

CLATHRATE INCLUSION OF FERROCENE AND CYMANTRENE

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Cymantrene is found to incorporate into a ferrocene clathrate of thiourea. Inclusion of cymantrene in the absence of ferrocene does not occur. A novel proof of clathration is demonstrated utilizing photochemical decarbonylation.

A recent report by Clement, Claude, and Mazieres¹ on the clathration of ferrocene and nickelocene in a thiourea host lattice prompts us to report our findings in the same general area. Ferrocene can be incorporated into a thiourea host as a clathrate inclusion compound in the form of relatively long (9 mm) pale orange needles, m.p. = 172-175° (uncorrected). The capacity of thiourea for clathrating assorted organic molecules such as paraffins, fatty acids, etc. has been known for a long time,^{2,3} but the incorporation of π -metallocenes has only just now been realized.

We have found that, in analogy to the behavior of nickelocene, cyclopentadienylmanganese tricarbonyl ("cymantrene") does not form a thiourea clathrate in the absence of ferrocene. However, cymantrene can be incorporated in the clathrate when ferrocene is present in a ratio of ca 4:1, ferrocene: cymantrene. For instance, in a typical experiment, a ten ml solution of 50% saturated thiourea in reagent-grade methanol containing 0.08 g ferrocene and 0.02 g cymantrene is cooled to -15° for several hours. The resultant yellow needles are filtered and washed with cold methanol then dried under vacuum, m.p. = 172-175° (with a thermochromic transition, yellow and orange at ca 120°); i.r. (KBr) 3310, 3250, 3160, 2030 (w), 1940 (w), 1630 (m), 1615, 1490 (m), 1400 (w), 1120 (m), 1100 (m), 1010 (w), 860 (m), 840 (m), 720, 650 (m), 610 (m), 495 cm⁻¹ (m) (all bands strong unless noted otherwise).

The unequivocal presence of cymantrene is shown by the well-known⁴ CO bands at 2030 and 1940 cm⁻¹. All attempts at incorporating substituted cymantrenes or ferrocenes failed. For example, benzoylferrocene simply cocrystallizes under these conditions and no clathration occurs.

The carbonyl moieties in cymantrene are well-known to be photochemically unstable^{5,6}—hence, to ensure that our system was indeed a clathrate rather than a surface--absorbed contaminant of cymantrene, we used a 450 W Hanovia mercury lamp and irradiated through

quartz a slurry of the cymantrene/ferrocene clathrate in methylcyclohexane (which we have found does not enter the clathrate). There is no "dark" reaction--the 2030 and 1940 cm^{-1} bands remaining unchanged after ca 3 hrs in methylcyclohexane; but, after only one hour of irradiation a significant loss of the CO bands occurred--proving the presence of cymantrene as a clathrated species in the host thiourea lattice. We believe this is the first example of a photochemical reaction on a photolabile but clathrated species and hence offers the possibility of interesting future work.

References

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