexes would work as an effective CO source.⁶ As shown in Table 1, Co₂(CO)₈ itself was not effective, presumably due to its thermal instability; however, it was found that the presence of diphenylacetylene–Co₂(CO)₆ complex as a source of CO improved the yield of the tropone derivative **4** considerably. By carrying out the reaction in the presence of 3 equiv of diphenylacetylene–Co₂(CO)₆ complex, we obtained **4** in 85% yield. Furthermore, by heating the reaction mixture rapidly to 80 °C, we have succeeded in obtaining the product in 94% yield. Although the exact mechanism for the transfer of CO from the alkyne–Co₂(CO)₆ complex to palladium is not clear, the complex works as a thermally stable CO source in this reaction, and furthermore, it is possible that some positive interaction between palladium and the alkyne–Co₂(CO)₆ complex is operating.

We next examined the preparation of several other cobalt-complexed 4,5-didehydrotropone derivatives according to the above optimized procedure with the results summarized in Table 2. Tricyclic didehydrobenzotropone derivative **12**, didehydrobenzotropone **13**, and monocyclic didehydrotropone derivative **14** were obtained in good yield by this procedure. However, the

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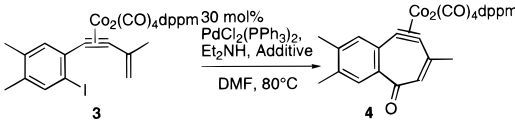
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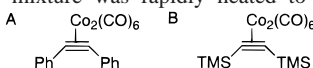
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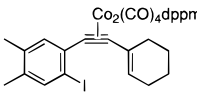
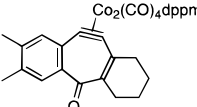
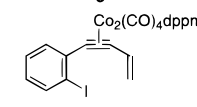
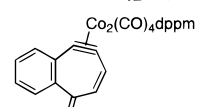
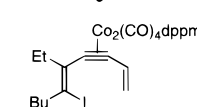
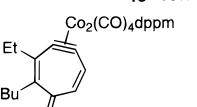
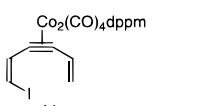
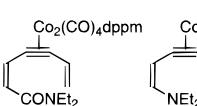
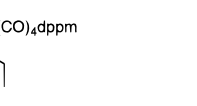
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Table 1. Effect of Additives on the Carbonylative Cyclization


entry	additive	yield of 4 (%)
1	1 atm CO	50
2	1.0 equiv of A	70
3	1.0 equiv of B	64
4	1.7 equiv of A	72
5	3.0 equiv of A	85
6	3.0 equiv of A ^a	94

^a The reaction mixture was rapidly heated to 80 °C. Additive;

**Table 2.** Synthesis of Cobalt Complexes of 4,5-Didehydrotropone Derivatives

Substrate	Product
	 12 56% ^a
	 13 95% ^a
	 14 61% ^b
	 15
	 16
	75% combined yield ^b

^a PdCl₂(PPh₃)₂, 30 mol %; Et₃NH, 30 equiv; DMF, 0.01 M; diphenylacetylene Co complex, 3 equiv. ^b PdCl₂(PPh₃)₂, 30 mol %; Et₃NH, 30 equiv; Toluene, 0.01 M; diphenylacetylene Co complex, 3 equiv.

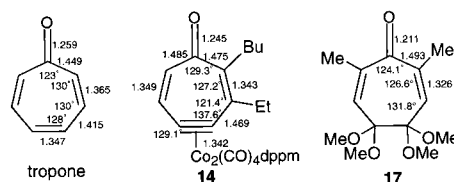
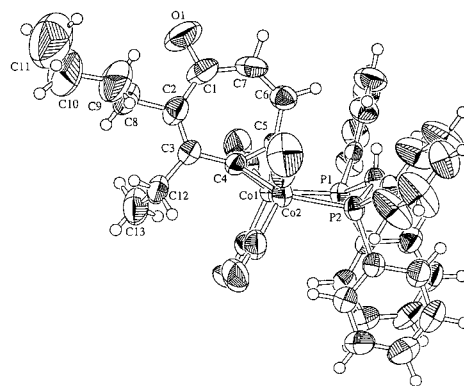
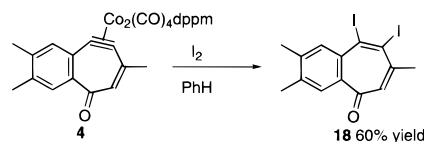
parent didehydrotropone complex itself could not be obtained and aminated products **15** and **16** were formed instead.

In Figure 1 are shown the structural data obtained from the X-ray analysis of complex **14** and the bond angles and lengths of tropone itself⁷ and a cyclohepta-2,6-dien-1-one derivative **17**⁸ for comparison. The X-ray data shows that the seven-membered ring is nearly planar and the bond angles of the alkyne part are 138° and 129°, that is to say considerably smaller than the corresponding average value for an acyclic alkyne cobalt complex. (~140°) The bond length of the carbonyl group of **14** is 1.245(6) Å, which is closer to that of tropone itself (1.259 Å) rather than that of **17** (1.211(3) Å). The most characteristic feature of the complex **14** is the exceptionally low frequency (1579 cm⁻¹)⁹ for the carbonyl stretching in the IR spectrum. Strong electron-donation from the alkyne-CO₂(CO)₄dppm part to the carbonyl group is occurring.

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**Figure 1.** X-ray data of **14** and comparison of the structure with related compounds.**Scheme 3**

Finally we turned our attention to the generation and reaction of decomplexed 4,5-didehydrotropone. It is known that acyclic alkyne-CO₂(CO)₆ complexes can be decomplexed by treatment with iodine to regenerate the parent alkynes.¹⁰ In the expectation that iodine would work both as a decomplexing reagent for the complex and a trapping reagent for the generated 4,5-didehydrotropone, we slowly added a benzene solution of didehydrotropone-CO₂(CO)₄dppm complex **4** to a benzene solution of iodine at room temperature. The reaction gave in 60% yield 4,5-diiodotropone **18**, which is thought to be produced by trapping of the liberated didehydrotropone with I₂¹¹ (Scheme 3). As there is no good method for the preparation of such cyclic diiodides, strained alkyne cobalt complexes should provide a useful general synthetic intermediate.

In conclusion, we have developed a new method for the preparation of 4,5-didehydrotropone-CO₂(CO)₄dppm complexes by the carbonylative Heck reaction in the presence of diphenylacetylene-CO₂(CO)₆ as a carbonyl source. Further studies on the transformation of the 4,5-didehydrotropone-CO₂(CO)₄dppm complexes are in progress.

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Supporting Information Available: Details of the X-ray data of **14** and procedures for the preparation of 4,5-didehydrotropone-CO₂(CO)₄dppm complexes **12**, **13**, and **14** including the preparation of the precursors (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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