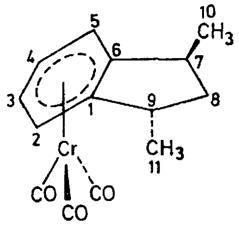
Some Applications of ^{13}C-Fourier Nuclear Magnetic Resonance to Stereochemical Problems of Transition Metal–Olefin Complexes

By **Edward W. Randall** * and **Edward Rosenberg**, Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS
Luciano Milone, Instituto Chimica Generale e Inorganica, Corso Massimo di Azeglio 48, CAP 10125, Torino, Italy

The ^{13}C n.m.r. of tricarbonyl(*trans*-1,3-π-dimethylindane)chromium (I), tricarbonyl(π-cyclo-octatetraene)-tungsten (II) and tricarbonyl(π-allyl)iron(II) iodide (III) and their corresponding free ligands have been studied. The spectrum of (I) shows a separate resonance for every carbon in the ligand ring. The spectrum of (II) shows a temperature dependence (0—90 °C) consistent with its classification as a ' fluxional ' organometallic molecule. The spectrum of (III) in both the hydrocarbon and carbonyl regions shows the presence of two isomers consistent with previous investigations of this compound.

THE potential of ^{13}C n.m.r. as a structural tool in organometallic chemistry has become apparent.[1-4] Relatively few examples, however, of the applications of this technique to unsolved structural problems in organometallic chemistry have appeared.[3,4] We have examined the ^{13}C n.m.r. spectra of three organometallic compounds each of which exhibits a different type of stereochemical behaviour peculiar to π-olefin complexes of the transition metals. We report our findings on these known systems in the hope that the examples presented here will help to point out the advantages and disadvantages of ^{13}C n.m.r. as a structural tool when compared with proton n.m.r. and hence with other spectroscopic techniques.

^{13}C *N.m.r. of Tricarbonyl*(trans-1,3-*dimethylindane*)-*chromium*.—The ^{13}C n.m.r. of *trans*-1,3-dimethylindane shows six resonances as assigned in Table 1. Thus the intrinsic diastereoisomerism present in this molecule does not lead to detectable chemical shift differences in the ring carbons even at the asymmetric centres themselves. Complexation of this ligand with the Cr(CO)$_3$ moiety to give complex (I) [5] removes the degeneracy in the ring carbons and eleven resonances are obtained for the π-ligand [see Table 1 and Figure 1(a)]. This confirms the suggested *trans*-disposition of the ligand methyl groups [5] and leads to the conclusion that intra- or inter-molecular ligand exchange is very slow on the ^{13}C n.m.r. time scale. Similar conclusions can be reached from the ^{1}H n.m.r. data where two doublets at 0·95 and 1·05 p.p.m. are resolved, but the remainder of the spectrum is very complex.



(I)

TABLE 1

^{13}C-Chemical shifts of free and complexed *trans*-1,3-dimethylindane [a]

Compound	δCH$_3$	δCH	δCH$_2$	δAryl C(1,6)	δAryl C(2,5)	δAryl C(3,4)	δCO
trans-1,3-Dimethylindane	20·7	38·6	44·0	137·6	126·8	123·9	
Complex (I)	18·6	36·3	41·3	122·4	95·3	87·0	235·0
	21·5	38·2		119·2	91·7	88·9	

[a] $\pm$0·1 P.p.m. downfield (positive) with respect to internal tetramethylsilane. Measured in CDCl$_3$ containing 10% C$_6$F$_6$ (for ^{19}F-lock) and 5% tetramethylsilane.

The hydrocarbon resonances in (I) can be readily assigned by the use of off-centre double resonance [Figure 1(b)].[6] All the resonances are shifted to high field, this effect being greatest for the aromatic resonances directly bound to chromium as has been previously observed.[2,7] One can infer from these data that ^{13}C n.m.r. shifts are very sensitive to molecular asymmetry in transition metal organometallic species. It has in fact been observed that the presence of a transition metal

---

[1] O. A. Gansow, A. R. Burke, and G. N. La Mar, *J.C.S. Chem. Comm.*, 1972, 456 and references therein.

[2] L. F. Farnell, E. W. Randall, and E. Rosenberg, *Chem. Comm.*, 1971, 1078.

[3] M. Evans, M. Hursthouse, E. W. Randall, E. Rosenberg, L. Milone, and M. Valle, *J.C.S. Chem. Comm.*, 1972, 545.

[4] O. A. Gansow, A. R. Burke, and W. D. Vennon, *J. Amer. Chem. Soc.*, 1972, **94**, 2550.

[5] W. R. Jackson, unpublished results.

