The existence of CMP glycosides of *N,O*-acylneuraminic acids has been demonstrated;[26] for analogous reasons it has to be expected that these have the β configuration too. Taking into account the fact that in glycoconjugates only α-NeuAc residues occur[27] the β-glycosidic configuration of CMP-NeuAc is in accordance with the assumption that NeuAc residues are transferred to the acceptor molecule via a "single displacement mechanism" with inversion of configuration.[6] So far, there is no evidence that a lipid intermediate is involved in this biosynthesis step since a twofold inversion of configuration would lead to sialic acid residues in β linkages to glycoconjugates. It has been reported that in the biosynthesis of colominic acid (an $\alpha(2 \rightarrow 8)$ linked NeuAc polymer) by *Escherichia coli*[28] sialylundecaprenyl phosphate plays a role. In view of the foregoing this intermediate probably only acts as an acceptor molecule for additional NeuAc residues, thus initiating the polymer formation.

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References and Notes

(1) Dedicated to Professor Dr. E. Havinga on the occasion of his 70th birthday.

(2) Part of this work was presented at the IXth International Symposium on Carbohydrate Chemistry, London, April 10–14, 1978, Abstracts of Papers D7.

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^{13}C NMR Relaxation Mechanisms in Methyl–Transition Metal Compounds

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Abstract: The ^{13}C NMR relaxation mechanisms in transition metal–methyl compounds have been investigated. The methyl carbons in *cis*-$Os(CO)_4(CH_3)_2$, $(\pi\text{-}C_5H_5)Mo(CO)_3CH_3$, $(\pi\text{-}C_5H_5)Fe(CO)_2CH_3$, $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$, and CH_3AuPPh_3 relax by the dipolar and spin-rotation mechanisms. The methyl carbon in $CH_3Re(CO)_5$ shows an additional contribution due to scalar relaxation of the second kind. The relaxation of the methyl and methylene carbons in the tautomeric clusters $Os_3(CO)_{10}(CH_3)(H) \rightleftarrows Os_3(CO)_{10}(CH_2)(H)_2$ is strictly dipolar. Estimates of the methyl rotation barriers from the spin-rotation relaxation times are reported.

Introduction

The use of ^{13}C NMR relaxation times as probes of the structures and dynamics of organic and main-group organometallic compounds is well established.[2] However, only a few studies involving transition-metal organometallic compounds have appeared,[3,4] and to our knowledge only one involving an alkyl carbon σ bonded to a transition metal.[5] We have thus undertaken studies to determine the ^{13}C(methyl) relaxation mechanisms of a number of representative transition metal–methyl complexes. In a preliminary communication[6] we reported the ^{13}C T_1's and η_{CH}'s for the methyl carbons in $(\pi\text{-}C_5H_5)Fe(CO)_2CH_3$, $(\pi\text{-}C_5H_5)Mo(CO)_3CH_3$, $Os(CO)_4(CH_3)_2$, and $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$. Herein we report variable-temperature (and in several instances variable-field) relaxation studies of the above compounds as well as of CH_3AuPPh_3, $CH_3Re(CO)_5$, and $Os_3(CO)_{10}(CH_3)(H)$.

Potential Relaxation Mechanisms for Methyl Carbons. A major contribution to the spin-lattice relaxation rate R_1 ($1/T_1$) of the methyl carbons in transition metal–methyl complexes is expected to be dipole–dipole relaxation R_1^{DD}, due to the methyl hydrogens.[6,7] In the extreme narrowing limit this

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rate is given by eq 1, in which τ_c is the carbon-hydrogen reorientation correlation time.[2b] R_1^{DD} and the non-dipole-dipole contribution R_1^{other} can be determined from R_1 and the nuclear Overhauser enhancement η_{CH} by eq 2.[8] However, when η_{CH} is near the theoretical maximum of 1.99 (i.e., the non-dipole-dipole contribution is small), there is a large uncertainty in the calculated value of R_1^{other}.

$$\frac{1}{T_1^{DD}} = R_1^{DD} = \hbar^2\gamma_C^2\gamma_H^2 \sum_{\text{all H}} r_{CH}^{-6}\tau_c \tag{1}$$

$$\frac{1}{T_1^{other}} = R_1^{other} = \frac{1}{T_1} - \frac{1}{T_1^{DD}} = \frac{1}{T_1}\left[1 - \frac{2\gamma_C\eta_{CH}}{\gamma_H}\right] \tag{2}$$

The reorientation correlation time τ_c is temperature dependent (eq 3)[9] and thus the dipolar contribution decreases with increasing temperature (eq 4).

$$\tau_c = \tau_0 \exp(E_A/RT) \tag{3}$$

$$\ln (R_1^{DD}) = E_A/RT + \text{constant} \tag{4}$$

Possible non-dipole-dipole mechanisms[2a,9] for a methyl carbon include chemical shift anisotropy, spin rotation, and scalar relaxation. The first contribution is field dependent and is described by eq 5, in which $\sigma_\parallel$ and $\sigma_\perp$ are the shielding tensor components and the extreme narrowing limit is assumed. It has been shown to be negligible for organic methyl carbons[10] and is small for first-row transition-metal carbonyl carbons.[11]

$$\frac{1}{T_1^{CSA}} = R_1^{CSA} = \frac{2}{15}\gamma_C^2H_0^2(\sigma_\parallel - \sigma_\perp)^2\tau_c \tag{5}$$

