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Preliminary communication

^{13}C RELAXATION MECHANISMS IN METHYL-TRANSITION METAL COMPLEXES: HIGH BARRIERS TO ROTATION ABOUT METAL—CARBON σ BONDS

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Summary

^{13}C T_1 and η(CH) have been measured for the methyl carbon in *cis*-$\mathrm{Os(CO)_4(CH_3)_2}$, $(\pi\text{-}\mathrm{C_5H_5})\mathrm{Fe(CO)_2CH_3}$, $(\pi\text{-}\mathrm{C_5H_5})\mathrm{Mo(CO)_3CH_3}$ and $(\pi\text{-}\mathrm{C_5H_5})_2\mathrm{Zr(CH_3)_2}$. From this data, barriers to methyl rotation are estimated to be 4.4 ± 0.7, 5.4 ± 2, > 6, and > 6 kcal/mol, respectively. It appears that such barriers can be substantial even in uncrowded molecules.

Although the observation of ^{13}C NMR spectra has become a routine and informative tool for the organometallic chemist, interest has largely centered upon chemical shifts and coupling constants. The quantitative study of organometallic ^{13}C T_1's has, to our knowledge, been confined to a few simple metal carbonyls and substituted ferrocenes [1—3].

However, measurement of the relatively short relaxation times of proton-bearing organometallic carbons not only will facilitate the acquisition and interpretation of spectra but should yield important information about molecular motions. In particular it has allowed us to reach the following conclusion: barriers to rotation about transition-metal-to-methyl carbon bonds can be substantial even in uncrowded molecules, and quite large (> 6 kcal/mol) when there is appreciable steric hindrance[**].

We have carried out T_1 measurements on a number of representative methyl-transition metal complexes, using 180°—τ—90° pulse sequences and analyzing

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[**] From rotational wings observed in solution IR, a V_0 of 770 cal/mol has been reported for $\mathrm{Au_2(CH_3)_4I_2}$ [4a]. Similarly it has been concluded from the absence of gas phase rotational fine structure on the antisymmetric methyl stretching band that $\mathrm{CH_3Mn(CO)_5}$ (which, as its barrier to internal rotation is presumably 12-fold, would be expected to have a much lower V_0 than any of the compounds in the present study) has a V_0 much greater than RT (a very approximate method of analysis yielded 2.7 kcal/mol) [4b]. Unfortunately, $\mathrm{CH_3Mn(CO)_5}$ cannot be studied by the method described in this paper because of the expected large T_1 contribution from scalar relaxation of the second kind; calculations do suggest that $\mathrm{CH_3Re(CO)_5}$ can be studied successfully.

the data by exponential curve-fitting using an iterative non-linear least-squares procedure [5]. Nuclear Overhauser enhancement factors η have been measured by gated decoupling (with intervals of 10 T_1 between pulses [6]), employing short spectral ranges (including only the methyl-carbon resonance) and 32 K Fourier transforms to insure adequate digitization (at least 50 points per peak) and accurate integrals.

Contributions to spin-lattice relaxation (T_1(other)) other than dipolar C—H can be determined by eq. 1.

$$\frac{1}{T_1(\text{other})} = \frac{1}{T_1(\text{obs})} \left[1 - \frac{2\gamma_C}{\gamma_H}\eta\right] \tag{1}$$

In the absence of any spin-1/2 nuclei other than C and H, and in the absence of spin > 1/2 nuclei capable of causing scalar relaxation of the second kind [7], the only significant contribution to T_1(other) will be from relaxation by spin rotation. Furthermore, for such large, high-molecular-weight molecules, T_1(SR) for the methyl carbon will arise almost exclusively from rotation about the metal—carbon bond [8, 9] (the assumption that T_1(SR) arises from internal rotation has been shown to be quantitatively correct for toluene [10]).

The observed T_1's and the T_1(DD) and T_1(SR) values thus computed are given in Table 1. The T_1's vary by a factor of 5. In light of eq. 2 (for isotropic dipole—dipole contributions) and the minimum methyl-carbon—cyclopentadienyl-hydrogen distances calculated from X-ray data for closely related molecules

$$\frac{1}{T_1(\text{DD})} = h^2 \gamma_C^2 \gamma_H^2 \sum r_{CH}^{-6} \tau_C \tag{2}$$

[11—13] (2.8 Å for (π-C_5H_5)Mo$(CO)_3CH_3$, 3.0 Å for (π-C_5H_5)Fe$(CO)_2CH_3$, and 3.2 Å for (π-$C_5H_5)_2$Zr$(CH_3)_2$), no hydrogens contribute to T_1(DD) other than those directly bonded to carbon.

