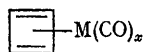


## Cyclobutadiene-Metal Carbonyl Complexes

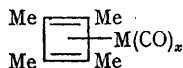
By R. G. AMIET, P. C. REEVES, and R. PETTIT\*

(Department of Chemistry, University of Texas, Austin, Texas 78712)

THE reaction of 3,4-dichlorocyclobutenes with di-iron enneacarbonyl appears to be a general method for the preparation of cyclobutadiene-iron tricarbonyl (Ia) and its derivatives;<sup>1</sup> however, cyclobutadiene complexes of other metal carbonyls are not available through analogous direct reactions. The complex (Ia) is also produced by the reaction of dichlorocyclobutene and sodium tetracarbonyl ferrate  $[\text{Na}_2\text{Fe}(\text{CO})_4]$ , apparently *via* a double nucleophilic displacement process; while this latter reaction offers no particular advantage for the synthesis of the complex (Ia), we have found that the method can be used for the preparation of cyclobutadiene complexes of other metals.



(I)	M	x
(a)	Fe	3
(b)	Ru	3
(c)	Mo	4
(d)	W	4



(II)	M	x
(a)	Fe	3
(b)	Cr	3
(c)	Mo	4
(d)	W	4

Sodium pentacarbonylmolybdate, prepared by reaction of  $\text{Mo}(\text{CO})_6$  with sodium in liquid ammonia,<sup>2</sup> reacts with dichlorocyclobutene to give cyclobutadienemolybdenum tetracarbonyl (Ic) as an orange-red solid, m.p. 17°. Better yields (35%) of this complex are obtained when the carbonyl salt is prepared through reaction of  $\text{Mo}(\text{CO})_6$  and sodium amalgam in refluxing tetrahydrofuran.

Reaction of  $\text{Ru}_3(\text{CO})_{12}$ ,<sup>3</sup>  $\text{W}(\text{CO})_6$ ,  $\text{Mo}(\text{CO})_6$ , and

$\text{Cr}(\text{CO})_6$  with Na-Hg in tetrahydrofuran and subsequent treatment with dichlorocyclobutene or tetramethyldichlorocyclobutene afforded the new cyclobutadiene complexes listed in the Table. The yields in these reactions varied from 1% for (Id) to 35% for (Ic).† The pertinent physical properties of the new complexes are given and, in addition, the mass spectrum of each compound displayed a strong parent molecular ion and prominent fragments corresponding to successive loss of CO groups.

The new cyclobutadiene complexes are stable for prolonged periods when kept in an inert atmosphere. However, while extensive investigation has not been completed, it is apparent that their chemical properties, notably their aromatic behaviour, may differ considerably from that of the iron carbonyl complex. For example, under conditions where cyclobutadiene-iron tricarbonyl reacts with  $\text{MeCOCl}$  and  $\text{AlCl}_3$  to yield the acetyl derivative<sup>4</sup> in better than 95% yield; the molybdenum complex (Ic) yields no such derivative. An X-ray investigation<sup>4</sup> of cyclobutadiene- $\text{Mo}(\text{CO})_3\text{-PPh}_3$  [prepared by irradiation of (Ic) in the presence of  $\text{PPh}_3$ ] reveals that the cyclobutadiene ring has a square configuration as in the case of the Fe complex; the difference in chemical "aromaticity" is thus not ascribed to any basic difference in the nature of the  $\text{C}_4\text{H}_4$  ligands.

We thank the National Science Foundation and the Robert A. Welch Foundation for financial support and Badische Anilin und Soda Fabrik for a generous gift of cyclo-octatetraene.

(Received, October 2nd, 1967; Com. 1047.)

TABLE. Spectroscopic properties of cyclobutadiene-metal carbonyl complexes

Compound	N.m.r. ( $\tau$ )		I.r. [ $\nu(\text{C}=\text{O})$ cm. <sup>-1</sup> ]		
(Ia) .. .. .	6.09		2055		
(Ib) .. .. .	5.87	2061		1995	
(Ic) .. .. .	5.94	2064		1994	1950
(Id) .. .. .	5.98	2068		1983	1950
(IIa) .. .. .	8.24		1961		2030
(IIb) .. .. .	8.15	2039		1949	1941
(IIc) .. .. .	8.06	2044		1971	1927
(IID) .. .. .	7.86	2043		1965	1926

† Whether the very low yields in certain cases is due to initial poor yields of the required dianions or because of their subsequent reaction with the dichlorocyclobutene has not yet been determined.

<sup>1</sup> L. Watts and R. Pettit, "Advances in Chemistry Series, No. 62: Werner Centennial" 1966, p. 549.

<sup>2</sup> H. Behrens and R. Weber, *Z. anorg. Chem.*, 1957, **291**, 122.

<sup>3</sup> M. I. Bruce and F. G. A. Stone, *Chem. Comm.*, 1966, 684.

<sup>4</sup> R. Davis, personal communication.