

Preliminary Communication

THE REACTION OF ACETYLENES WITH BIS[ $(\eta^5\text{-CYCLOPENTADIENYL})\text{DICARBONYLCHROMIUM}$ ]

JOHN S. BRADLEY

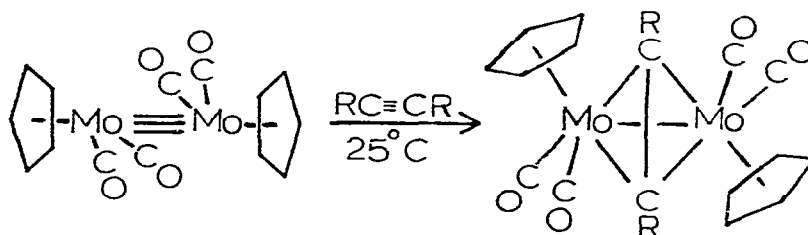
Exxon Research and Engineering Company, Corporate Research Laboratories, Linden,  
 New Jersey 07036

(Received January 18, 1978)

Summary

The reaction between  $[\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_2]_2$  and acetylenes proceeds readily in refluxing toluene, to produce a series of binuclear chromacyclopentadiene complexes, the first examples of chromium metallacycles to be isolated.

The chemistry of complexes of the Group VI metals containing multiple metal-metal bonds has been developed by Cotton et al. [1] and by others [2]. Among the reports of the reactivity of these compounds are examples in which triple metal-metal bonds of  $[\text{CpMo}(\text{CO})_2]_2$  and its tungsten analog have been shown to be reactive toward various small molecules. In particular, these compounds react readily with acetylenes [3], one molecule of the acetylene adding across the triple metal-metal bond to give an adduct with a quasitetrahedral  $\text{M}_2\text{C}_2$  core [4], e.g.:



In contrast,  $[\text{CpCr}(\text{CO})_2]_2$  is reportedly inert to acetylenes [3]. We wish to report that, in fact, a variety of acetylenes react readily with  $[\text{CpCr}(\text{CO})_2]_2$  (I) in refluxing toluene, resulting in the coupling of two acetylene

molecules across the  $\text{Cr}_2$  unit in an  $\eta^5$ -chromole chromium complex.

The addition of two equivalents of phenylacetylene to a dark green solution of I in refluxing toluene, under nitrogen, produces a deep red air-sensitive solution after several minutes. The two infrared carbonyl bands of I ( $1915\text{ cm}^{-1}$ ,  $1890\text{ cm}^{-1}$ ) are replaced by a single band at  $1810\text{ cm}^{-1}$ ; no other carbonyl containing species are detected during the course of the reaction. The product, of stoichiometry  $(\text{C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})(\text{C}_6\text{H}_5\text{O}_2\text{H})_2$ , (II) was isolated in 55% yield as red-black needles by crystallization from hexane\*; infrared spectrum  $1803\text{ cm}^{-1}$  (methylcyclohexane); mass spectrum (70 ev,  $200^\circ\text{C}$ ) parent ion 466, M-CO m/e 438;  $^1\text{H}$  nmr ( $\tau$ , in  $\text{CD}_2\text{Cl}_2$ ) 5.20 (s, 5 H), 5.33 (s, 5 H) (due to non-equivalent Cp rings), 2.8 (m, 12 H). The molecule is fluxional, and the two non-equivalent Cp resonances coalesce reversibly at  $140^\circ\text{C}$  in *o*-dichlorobenzene.

The  $^{13}\text{C}$  nmr spectrum clearly shows that the two acetylene molecules incorporated into II are coupled. In addition to resonances at 316 ppm (TMS) (s, carbonyl) and at 98.3 ppm and 96.3 ppm (d,  $J = 170\text{ Hz}$ , Cp rings) plus a series of overlapping doublets (128-124 ppm,  $J = 160\text{ Hz}$ , *o*-*m*-*p*-phenyl carbons) there are resonances at 207 ppm(s), 194 ppm (d,  $J = 160\text{ Hz}$ ) 107 ppm(s) and 87 ppm (d,  $J = 160\text{ Hz}$ ). These are assigned to the formerly sp carbons of the acetylene molecules, now  $\text{sp}^2$  hybridized and coupled in a 2,4-diphenylchromacyclopentadiene ring. The two lower field lines are assigned to the  $\alpha$ -carbons  $\text{C}_2$  and  $\text{C}_5$ ; the two higher field lines to the  $\beta$ -carbons  $\text{C}_3$  and  $\text{C}_4$ . Two remaining resonances in the spectrum at 151 ppm(s) and 139 ppm(s) are assigned to the *ipso*-carbons of the  $\text{C}_2$  and  $\text{C}_4$  phenyl rings. On the basis of these data, II is assigned the structure shown in Figure I.