[6] E. W. Randall, *Chem. in Britain*, 1971, **7**, 371.

[7] B. E. Mann, *Chem. Comm.*, 1971, 976.

increases the already large shift range for carbon resonances as a result of shielding by the metal.[2,8] It is not possible at present, however, to ascertain whether the methyl group *syn* or *anti* to the $Cr(CO)_3$ group is at higher field or how the remaining resonances are influenced.

We have also observed the ^{13}C n.m.r. spectrum of the carbonyl region of complex (I) at −80 °C. Although slight broadening of the single carbonyl resonance was observed at this temperature, we were unable to resolve the expected separate resonances for the conformation of (I) shown in the diagram. Further lowering of the temperature was precluded by the limited solubility of (I) at low temperatures. This result does suggest that the barrier to rotation around the transition metal–arene bond is quite low even in this relatively crowded complex.

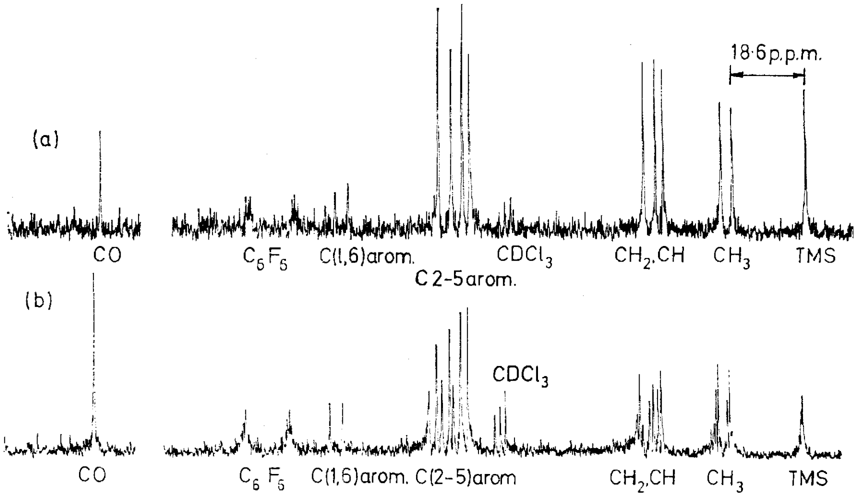
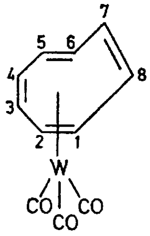


FIGURE 1 (a), 5 kHz proton noise decoupled ^{13}C n.m.r. of tricarbonyl(π-1,3-dimethylindane)chromium (accumulation time: 30 min); (b), 5 kHz ' off-centre ' double resonance ^{13}C n.m.r .of tricarbonyl(π-1,3-dimethylindane)chromium (accumulation time: 60 min)

^{13}C *N.m.r. of Tricarbonyl*(1—6-*η-cyclo-octatetraene*)*tungsten*.—The ' fluxional ' behaviour of complex (II) was first inferred from ^1H n.m.r. data where the two complex multiplets observed at 0 °C collapsed to a singlet at 95 °C.[9] This led to the postulate that the structure in solution was:



(II)

This was later borne out by *X*-ray crystal studies.[10] More work on methyl substituted derivatives of (π-C_8H_8)$M(CO)_3$ (M = Cr or Mo) suggested rotation of the ring *via* 1–2 shift mechanism.[11] We have obtained the ^{13}C n.m.r. of the cyclo-octatetraene ring in (II) in the range of 0—90 °C and find that our results support the conclusions drawn from ^1H n.m.r.

At 0 °C in pentafluorobromobenzene three resonances for the ring carbons are observed (Table 2). The resonance at 99·6 p.p.m. is partially resolved into two resonances in [$^2H_8$]toluene. Although it is not possible to assign definitively these resonances, results for other π-olefin complexes suggest that the terminally co-ordinated carbons are always shifted to highest field with the central carbons of the olefin being less shifted and unco-ordinated olefins being found at lower fields.[2,7] We assign the resonances of (II) accordingly. All the resonances are found to substantially higher fields than in cyclo-octatetraene itself as would be expected from previous results.[7] As the temperature is raised there is an apparently symmetrical collapse of the resonances to a singlet; observed as a shoulder on the A_2B_2X multiplet of C(1) of the solvent C_6F_5Br. The shift of 95·6 p.p.m. of this resonance is in good agreement with the calculated arithmetic mean of 96·2 p.p.m. Symmetrical collapse supports the 1,2-shift mechanism previously proposed.[11]

