

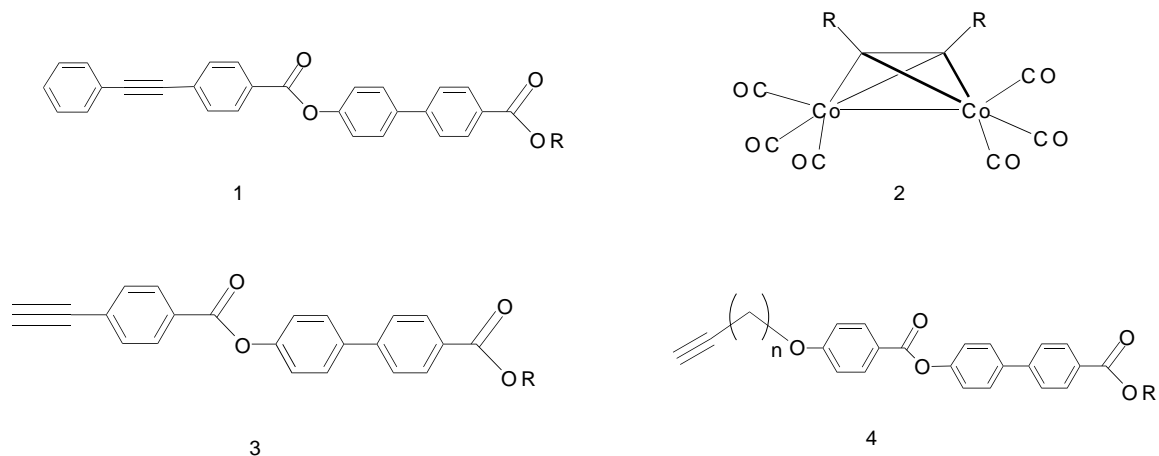
STRUCTURE-PROPERTY STUDIES ON THE DICOBALT HEXACARBONYL COMPLEXES OF A SERIES OF ALKYNE CONTAINING LIQUID CRYSTALS

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There has been a great deal of interest in metallomesogens over the past fifteen to twenty years due to their potential to exhibit unique physical properties¹. Most of the metallomesogens reported possess a metal center that adopts a square planar or linear geometry. In the absence of desymmetrizing groups, these complexes tend to melt at much higher temperatures than their organic precursors. There are far fewer examples of metallomesogens in which the geometry about the metal is octahedral. The incorporation of an octahedral metal center significantly broadens the molecule. In many cases, this lowers the phase transition temperatures of the complex relative to the organic precursor²; liquid crystallinity is sometimes destroyed entirely. Nevertheless, we are greatly interested in preparing metallomesogens possessing an octahedral metal center because it may allow for the possibility of obtaining liquid crystallinity at or near room temperature. For the past several years, we have been studying the phase behavior of $\text{Co}_2(\text{CO})_6$ complexes of liquid crystalline alkynes because alkyne complexes of this cobalt fragment are relatively stable³.



Bruce and Deschenaux have demonstrated that, in cases where the octahedral metal center significantly disrupts molecular anisotropy, it is necessary to have at least four aromatic rings present in order to maintain liquid crystallinity in the metal complex². We therefore initiated our studies by preparing a homologous series of diphenylacetylene derivatives, 1⁴. While the organic compounds exhibit broad mesophase ranges and clearing temperatures above 200 °C, the dicobalt hexacarbonyl complexes melt directly to an isotropic liquid at temperatures below 100 °C. We attribute this behavior to the very large kink that is introduced upon incorporation of the cobalt fragment (see compound 2).

Next, a series of ethynyl benzoate derivatives, **3**, was prepared with the hope that less disruption might occur upon metal incorporation. Unfortunately, the dicobalt hexacarbonyl complexes of **3** also exhibit no mesomorphism. We then designed and synthesized a series of organic derivatives in which the alkyne was separated from the aromatic core by an aliphatic tether, **4**. When $n = 4$, the cobalt derivatives exhibit enantiotropic liquid crystalline behavior. Upon cooling, the mesophase remains present to room temperature with the crystalline phase reforming after several hours. We have been unable to identify the nature of the mesophase based on the microscopic texture; however, the phase is clearly fluid as it readily shears upon application of light pressure on the cover slip. Derivatives where $n = 3$ and $n = 2$ have also been prepared and the dicobalt complexes of these species are mesomorphic as well. However, only monotropic behavior is observed for the latter compounds.

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