For the molecules studied in this work, the spin-rotation contribution R_1^{SR} to the methyl carbon relaxation will be predominantly due to internal rotation of the methyl group about the M-C bond.[12,13] In the extreme narrowing limit the magnitude of this contribution is given to reasonable accuracy by

$$\frac{1}{T_1^{SR}} = R_1^{SR} = \frac{8\pi^2k_BT(C_\parallel^2I_\parallel\tau_\parallel)}{3\hbar^2} \tag{6}$$

where $C_\parallel$ is the axial component of the spin-rotation coupling tensor, and $\tau_\parallel$ is the angular momentum correlation time for rotation about the symmetry axis, in this case the M-C bond.[12] Substitution of an approximate expression for $\tau_\parallel$, eq 7 (in which $I_\parallel$ is the moment of inertia about the M-C bond, k_B is the Boltzmann constant, and β is an empirical parameter[12,13]), into eq 6 gives the temperature dependence of R_1^{SR}, eq 8. In

$$\tau_\parallel = \beta\sqrt{\frac{I_\parallel}{k_BT}} \tag{7}$$

$$R_1^{SR} \propto \sqrt{T} \tag{8}$$

contrast with other relaxation mechanisms this contribution increases with increasing temperature. For organic methyl carbons R_1^{SR} approaches the limiting value of $\frac{1}{25}$ s^{-1} (at 38 °C) when the barrier to methyl rotation is very low (i.e., the methyl group is a free rotor) and increases approximately linearly with the barrier to rotation V_0.[12]

Scalar relaxation of the second kind is possible for methyl carbons that are bonded to metals with quadrupole moments, but is likely to be important only in $CH_3Re(CO)_5$.[14,15] In the extreme narrowing limit this relaxation mechanism is described by

$$\frac{1}{T_1^{SC}} = R_1^{SC} = \frac{8\pi^2J^2I(I+1)}{3}\left\{\frac{T_1^Q}{1 + (\Delta\omega T_1^Q)^2}\right\} \tag{9}$$

in which T_1^Q and I are the relaxation time and spin of the quadrupolar nucleus, J is the coupling constant between it and the relaxing nucleus, and $\Delta\omega$ is the difference in their Larmor frequencies.[9]

T_1^Q(Re) is not known, but it can be estimated from the $T_1^Q(^{55}Mn)$ in $CH_3Mn(CO)_5$. The quadrupolar relaxation rate

$$\frac{1}{T_1^Q} = R_1^Q = \frac{3}{40}\frac{(2I+1)}{I^2(2I-1)}\left(1 + \frac{\eta^2}{3}\right)(Q')^2\tau_{c,\text{molecular}} \tag{10}$$

(in which η is the asymmetry parameter and Q' is the quadrupole coupling constant[9]) is proportional to $(Q')^2$ when η is small and τ_c is constant.[16] The Re isotopes and ^{55}Mn all have $I = \frac{5}{2}$ and for corresponding compounds $Q'(\text{Re})/Q'(\text{Mn}) \approx 10$,[15] so T_1^Q(Re) and T_1^Q(Mn) are approximately related by eq 11.

$$\frac{1}{T_1^Q(\text{Re})} = R_1^Q(\text{Re}) = \frac{Q'(\text{Re})^2}{Q'(\text{Mn})^2}\frac{1}{T_1^Q(\text{Mn})} \approx \frac{100}{T_1^Q(\text{Mn})} \tag{11}$$

T_1^Q(Mn) in $CH_3Mn(CO)_5$ can be estimated from the ^{55}Mn line width (1.69 G at 14.86 MHz)[17] to be 180 μs, which gives $T_1^Q(\text{Re}) \approx 1.8$ μs. For $CH_3Re(CO)_5$ in a 23.5-kG field $\Delta\omega$ = 15.6 Mrad/s (weighted average for ^{187}Re and ^{185}Re) and $(\Delta\omega T_1^Q)^2 \approx 790 \gg 1$, so that eq 9 reduces to

$$R_1^{SC} = \frac{8\pi^2}{3}\frac{J^2I(I+1)}{(\Delta\omega)^2T_1^Q} \propto \frac{\tau_{c,\text{molecular}}}{(\Delta\omega)^2} \tag{12}$$

Thus the scalar contribution to the ^{13}C relaxation in $CH_3Re(CO)_5$ should be both temperature ($\tau_{c,\text{molecular}} \propto \exp(E_{A,\text{molecular}}/RT)$) and field ($(\Delta\omega)^2 \propto H_0^2$) dependent.