Confirmation of these assignments is obtained from the  $^{13}\text{C}\{^1\text{H}\}$  spectrum of III, the diphenylacetylene analog of II, which was isolated in 65% yield from the reaction of diphenylacetylene with  $[\text{CpCr}(\text{CO})_2]_2$ . The cyclopentadiene resonances remain non-equivalent (101 ppm, 99 ppm) while the four resonances assigned to the chromacycle in II are reduced to two (213 ppm, 111 ppm) assigned to  $\text{C}_{2,5}$  and  $\text{C}_{3,4}$ . The two resonances due to the *ipso*-carbons of the  $\text{C}_{2,5}$  and  $\text{C}_{3,4}$  phenyl groups are found at 150 ppm and 139 ppm.

Chemical corroboration of the coupling of the acetylenes is obtained by treating III with a solution of HCl in ether, which yields 1,2,3,4-tetra-phenylbuta-1,3-diene (m/e 358).

The identity of the chromole was confirmed by a crystallographic study. Crystals of III were grown from hexane solution and the structure was determined by Dr. Jan Troup of Molecular Structure Corporation, College Station, Texas. The molecule crystallizes in the orthorhombic space group

\*Satisfactory elemental analyses (C,H,Cr) were obtained for all new compounds.

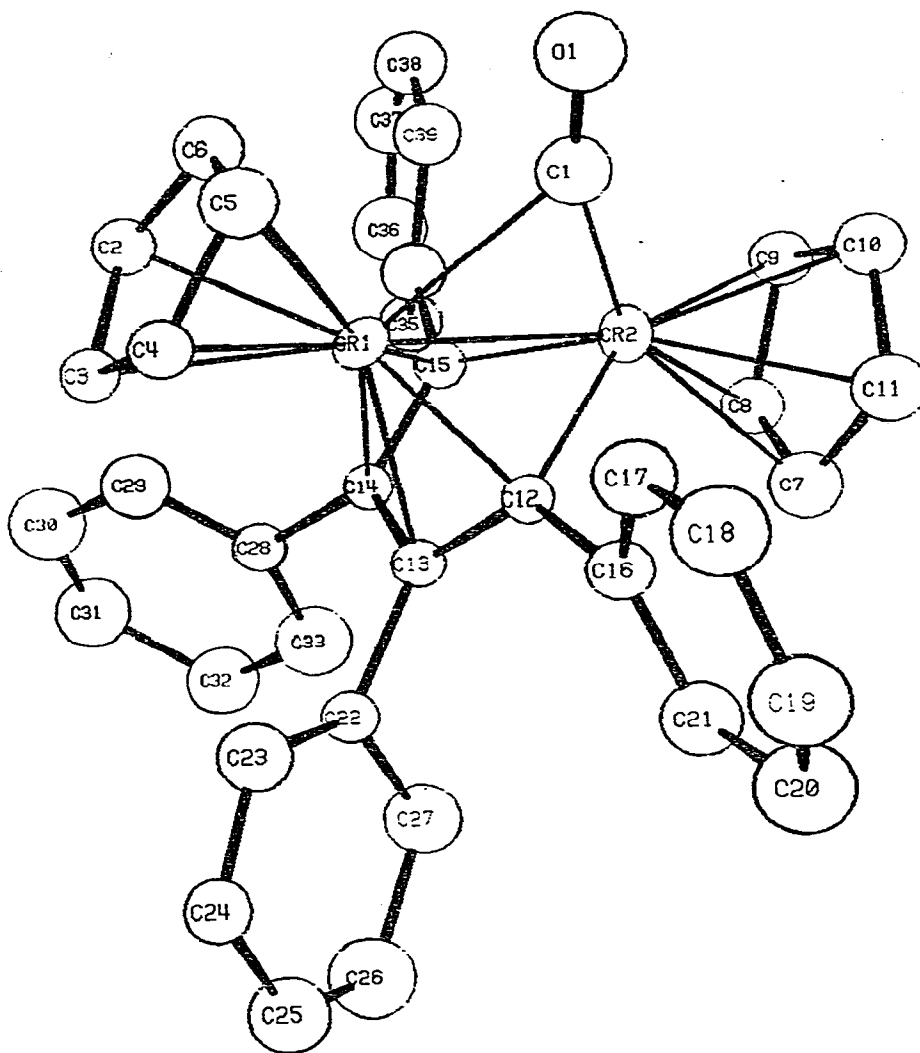


Figure I. Proposed Structure of  $\text{Cp}_2\text{Cr}_2(\text{CO})(\text{Ph}_2\text{C}_4\text{H}_2)$ . II.

