

Pentacarbonylmethyl(methylamino)carbenechromium

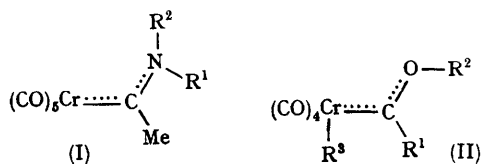
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PENTACARBONYLMETHYLAMINOCARBENECHROMIUM complexes (I) are formed when pentacarbonylmethylmethoxycarbenechromium (II; $R^1 = R^2 = \text{Me}$, $R^3 = \text{CO}$) is treated with amines. Thus the reaction with ammonia yields (I; $R^1 = R^2 = \text{H}$),¹ whilst derivatives with other substituents have been reported.²

The properties, chemical and structural, of those carbene complexes which contain an oxygen atom α

to the carbene carbon atom seem best to be described³ in terms primarily, of electron donation



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from the formally singlet sp^2 -hybridised carbene carbon atom to the metal, together with associated, but competitive, back-donations from both the metal and the oxygen into the empty p_z -orbital on the carbon. This results in partial double-bond character of both the metal-carbon and oxygen-carbon bonds. Because of the competitive nature of this back-donation, the metal-carbon bond has less double-bond character than in the simple metal carbonyls and thus the Cr-C distances in (II; $R^1 = \text{Ph}$, $R^2 = \text{Me}$, $R^3 = \text{CO}$)⁴ and in (II; $R^1 = R^2 = \text{Me}$, $R^3 = \text{PPh}_3$)⁵ are 2.04 Å ($\sigma = 0.03$ Å) which value is appreciably longer than the (still) partial double-bond separation, 1.92 Å,⁶ in $\text{Cr}(\text{CO})_6$.

We have determined the crystal structure of a methyl(methylamino)carbene complex (I; $R^1 = \text{Me}$, $R^2 = \text{H}$),[†] in the first place to determine the overall geometry of this new ligand, and secondly to observe the effect of replacement of oxygen by nitrogen on the competitive back-donation balance. The introduction of the more electropositive nitrogen should result in greater double-bond character of the C-N bond and less double-bond character of the Cr-C bond with a consequent lengthening of this distance in comparison with the oxygen complexes.

Crystal data: $\text{C}_8\text{H}_7\text{NO}_5\text{Cr}$, $M = 249.2$, monoclinic, $a = 6.79$, $b = 10.32$, $c = 16.27$ Å, $\beta = 106.8^\circ$, $U = 1091$ Å³, $Z = 4$, space group $\text{P}2_1/c$ (C_{2h}^5 , No. 14) by systematic absences. Three-dimensional intensities were collected partly by film methods (precession photographs taken with molybdenum radiation) and partly from a Stoe automatic Weissenberg instrument (with copper radiation). The structure was solved by the usual Fourier techniques of Patterson synthesis and heavy-atom method and refined by least-squares methods ($R = 8.8\%$ for 790 non-zero reflexions).

The analysis has established that the amino-carbene complexes are structural analogues of the oxycarbene complexes previously determined. The

$\text{Cr}-\text{C}-\begin{array}{l} \text{N} \\ \text{Me} \end{array}$ group is essentially planar and the bonding to the metal is through the carbon. The

Figure shows some bond lengths from which it is clear that the nitrogen-carbene carbon distance, 1.33 Å, corresponds to partial double-bond character (compare the N-Me value of 1.51 Å). The determined Cr-C distance of 2.09 Å is numerically greater than those reported for the oxygen

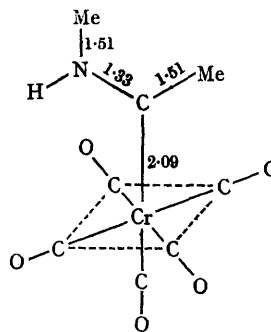


FIGURE. $\sigma(\text{Cr}-\text{C}) = 0.02$ Å
 $\sigma(\text{C}-\text{N}) = 0.03$ Å

complexes but, after allowance for the standard deviations involved in the different analyses, cannot be proved to be significantly longer with complete certainty. However if other analyses of related complexes currently under investigation show similar values, this lengthening may yet be established. The average Cr-C(carbonyl) distance, 1.85 Å, is close to the values found for the oxycarbene complexes.

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