

Preliminary communication

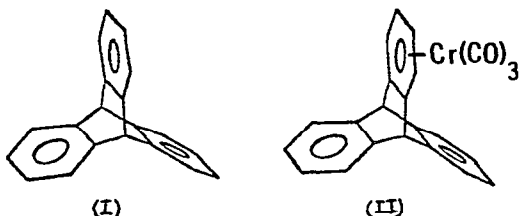
Triptycenetetracarbonylchromium(0)

RUDOLPH L. POHL and BENNETT R. WILLEFORD

Department of Chemistry, Bucknell University, Lewisburg, Pa. 17837 (U.S.A.)

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Triptycene (I) is a strained molecule. It became of interest to us to see if it were possible to form metal carbonyl complexes of this molecule whose rigidity imposes stringent steric requirements. There is also the possibility of forming complexes containing more than one metal atom. Though the π -electron clouds of each of the three aromatic rings cannot be further delocalized because of the saturated bridgehead carbons, the question of possible transannular interactions of the rings has been the subject of much study¹.



On refluxing triptycene with hexacarbonylchromium in *n*-butyl ether at 140° for 22 h, a bright yellow solid was isolated after filtration and evaporation of the solvent. Vacuum sublimation of this solid at 69° at 10⁻³ mm produced a very small amount of a substance of m.p. 60–64° (Found: C, 56.85; H, 4.24; Cr, 18.83). It has not yet been possible satisfactorily to characterize this substance. After further heating of the solid to 130° at 10⁻³ mm to sublime the unreacted triptycene, and several recrystallizations from 1/1 carbon tetrachloride/petroleum ether, triptycenetetracarbonylchromium(0) (II), m.p. 235–236° (dec.) was isolated in 37% yield. (Found: C, 70.39; H, 3.78; Cr, 13.46; mol. wt. (mass spec.) 390. C₂₃H₁₄CrO₃ calcd: C, 70.77; H, 3.61; Cr, 13.32%; mol. wt., 390). Prominent IR bands (Nujol mull) at 670s, 743s, 799m, 840m, 1165m, 1430m, 1860s, 1905s, and 1965s cm⁻¹. The complex sublimes with some decomposition at 140–150° at 10⁻³ mm. It is soluble in most organic solvents, is stable for days in air, but decomposes rapidly when exposed to sunlight.

In CDCl₃ solution, the PMR spectrum of triptycene shows an aromatic A₂B₂ pattern centered at τ 2.89 and a bridgehead singlet at τ 4.65 (lit. values, 2.94, 4.79 respec-

tively, in CS_2 ², 2.75, 4.40 respectively in acetone³). Triptycetricarbonylchromium in CDCl_3 solution gives an A_2B_2 pattern centered at $\tau 2.72$, a second A_2B_2 pattern centered at $\tau 4.60$, and a bridgehead singlet at $\tau 4.82$ in intensity ratios of 4/2/1. The carbonyl stretching region of the infrared shows strong bands at 1860, 1905 and 1965 cm^{-1} in the solid state but only two bands at 1910 and 1975 cm^{-1} in cyclohexane solution. The UV spectrum is similar to that of most other arene tricarbonylchromium complexes with absorptions at 324 nm ($\epsilon = 5.9 \cdot 10^3 \text{ l} \cdot \text{mole}^{-1} \cdot \text{cm}^{-1}$), and 277.5 and 270 nm ($\epsilon = 5.8 \cdot 10^3 \text{ l} \cdot \text{mole}^{-1} \cdot \text{cm}^{-1}$). The mass spectrum shows prominent peaks at m/e values of 390, 334, 306, and 254, corresponding to the molecular ion and successive loss of 2CO, 3CO, and $\text{Cr}(\text{CO})_3$ fragments, as well as at smaller values indicating fragmentation of the triptycene part of the molecule.

Assuming normal carbon-carbon bond distances in the triptycene molecule and the distances and angles characteristic of the tricarbonylchromium moiety found for benzenetricarbonylchromium⁴ and hexamethylbenzenetricarbonylchromium⁵, it can be calculated that the distance of closest approach of a carbonyl oxygen atom to the center of the adjacent aromatic ring is about 2 Å, while the maximum such distance is about 3.6 Å. Non-bonded interactions of the order of 2 Å would indicate that free rotation of the tricarbonylchromium group would be difficult. The barrier to rotation could be reduced considerably, either by a tilting of the tricarbonylchromium with respect to the plane of the ring to which it is bonded, or by significant distortion of the triptycene molecule itself. A single crystal X-ray study of this complex will be attempted soon.

We are currently studying the tricarbonylchromium complexes of several substituted triptycenes. We also believe that the photochemistry of triptycetricarbonylchromium will be interesting in the light of the recently published studies of the photochemical rearrangement of triptycene itself^{6,7}.

ACKNOWLEDGEMENT

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