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Preliminary communication

^{13}C—^{15}N COUPLING CONSTANTS IN METHYLDIMETHYLAMINOCARBENEPENTACARBONYL COMPLEXES OF CHROMIUM(0) AND TUNGSTEN(0)*

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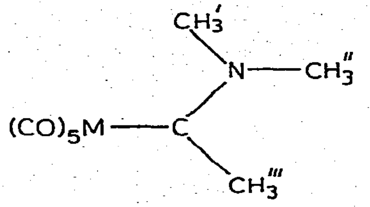
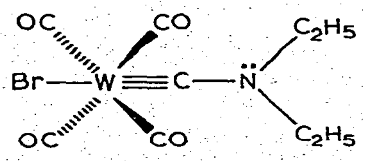
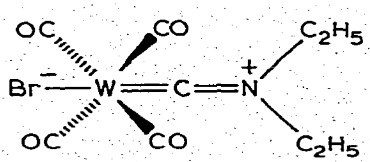
Nuclear spin coupling constants between different kinds of nuclei, such as ^{1}H, ^{13}C, ^{15}N, and ^{31}P are very important for structural investigations in that they provide information about the types of chemical bonding involved. In the present study, we have determined ^{13}C—^{15}N coupling constants for two methyldimethylaminocarbenepentacarbonyl complexes of chromium(0) and tungsten(0) (I and II) [1] for the purpose of subsequent comparison with the ^{13}C—^{15}N couplings of *trans*-bromodiethylaminocarbynetetracarbonyltungsten (III) [2]. Earlier IR and NMR investigations [2] suggest structure IIIb for this complex; however, deter-



(I) M = Cr
(II) M = W



(IIIa)



(IIIb)

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mination of the coupling between the carbyne carbon and the nitrogen should give a much more detailed picture of the bond type of the carbyne carbon.

The proton-decoupled ^{13}C NMR spectra of the carbene complexes I and II in benzene-d_6 solutions contained in glass bulbs were determined on our Bruker DSF-60 [3]. The Fourier transformation was carried out without weighting of the free-induction decay. The coupling constants obtained from the spectra are given in Table 1. The ^{13}C chemical shifts agreed well with those previously reported [2]. Both compounds show very similar couplings. No coupling could be detected between the nitrogen and the carbons of the *cis* and *trans* carbonyl groups, however, a coupling of 4.0 and 4.7 Hz between the nitrogen and carbene carbons were found. The $^2J(^{13}C—^{15}N)$ coupling from the nitrogen to the *C*-methyl carbons are small, 0.5 and 1.0 Hz.

Double-bond character and the associated hindered rotation about the carbene carbon to nitrogen bond makes the two *N*-methyl groups nonequivalent [4]. It is interesting that the location of the *N*-CH_3 group in the *syn* or in the *anti* position with respect to the transition metal has an important influence on the magnitude of the coupling between the *N*-methyl carbons and the nitrogen. The values are 12.4 and 12.5 Hz for the *syn* and 8.3 and 8.1 Hz for the *anti* coupling. If one assumes sp^2 hybridization of the nitrogen and sp^3 for hybridization for the methyl carbons [5, 6] and uses the equation for $^{15}N—^{13}C$ coupling, $\%S_N \cdot \%S_C \approx 80 \cdot {}^1J(^{15}N—^{13}C)$, where $\%S_N$ and $\%S_C$ are the amounts (%) of the *s*-character of the bonds formed by each atom [7], one predicts a coupling of 10.4 Hz which is almost exactly the average of the two different N—C(methyl) couplings. That the difference in steric location of the methyls should cause the respective bond hybridizations to change in equal and opposite directions would be possible, but surprising.

TABLE 1

^{13}C—^{15}N COUPLING CONSTANTS IN Hz OF I AND II IN BENZENE-d_6

M	C carbene	CO *trans*	CO *cis*	N—CH_3'	N—CH_3''	C—CH_3'''
Cr	4.0	< 0.25	< 0.26	12.4	8.3	0.5
W	4.7	< 0.25	< 0.25	12.5	8.1	1.0

The same equation applied to the N—C(carbene) coupling suggests that, if the nitrogen is sp^2 hybridized, then the carbene carbon to nitrogen bond has only 10% *s* character which if correct, would indicate that the metal is strongly bound by the 2*s* orbital of the carbene carbon.

Experimental

All preparations were carried out under dry nitrogen and argon. Compounds I and II were synthesized by a slight modification of the method of Klabunde and Fischer [1]. A small excess of 5 mmol of dimethylamine-^{15}N was added to a solution of 2.5 mmol of methylmethoxycarbenepentacarbonyl-chromium(0) or -tungsten(0) in pentane at −30°C. The mixture was stirred for 2 h at this temperature and the products purified by three recrystallizations from ether/pentane. The products were identified by their ^{13}C NMR spectra [8].

The NMR measurements were carried out in benzene-d_6 in sealed glass bulbs. For the carbene and the carbonyl carbons, the sweep width was 1000 Hz with a resolution of 0.25 Hz/point. For the methyl carbons the sweep width was 500 Hz and the resolution 0.18 Hz/point.

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