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Cyclopentadienyl Compounds of Chromium, Molybdenum and Tungsten

by

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Abstract

A new preparation of bis-cyclopentadienyl metal compounds from the reaction of cyclopentadiene and metal carbonyls is described, together with cyclopentadienyl compounds of Cr, Mo, W and Co.

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This report is being submitted to the Journal of the American Chemical Society.

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## Cyclopentadienyl Compounds of Chromium, Molybdenum and Tungsten

Sir,

Bis-cyclopentadienyl compounds of some transitional elements have been prepared by two methods. Firstly, the reaction of cyclopentadienyl-magnesium halides with the metal halides,<sup>1,3</sup> or acetylacetonates,<sup>2,3</sup>

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(1) T. J. Kealy, P. L. Pauson, *Nature* 168, 1039 (1951).

(2) G. Wilkinson, *This Journal* 74 (a) 6146, (b) 6148 (1952).

(3) G. Wilkinson, P. L. Pauson, J. M. Birmingham, F. A. Cotton, *This Journal* 75, 1011 (1953).

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leads to compounds of the type  $[(C_5H_5)_2M^n]X_{n-2}$ , where  $n = 2$  to  $5$  is the oxidation state of the metal  $M$ , and  $X$  is a halogen, e.g.  $(C_5H_5)_2Ni^{II}$ ,  $(C_5H_5)_2Rh^{III}Br$ ,  $(C_5H_5)_2Ti^{IV}Br_2$ ,  $(C_5H_5)_2Nb^VBr_3$ ; in the cases of  $FeCl_3$  and  $Ru$  III acetylacetonate, reduction to the neutral compound  $(C_5H_5)_2M$  occurs.

Secondly, the direct reaction of cyclopentadiene with an iron catalyst at  $375^\circ C$  forms  $(C_5H_5)_2Fe$ .<sup>4</sup>

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(4) S. A. Miller, J. A. Tebboth, J. F. Tremaine, *J. Chem. Soc.* 632 (1952).

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A third preparative method has been found in the vapor phase reaction of cyclopentadiene with metal carbonyls at elevated temperatures.

On passing  $Cr(CO)_6$  vapor and cyclopentadiene in nitrogen through a tube at  $320-380^\circ C$ , scarlet crystals of  $(C_5H_5)_2Cr$  (m.p.  $170^\circ$ , Anal. calc. Cr 28.50, found Cr. 28.47) appear on a cooling probe. The compound sublimes in vacuum at  $50^\circ C$  and is thermally stable to at least  $400^\circ C$ ; it is exceedingly sensitive to air, being pyrophoric when finely divided. It is soluble in thoroughly deoxygenated organic solvents without appreciable

decomposition; in  $\text{CS}_2$  solution, the infrared absorption spectrum is strikingly similar to that of other  $(\text{C}_5\text{H}_5)_2\text{M}$  compounds.<sup>2a</sup> With water, there is only a very slow reaction but dilute acids cause effervescence liberating cyclopentadiene; there is no evidence for the formation of a bis-cyclopentadienylchromium III cation. The compound is paramagnetic  $\chi_{\text{mol}}^{27^\circ} = +3580 \times 10^{-6}$  cgsu, suggesting two unpaired electron spins.

With  $\text{Mo}(\text{CO})_6$ , the reaction at  $375^\circ\text{C}$  gives, on the probe, the dark green  $(\text{C}_5\text{H}_5)_2\text{Mo}$  [Anal. Calcd. Mo 42.45, found 42.50], readily volatile above  $90^\circ$  in vacuum; it dissolves in acids being oxidized to bis-cyclopentadienylmolybdenum cations. Within the heated portion of the tube remain dark red needles of a stable compound  $\text{C}_{15}\text{H}_{10}\text{O}_5\text{Mo}_2$  [m.p.  $217^\circ$  d. Anal. Calc. C, 38.95, H 2.16, Mo 41.45; found C 38.85, H 2.14, Mo 41.40], which is volatile in vacuum only above  $150^\circ\text{C}$ . The compound is crystallized from  $\text{CHCl}_3$ ,  $\text{CCl}_4$  or ligroin; it dissolves in pyridine, but does not undergo carbonyl substitution on boiling; it is unaffected by water and dilute acids or bases, and is decomposed on oxidation. The molecular weight by cryoscopy in benzene is  $455 \pm 20$  (calc. 461.0); it is diamagnetic,  $\chi_{\text{mol}}^{25^\circ} = -210 \times 10^{-6}$  cgsu.

A similar compound  $\text{C}_{16}\text{H}_{10}\text{O}_6\text{W}_2$ , [m.p.  $240^\circ$  d. Anal. Calc. C, 28.86, H, 1.50, W 55.25; found C, 28.94, H 1.68, W 55.23], also dark red in color is formed using  $\text{W}(\text{CO})_6$  at  $350^\circ\text{C}$ , and is crystallized from  $\text{CHCl}_3$ . The molecular weight by cryoscopy in benzene is  $650 \pm 20$  (calc. 666.0); it is diamagnetic,  $\chi_{\text{mol}}^{25^\circ} = -220 \times 10^{-6}$  cgsu. The chemical properties are similar to those of the molybdenum compound.

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The infrared spectra of these two red compounds are remarkably similar; both show a single C-H stretching frequency, and have other bands in positions similar to those in bis-cyclopentadienyl compounds. In addition, however, both have two intense bands in the C-O stretching region; for the molybdenum compound, there is a sharp band at  $1960\text{ cm}^{-1}$  and a broader one of comparable intensity at  $1916\text{ cm}^{-1}$ , while in the tungsten compound, the analogous bands are at  $1959$  and  $1911\text{ cm}^{-1}$  respectively.

The structures of these cyclopentadienyl carbonyls are, perhaps, best formulated as "triple decker" sandwiches, with a cyclopentadienyl ring on each metal atom with five and six bridging carbonyl groups in the molybdenum and tungsten compounds, respectively, e.g.  $\text{C}_5\text{H}_5\text{W}(\text{CO})_6\text{WC}_5\text{H}_5$ , bis(cyclopentadienyl)- $\mu$ -pentacarbonmonoxide-bi-tungsten (I). The diamagnetism of these compounds would be accounted for if a cyclopentadienyl radical contributes one electron and the cyclic carbonyl system furnishes on the average, three electrons, to each neutral metal atom, four of the d orbitals being used in this bonding, with the fifth filled and not involved in bonding. Partial bonding between the carbon atoms of the carbonyl groups seems implied, and interaction between these groups may explain the observed C-O stretching frequencies; it is to be noted that certain  $\alpha$ -diketones show two C-O frequencies.

The carbonyl method of preparation of  $(\text{C}_5\text{H}_5)_2\text{M}$  compounds has been applied<sup>5</sup> to iron, using  $\text{Fe}(\text{CO})_5$ , and to cobalt using  $\text{Co}_2(\text{CO})_8$ . Bis-

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(5) In collaboration with Dr. P. L. Pauson.

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cyclopentadienyl cobalt (Anal. calc. Co 31.15, found Co 31.20) forms

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lustrous, almost black crystals, subliming readily in vacuum above 40°; it is oxidized in air and with acids gives hydrogen, some cyclopentadiene and the cobalticinium ion; it is paramagnetic,  $\chi_{\text{mol}}^{26^\circ} = +1730 + 10^{-6}$  cgsu, suggesting a single unpaired electron.

I am indebted to Drs. E. O. Brinn and M. Lynch of the Linde Air Products Co., Tonawanda, N.Y., for their kind gifts of metal carbonyls.

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