TABLE 2

^{13}C-Chemical shifts of tricarbonyl(1—6-η-cyclo-octatetraene)tungsten [a]

	Temp. (°C)	δ (C1,6)	δ C(2,5)	δ C(3,4)	δ C(7,8)	δCO
$C_8H_8W(CO)_3$ [b]	0	81·9	98·3	98·5	101·6	
$C_8H_8W(CO)_3$ [c]	0	83·1	99·6	99·6	102·9	193·8
$C_8H_8W(CO)_3$ [c]	90		95·6 [d]		(96·2) [e]	
C_8H_8 [b]	35			132·6 [d]		

[a] ±0·1 P.p.m. downfield (positive) with respect to internal tetramethylsilane. [b] In [$^2H_8$]toluene. [c] In C_6F_5Br. [d] All resonances equivalent on ^{13}C n.m.r. time scale. [e] Calculated average of shifts observed at 0 °C.

---

[8] E. W. Randall and E. Rosenberg, unpublished work.

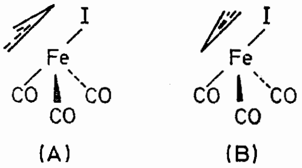
[9] R. B. King, *J. Organometallic Chem.*, 1967, **8**, 129.

[10] J. S. McKechnie and I. C. Paul, *J. Amer. Chem. Soc.*, 1966, **88**, 5927.

[11] F. A. Cotton, A. Musco, and J. W. Faller, *J. Amer. Chem. Soc.*, 1968, **90**, 1438.

It should be noted here that the resonances of the ' frozen ' structure remain reasonably sharp up to 30 °C while this is not the case for the ^{1}H n.m.r. spectrum where separate resonances could be observed only at 0 °C.[9] This follows from the generally greater chemical shift differences in ^{13}C n.m.r. which widens the scope of dynamic processes amenable to study by n.m.r.

^{13}C *N.m.r. of Tricarbonyl(π-allyl)iron*(II) *Iodide*.—The complex ^{1}H n.m.r. spectrum of (III) was first interpreted as evidence for a σ–π-allyl or monomer–dimer equilibrium.[12] A more detailed investigation [13] of the ^{1}H n.m.r. data led to the suggestion of an equilibrium between two rotational isomers of the type:



(III)

The major isomer (between 1·8 and 2·0 : 1) was deduced to have the same configuration as in the solid state. The structure in the solid corresponds to minimum interaction between the central hydrogen atom of the allyl groups and the iodine atom with iodine in one of the axial positions, the allyl group occupying two adjacent octahedral sites and two equivalent CO *trans* to the allyl group (B).[15] The slight asymmetry of the allyl group indicated by C_1–C_2, C_2–C_3, C_1–Fe, and C_3–Fe bond lengths was attributed to intermolecular crystal lattice interactions.

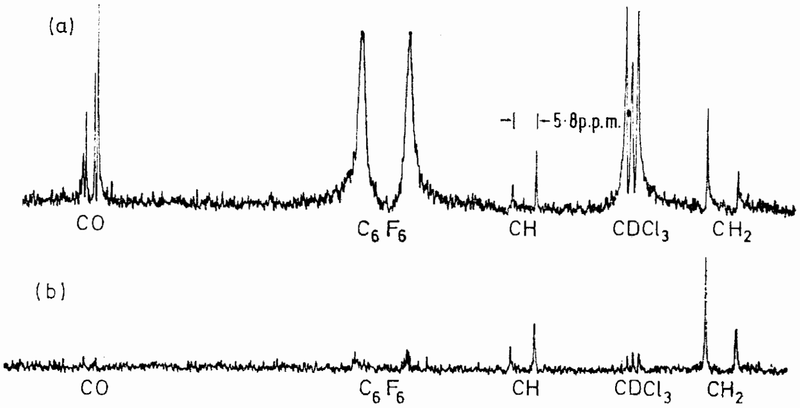


FIGURE 2 (a), 5 kHz proton noise decoupled ^{13}C n.m.r. of tricarbonyl(π-allyl)iron(II) iodide (in 75% $CDCl_3$ + 20% C_6F_6 + 5% tetramethylsilane); 0·1M in tris(acetylacetonato)chromium(III) (accumulation time: 10 min); (b), 5 kHz proton noise decoupled ^{13}C n.m.r. of tricarbonyl(π-allyl)iron(II) iodide (in 75% $CDCl_3$ + 20% C_6F_6 + 5% tetramethylsilane; accumulation time: 10 min)

TABLE 3

^{13}C-Chemical shifts [a] of tricarbonyl(π-allyl)iron(II) iodide

	δCH_2	δCH	δCO (*cis*) [b]	δCO (*trans*) [b]
$Fe(CO)_3(C_3H_5)I$ Isomer (B)	52·6	106·6	207·6	210·4
$Fe(CO)_3(C_3H_5)I$ Isomer (A)	59·7	100·8	206·8	209·9

[a] ±0·1 P.p.m. downfield (positive) with respect to internal tetramethylsilane. [b] *cis*- and *trans*- Refer to the relationship of the CO group to I for both isomers.

