

## $(\eta^4\text{-Cyclobutadiene})(\eta^5\text{-cyclopentadienyl})\text{dicarbonylvanadium}$

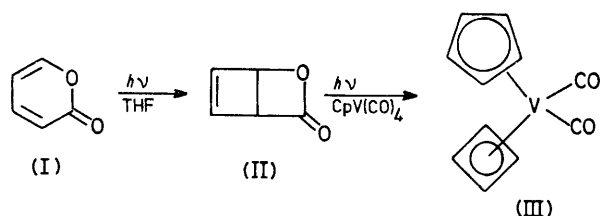
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**Summary** The synthesis and properties of  $[(\eta^4\text{-C}_4\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_2]$ , the first unsubstituted cyclobutadiene complex of an early transition metal, are described.

THE formation, reactions and structures of  $\eta$ -cyclobutadiene-metal complexes continues to be a highly active area of organic and organometallic chemistry.<sup>1</sup> In contrast to an extensive chemistry of cyclobutadiene derivatives of the middle and late transition metals which has been developed in recent years, the known cyclobutadiene analogues of the early transition metals (groups 4B and 5B) are currently limited to only three tetraphenylcyclobutadiene derivatives of titanium,<sup>2</sup> vanadium,<sup>3</sup> and niobium.<sup>4</sup> We now report the formation of the first unsubstituted cyclobutadiene complex of a group 5B metal,  $(\eta^4\text{-cyclobutadiene})(\eta^5\text{-cyclopentadienyl})\text{dicarbonylvanadium}$  (III).

The synthesis of (III) utilizes a procedure used previously for preparing cyclobutadiene derivatives of iron,<sup>5</sup> cobalt,<sup>6</sup> and rhodium.<sup>7</sup> In a typical experiment, 10 mmol of  $\alpha$ -pyrone (I) was converted into its photo-isomer (II) by photolysis in 400 ml of dry, oxygen-free tetrahydrofuran (THF) at 0 °C for 4 h, followed by an additional photolysis



for 30 min at 0 °C in the presence of 3.5 mmol of  $[(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4]$ . The product can be purified by chromatography on alumina under nitrogen followed by vacuum sublimation. In some runs, the product was slightly contaminated with unchanged  $[(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4]$ . Yields of (III) prepared in this manner ranged from 31 to 56%.

The cyclobutadiene complex (III) is a bright orange, moderately air-sensitive compound which slowly decomposes on heating in the solid state. It sublimes readily at room temperature and  $10^{-3}$  Torr, and is soluble in all common organic solvents. The i.r. spectrum (THF) of (III) shows two carbonyl frequencies at 1970 and 1905  $\text{cm}^{-1}$ . The  $^1\text{H}$  n.m.r. spectrum ( $\text{C}_6\text{D}_6$ ) exhibits two sharp singlets

at  $\tau$  5.55 (5H, C<sub>5</sub>H<sub>5</sub>) and 6.65 (4H, C<sub>4</sub>H<sub>4</sub>). Additional evidence for the product being (III) was provided by its high resolution mass spectrum ( $M^+$ , calc. 224.00422, found 224.00325), by satisfactory elemental analyses, and by strong mass spectral fragmentation peaks at  $m/e$  196 ( $M - CO$ ), 168 ( $M - 2CO$ ), 142 ( $M - 2CO - C_2H_2$ ), and 116 (C<sub>5</sub>H<sub>5</sub>V)<sup>+</sup>. Similar photolysis of (II) and [ $\eta^5$ -C<sub>5</sub>H<sub>5</sub>C(O)Me}V(CO)<sub>4</sub>]<sup>8</sup> readily produces an acetyl analogue of (III) [ $\nu_{CO}$  1995, 1935, and 1675 cm<sup>-1</sup>;  $\tau$  (CDCl<sub>3</sub>) 7.25

(3H, s, Me), 6.35 (4H, s, C<sub>4</sub>H<sub>4</sub>), 5.01 (2H, t, H<sub>3,4</sub>), and 4.35 (2H, t, H<sub>2,5</sub>)]. The chemical reactivity of (III) and extensions of the method to other group 4B and 5B metal carbonyls are under investigation.

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