$P_{\text{bcn}}$  with  $\underline{a} = 19.545(4)\text{\AA}$ ,  $\underline{b} = 20.323(3)\text{\AA}$ ,  $\underline{c} = 16.663(3)\text{\AA}$ ,  $V = 5519\text{\AA}^3$ ,  
 $\rho_{\text{(calc)}} = 1.242 \text{ g cm}^{-3}$  for  $Z = 8$  and  $\text{mw} = 618.67$ . A total of 6922 independent reflections was collected; 1826 reflections having  $F_0^2 > 3\sigma(F_0^2)$  were used in the refinement. All non-hydrogen atoms were located and refined. Anisotropic thermal parameters were assigned only to Cr atoms, the remaining atoms having been refined isotropically. The current R value is .113 and the molecular configuration obtained at this stage of refinement (Figure II) confirms the structural features proposed on the basis of the above data. The Cr-Cr distance of  $2.337(3)\text{\AA}$  is consistent with a triple metal-metal bond; the chromole ring  $\text{Cr}(2)\text{C}(12)\text{C}(13)\text{C}(14)\text{C}(15)$  is evident, and it is bonded  $n^5$  to

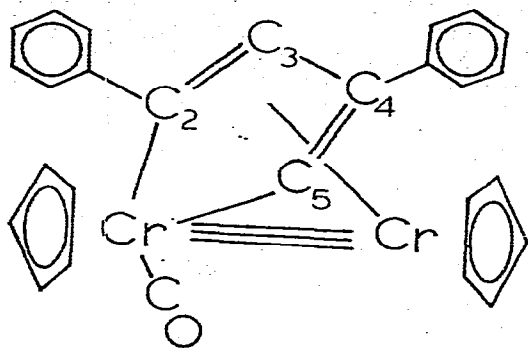


Figure II. Molecular Structure of  $\text{Cp}_2\text{Cr}_2(\text{CO})(\text{Ph}_4\text{C}_4)$ , III.

the second chromium in an  $\eta^5$ -chromacyclopentadiene- $\eta^5$ -cyclopentadienyl chromium complex. The carbonyl is bonded in a semi-bridging fashion between the two chromium atoms ( $\text{Cr}(1)\text{-C}(1) = 2.38(2)\text{\AA}$ ,  $\text{Cr}(2)\text{-C}(1) = 1.90(2)\text{\AA}$ ,  $\angle\text{Cr}(2)\text{C}(1)\text{O}(1) = 164^\circ$ ). In the light of the asymmetry of the molecule this is not surprising, and the carbonyl-stretching frequency of  $1815\text{ cm}^{-1}$  is consistent with this bonding mode [5].

A variety of acetylenes react similarly with I, giving the analogous chromoles. Although metallacyclopentadienes are known for a number of metals, this is the first report of the isolation and characterization of such a chromium heterocycle. Metallacyclopentadienes have been shown to be intermediates in the catalytic trimerization of acetylenes to arenes [6] and in the formation of  $\pi$ -cyclopentadienone and  $\pi$ -cyclobutadiene complexes from acetylenes [7]; these and other aspects of the chemistry of the  $\eta^5$ -chromole chromium system are under investigation.

#### Acknowledgements

The author wishes to thank Prof. M. D. Rausch for helpful discussions, and acknowledges with thanks the expert technical assistance of Ernestine Hill.

#### References

1. F. A. Cotton, S. Koch, K. Mertis, M. Miller and G. Wilkinson, *J. Am. Chem. Soc.*, **99** (1977), 4989, and references cited therein.
- 2a. D. S. Ginley and M. S. Wrighton, *J. Am. Chem. Soc.*, **97** (1975), 3533  
 b. R. J. Klingler, W. Butler and M. D. Curtis, *ibid.*, **97** (1975), 3535.

3. D. S. Ginley, C. R. Bock and M. S. Wrighton, *Inorg. Chim. Acta.*, 23 (1977), 85.
4. W. I. Bailey, F. A. Cotton, J. D. Jamerson and J. R. Kolb, *J. Organometal. Chem.*, 121 (1976), C23.
5. F. A. Cotton, *Prog. Inorg. Chem.*, 21 (1976), 1.
6. D. R. McAlister, J. G. Bercaw and R. G. Bergman, *J. Am. Chem. Soc.*, 99 (1977), 1666.
- 7a. S. McVey and P. M. Maitlis, *J. Organometal. Chem.*, 19 (1969), 169.
- b. M. D. Rausch and R. A. Genetti, *J. Am. Chem. Soc.*, 89 (1967), 5502.