The hydrocarbon region of the ^{13}C n.m.r. spectra obtained for (III) shows two CH and two CH_2 resonances. The higher intensity CH resonance being to higher field than the lower intensity one with the opposite being the case for the CH_2 resonances. If we accept the idea that the bulky iodine atom induces an upfield shift on the more proximate carbons by a steric mechanism we assign the higher intensity isomer to (A), thus reversing the ^{1}H n.m.r. assignment. The ^{13}C n.m.r. of (III) in the carbonyl region shows two sets of two resonances with integrated intensities within each set of 1·5 : 1 (in fair accord with the relative intensities of ^{1}H n.m.r. results). The intensity ratio between the sets, *i.e.*, between one resonance in one set to a corresponding resonance in the other set is 2 : 1. We assign the high field set to the resonances of the two CO groups *cis* to the iodine in isomers (A) and (B), and the set at low field to the CO group *trans* to the iodine. This assignment is based not only on intensities since it has been found that CO *trans*- to CO is generally to high field of CO *trans*- to another ligand.[16] Finally the ^{13}C n.m.r. spectra obtained for (III) provide one excellent example of the use of the shiftless relaxation reagent tris(acetylacetonato)chromium(III).[1] There is an at least 10 : 1 signal-to-noise enhancement for the carbons not bound to protons (*e.g.*, CO) due to the shortening of long longitudinal relaxation times which make this type of resonance difficult to detect.

General Conclusions.—The results obtained for the three systems studied here point to the higher sensitivity

---

[12] F. G. A. Stone and R. A. Plowman, *Z. Naturforsch.* (*B*), 1962, **17**, 575.

[13] A. N. Nesmeyanow, Yu. A. Ustynynk, I. I. Kritskaya, and G. A. Schembelov, *J. Organometallic Chem.*, 1968, **14**, 395.

[14] J. D. Cotton, D. Doddrell, R. L. Heazlewood, and W. Kitching, *Austral. J. Chem.*, 1969, **22**, 1785.

[15] M. Kh. Minasyou, Yu. A. Struchkov, I. I. Kritskaya, and R. L. Avoyan, *Zhur. strukt. Khim.*, 1966 **7**, 840.

[16] P. S. Braterman, D. W. Milne, E. W. Randall, and E. Rosenberg, *J.C.S. Dalton*, 1973, 1027.

of ^{13}C n.m.r. to stereochemical changes within a molecule when compared to ^{1}H n.m.r. and to the more complete picture of a molecule obtained by observing all the carbon containing ligands. The greater simplicity of ^{13}C n.m.r. spectra can also be an advantage but sometimes leads to ambiguities in assignment. Finally on the debit side are the sometimes lengthy accumulation times necessary for compounds of moderate solubility [*e.g.* complex (II)] and the necessity of sometimes having to add ' inert ' paramagnetic shiftless relaxation reagents in order to obtain resonances for carbons not bound to protons.

EXPERIMENTAL

Tricarbonyl(1—6-η-cyclo-octatetraene)tungsten and tricarbonyl(π-allyl)iron(II) iodide were synthesised by published procedures.[9,12] All solutions were prepared in 10 mm tubes in an inert atmosphere using dry (molecular sieves), degassed solvents.

Spectra.—Spectra were measured on a Bruker HFX 13 spectrometer operating in the Fourier Transform mode at 22·63 MHz. Proton noise decoupling was obtained using a 90 MHz broad band decoupler. Sample temperature was monitored by a chromel–alumel thermocouple inserted *ca.* 1 cm from the sample tube, the sample being cooled by blown precooled nitrogen, and the standard Bruker BST-100/700 temperature control unit. Temperatures in the range of 0—90 °C were checked against a thermometer in a sample tube containing the same solvent to be used for a given run and were found to agree to within ±3 °C.

The assignments for the aromatic resonances in (I) were made using known substituent parameters.[6]

We are grateful to Dr. W. R. Jackson for suggesting that we study complex (I) and for a sample of the complex, to the S.R.C. for financial support and the British Council for a grant (to L. M.).

[2/2895 *Received, 28th December,* 1972]