

CARBON-13 NMR SPECTRA OF CHROMIUM PENTACARBONYL CARBENOID COMPLEXES

D. J. CIAPPENELLI

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (U.S.A.)

F. A. COTTON* and L. KRUCZYNSKI**

Department of Chemistry, Texas A&M University, College Station, Texas 77843 (U.S.A.)

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SUMMARY

The carbon-13 NMR spectra of six carbenoid complexes of the type $(OC)_5Cr(CXX')$ have been recorded. The carbenoid carbon atoms are all markedly deshielded (chemical shifts *vs.* TMS in the range -271 to -360). With only one minor inversion of uncertain significance, the chemical shifts correlate well with the expected ability of the X and X' groups to engage in dative π bonding to the carbenoid carbon atom. The longitudinal relaxation times for both carbenoid and carbonyl carbon atoms in $(OC)_5Cr[C(CH_3)(OC_2H_5)]$ are 1-2 sec. The chemical shift difference for carbonyl carbon atoms *cis* and *trans* to the carbenoid ligand is essentially invariant in the six compounds.

INTRODUCTION

The carbenoid complexes*** of the type $(OC)_5Cr(CXX')$ are of interest because they afford the opportunity to investigate two significant aspects of ^{13}C NMR spectroscopy as applied to organometallic and metal carbonyl chemistry. First, the chemical shifts of the carbenoid carbon atoms as a class and as a function of the appended X and X' groups merit study in order to advance our understanding of the electronic structures of metal-carbenoid complexes. Second, the chemical shift differences for carbonyl carbon atoms *cis* and *trans* to a substituent have not been systematically studied and data for a homologous series of representative compounds are of interest.

EXPERIMENTAL

The six compounds we have investigated are listed in Table 1 where the observed chemical shift data are recorded. The compounds were prepared by literature

* Address correspondence to this author.

** Postdoctoral Fellow of the National Research Council of Canada, 1970-1972.

*** For general reviews of carbenoid complexes see ref. 1.

TABLE 1

¹³C CHEMICAL SHIFTS (in ppm vs. TMS) IN (OC)₅CrCXX' COMPOUNDS

No.	Compound		Carbene carbon atom	CO groups	
	X	X'		cis	trans
(I)	OC ₂ H ₅	C ₆ H ₅	-351 (-351 ^a)	-218 (-217 ^a)	-226 (-225 ^a)
(II)	OC ₂ H ₅	CH ₃	-357 (-360 ^a) (-362 ^b)	-217 (-217 ^a) (-218 ^b)	-226 (-224 ^a) (-224 ^b)
(III) ^c	NHCH ₃	C ₆ H ₅	-289	-218	-224
(IV) ^c	NHCH ₃	CH ₃	-276	-218	-223
(V) ^c	NH(CHMe ₂)	CH ₃	-274	-218	-224
(VI)	N(CH ₃) ₂	CH ₃	-271	-218	-224

^a For analogous (OCH₃) compound in benzene³. ^b For the same compound in CHCl₃⁵. ^c These data are all for the *cis* configuration of the carbenoid group.

methods¹. Solutions were passed through a short Florisil column into the NMR tube under N₂ purge to eliminate paramagnetic impurities. The ¹³C NMR spectra were recorded on a Bruker HFX-90 spectrometer interfaced with a Digilab NMR-3 FTS computer with a 256K disc. We are grateful to Dr. D. Traficante for guidance in the operation of this instrumentation. Each compound was examined as a saturated THF solution in a 10 mm tube; a capillary of C₆F₆ was used as a reference lock. A 20° tip angle and a delay of 1–2 sec between pulses were used; an average of 1500 pulses was used to record each spectrum. Broadband (noise) decoupling of protons was used except in T₁ measurements where the "progressive saturation" technique² was employed. Chemical shifts were actually measured against internal CS₂, but are reported *vs.* TMS in Table 1 to facilitate comparison with the literature. The correction made was, $\delta(\text{CS}_2) - \delta(\text{TMS}) = -194.0$ ppm; *e.g.*, a value of -157 ppm *vs.* CS₂ (measured) is reported as -351 ppm *vs.* TMS. The shifts reported are believed to be accurate to ± 1 ppm.

RESULTS

It is well known that detailed interpretation of ¹³C chemical shifts (and those for other non-hydrogen atoms, such as ³¹P) is not straightforward. Both ground state electron density and the mixing in of paramagnetic excited states under the influence of the applied magnetic field contribute to the observed shifts. In these carbenoid complexes, it appears that the latter effect may be either sufficiently constant or covariant with the former, so that a fair correlation of the chemical shifts with ground state electron density exists.