The results do make qualitative sense in motional terms. In those cases such as (π-C_5H_5Mo$(CO)_3CH_3$, where methyl rotation is so hindered that no spin-rotation contribution is observed, the effective τ_c for $^{13}CH_3$ is increased and T_1(DD) is decreased, whereas in cases of relatively rapid CH_3 rotation, such as Os$(CO)_4(CH_3)_2$, the internal motion decreases the effective τ_c and this increases T_1(DD).

TABLE 1

^{13}C SPIN-LATTICE RELAXATION DATA

Compound	T_1(obs) (sec) [a,b]	η [c]	T_1(DD) (sec)	T_1(SR) (sec) [d]	V_0 (kcal/mol) [e]
cis-Os$(CO)_4(CH_3)_2$	16.3	1.52	21.4	69	4.4 ± 0.7
(π-C_5H_5)Fe$(CO)_2CH_3$	6.3	1.83	6.9	78	5.4 ± 2
(π-C_5H_5)Mo$(CO)_3CH_3$	3.4	1.99	<3.5	>170	>6 [f]
(π-$C_5H_5)_2$Zr$(CH_3)_2$	9.9	1.99	<10.1	>490	>6 [f]

[a] Solvent C_6D_8, probe temperature 34°C. [b] The recovery of the magnetization of solvent carbons was monitored to ensure that there were no effects due to adventitious paramagnetic impurities. [c] All NOE's ± 0.05. [d] Calculated from eq. 1, assuming T_1(other) = T_1(SR). [e] Calculated from eq. 3. [f] While values can be estimated, they may not be valid since the correlation expressed in eq. 3 includes only compounds with methyl rotation barriers < 6 kcal/mol.

Fortunately, quantitative evaluation of the barriers to rotation is now possible by the use of the semi-empirical relationship (eq. 3) reported by Zens and Ellis [9]

$$V_0 = (T_1(\mathrm{SR}) - 25.61)/9.783 \qquad (3)$$

and developed by comparison of T_1(SR) with known (principally from microwave spectroscopy) barriers to rotation of methyl groups in small organic molecules. As the relationship involves phenomena confined to the methyl group (i.e., the effects of a barrier to rotation of any origin on the coupling between the carbon nuclear spin and the internal rotational magnetic field), it should be applicable to organometallic methyl groups without serious error, although there may be small effects arising from changes in hybridization at carbon and changes in H—C—H angles.

The resulting calculated barriers to rotation V_0 are given in Table 1. As the validity of eq. 3 has not been tested for V_0 of 6 kcal/mol and higher (there is no fundamental reason why the relationship should be linear and extrapolation is therefore clearly unwarranted), we prefer to report the barriers in those cases where there is no detectable relaxation by spin-rotation as "> 6 kcal/mol". The high barriers for both $(\pi\text{-}C_5H_5)Mo(CO)_3CH_3$ and $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ may reflect the substantial steric congestion in both complexes, as measured in the Mo case by the short methyl—cyclopentadienyl distance mentioned above, and in the Zr case by the large number of short nonbonded contacts. Even the less crowded Fe and Os complexes show appreciable barriers*. These results lend support to suggestions of restricted rotation about metal—carbon single bonds in conventional variable-temperature NMR studies, e.g. that of $[HMo(C_2H_4)_2(PhPCH{=}CHPPh_2)]^+$, where restricted rotation in an intermediate ethyl species has been proposed [14]. A number of such studies [15—17] had previously reported hindered rotation (barriers as high as 10.5 kcal/mol [15]) about transition metal—carbon σ bonds in sterically congested systems with bulky alkyl ligands.

Work is in progress on the application of this technique to $Au_2(CH_3)_4I_2$, for which IR studies suggest a low V_0 [4a], to $CH_3Re(CO)_5$, which, as its barrier to internal rotation is 12-fold, should have a very low V_0, and to the recently reported [18] $Os_3(CO)_{10}(H)CH_3$, in order to determine whether T_1 and V_0 are significantly different for bridging methyl groups.

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* V_0 for $(\pi\text{-}C_5H_5)Fe(CO)_2CH_3$ has been calculated as 2.9 kcal/mol [19].

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