The most obvious correlation with electron density is seen in the large increase in shielding (≈ 75 ppm) on going from C(R)(OR') to C(R)(NR'R') type compounds. The ability of an NRR' group to participate in dative π bonding to the carbene carbon atom is much greater than that of an OR group. This type of correlation has also been observed by Kreiter and Formacek³. A more refined display of this trend is seen

among compounds (IV), (V) and (VI) where there is a continuous upfield shift as the true (gas-phase) basicity⁴ of the amines, HNRR' , corresponding to the NRR' groups increases.

The data reported here compare satisfactorily with those few reported by others^{3,5} if some allowance is made for possible solvent effects of the magnitude (≤ 5 ppm) found for organic carbonyl compounds⁶.

The shifts of the carbonyl carbon atoms are not observably sensitive to the changes in X and X', even though these changes have a large effect on the shift of the carbenoid carbon atom. This perhaps weakens previous interpretations of physical data (*e.g.*, CO stretching frequencies) in which the CO groups were used as probes to sense electron density distributions in the carbenoid ligand.

There is one minor inconsistency in the results we are reporting. On keeping X constant and changing X' from phenyl to methyl we find decreased shielding when $\text{X} = \text{OC}_2\text{H}_5$ but increased shielding when $\text{X} = \text{NHCH}_3$. The former result is similar to that of Kreiter and Formacek for the corresponding compounds with $\text{X} = \text{OCH}_3$. These authors attributed the shift to π conjugation of the phenyl group with the carbenoid carbon atom. In a previous publication from the same laboratory⁷, it was indicated that conjugation of the phenyl group was probably small since varying the substituents on the phenyl group did not affect the CO stretching frequencies in the expected manner. However, as we noted above, CO stretching frequencies may be relatively insensitive to such an influence. In the only crystal structure reported for a carbenoid complex containing a $[\text{C}(\text{X})(\text{C}_6\text{H}_5)]$ ligand⁸ the plane of the phenyl ring is approximately perpendicular to the carbenoid plane, thus eliminating any conjugative interaction. However, in the same complex, $(\text{OC})_5\text{Cr}[\text{C}(\text{OCH}_3)(\text{C}_6\text{H}_5)]$, the carbenoid ligand has a *trans* configuration, and it thus appears that rotation of the phenyl group into coplanarity with the carbenoid group might occur in solution. In the case of the $[\text{C}(\text{NHCH}_3)\text{X}']$ complexes the configurations are all *cis* and no isomerization is possible due to relatively large C-NHCH₃ double bond character. It may be that this prevents the phenyl group from rotating into or sufficiently close to coplanarity to give significant conjugative interaction. In that case the less inductive C_6H_5 group would leave the carbenoid carbon atom less shielded than it is in the compound with $\text{X}' = \text{CH}_3$.

Quantitative evaluation of T_1 by the progressive saturation technique was carried out only for $(\text{OC})_5\text{CrC}(\text{OEt})\text{Me}$, because of the time required as compared to our available access to the spectrometer. For all three types of carbon atom directly bound to the chromium atom, we measured T_1 's in the range of 1-2 sec. This is notably shorter than the T_1 's which have been found in the vast majority of other metal carbonyls either in this laboratory⁹ or elsewhere^{5,10}.

The relaxation mechanisms¹¹ which most commonly account for short T_1 's (1-5 sec) are dipolar coupling (to spin-active species such as ¹H) or scalar coupling to quadrupolar nuclei (*e.g.*, ⁷⁹Br), neither of which is applicable here.

Of the two remaining important relaxation mechanisms, chemical shift anisotropy and spin-rotational interactions, the latter can be expected³ to be a contributing factor only for small molecules (¹³CS₂, ¹³CH₃OH) near their boiling points. We are left to conclude that chemical shift anisotropy plays a dominant role in the relaxation of ¹³C in the present case, and may eventually provide some valuable insight into the electronic structure of transition metal carbenoid species.

CONCLUDING REMARKS

The results we are reporting raise at least as many questions as they answer. Specifically, we think the following points should be pursued in further investigations. (1) A greater range of complexes should be examined to see if other small deviations from the overall monotonic relationship between chemical shift of the carbenoid carbon atom and the inductive character of the substituents occur. In the event that they do, a properly designed study may be able to reveal the cause. (2) Possible solvent effects on chemical shifts should be tested. Neither benzene nor THF is free of suspicion and a saturated hydrocarbon would probably be preferable to either. The possible influence of solvents is suggested by the powerful coordination of very basic solvents (e.g., THF and pyridine) to the Ge and Sn atoms in the $R_2MCr(CO)_5$ ($M = Ge, Sn$) molecules¹². (3) The surprisingly short longitudinal relaxation times observed suggest that further study of how T_1 's depend on the nature of substituents in substituted metal carbonyls generally, and other carbenoid complexes in particular, might be rewarding.

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