Results and Discussion

Dipole-Dipole and Spin-Rotation Relaxation. The variable-temperature data for all the $M-^{13}CH_3$ compounds studied are summarized in Table I. It is clear from the less than maximum values for η_{CH} that there is a significant nondipolar contribution to the relaxation. For $Os(CO)_4(CH_3)_2$, $(\pi\text{-}C_5H_5)Fe(CO)_2CH_3$, $(\pi\text{-}C_5H_5)Mo(CO)_3CH_3$, $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$, and CH_3AuPPh_3, T_1^{other} decreases markedly with increasing temperature, indicating that the spin-rotation contribution is substantial.

The high-field measurements (Table II) show that for $Os(CO)_4(CH_3)_2$ T_1 is field independent and thus that the chemical shift anisotropy contribution is negligible.[18] As this is the case where such a contribution is most likely to be detected ($Os(CO)_4(CH_3)_2$ has the largest T_1 of the compounds studied, and R_1^{CSA} is probably largest for carbons bonded to heavy metals[19,20]), and, as such effects are rarely important (see Introduction and ref 11), we conclude that relaxation by chemical shift anisotropy is negligible in the Fe, Mo, Zr, and Au compounds as well. We thus conclude that for the compounds above $T_1^{other} = T_1^{SR}$(internal). A plot (Figure 1) of R_1^{other} vs. $\sqrt{T}$ (eq 8) for $Os(CO)_4(CH_3)_2$ is not perfectly linear but, in view of the many approximations built into eq 6-8 and the large uncertainties in the calculated values of R_1^{other}, it offers satisfactory confirmation of our conclusion.

The dipole-dipole contributions show the expected temperature dependence (eq 4) and thus plots (Figure 2) of ln $(1/T_1^{DD})$ vs. $1/T$ are linear. The slopes give reasonable values for the reorientation activation energies (kcal/mol): 2.25 for $Os(CO)_4(CH_3)_2$, 3.45 for $CH_3Re(CO)_5$, 2.48 for $(\pi\text{-}C_5H_5)Fe(CO)_2CH_3$, 2.90 for $(\pi\text{-}C_5H_5)Mo(CO)_3CH_3$, 3.21 for $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$, and 2.84 for CH_3AuPPh_3. (The last two figures are based on only two experimental points.)

Relaxation Mechanisms in $^{13}CH_3Re(CO)_5$. The very low values of η_{CH} (Tables I and II) for $CH_3Re(CO)_5$ indicate that relaxation is predominantly nondipolar. By the argument of the previous section the chemical shift anisotropy contribution is probably small, so that spin-rotation and scalar relaxation of the second kind are the only nondipolar mechanisms possible:

$$R_1^{other} = R_1^{SR} + R_1^{SC} \tag{13}$$

Table I. Variable Temperature ^{13}C(Methyl) Relaxation Data at 25.1 MHz (23.5 kG)

compd		temp, °C							
		−30	0	29	38	50	63	70	90
cis-$Os(CO)_4(CH_3)_2$	$T_1{}^a$	8.47	12.9	13.7	14.8	17.5	17.3		14.0
	$\eta_{CH}{}^b$	1.77	1.46	1.18	1.12 ± 0.05	0.97	0.87		0.68
	$T_1{}^{DD\ c}$	9.57	17.7	23.2	26.3 ± 3	36.1	39.8		41.2
	$T_1{}^{other\ c}$	76.6 ± 20	48.4 ± 7	33.7 ± 4	33.8 ± 4	34.0 ± 3	30.6 ± 3		21.2 ± 2
$(\pi\text{-}C_5H_5)Fe(CO)_2CH_3$	T_1		4.24		7.33		8.80		
	η_{CH}		1.99		1.89 ± 0.02		1.77		
	$T_1{}^{DD}$		4.24		7.72 ± 0.5		9.89		
	$T_1{}^{other}$		>206[d]		150 ± 37		79		
$(\pi\text{-}C_5H_5)Mo(CO)_3CH_3$	T_1			4.41	5.13			7.22	
	η_{CH}			1.99	1.99 ± 0.02			1.81	
	$T_1{}^{DD}$			4.41	5.13 ± 0.3			7.94	
	$T_1{}^{other}$			>440[d]	>510[d]			80.0	
$(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$	T_1				10.0			14.2	
	η_{CH}				1.82 ± 0.02			1.60	
	$T_1{}^{DD}$				10.9 ± 0.6			17.7	
	$T_1{}^{other}$				120 ± 20			72.5	
CH_3AuPPh_3	T_1		3.22		4.6				
	η_{CH}		1.99		1.5 ± 0.05				
	$T_1{}^{DD}$		3.22		6.1 ± 0.5				
	$T_1{}^{other}$		>160[d]		19. ± 3				
$CH_3Re(CO)_5$	T_1		2.33	3.03		3.92			4.73
	η_{CH}		0.46	0.32		0.24			0.19
	$T_1{}^{DD}$		10.1	18.9		32.7			49.5
	$T_1{}^{other}$		3.03	3.61		4.45			5.24

[a] All T_1's are ±5%. [b] NOEs are ±0.05 or as indicated. [c] Calculated from eq 2. [d] Minimum limit estimated from eq 2 using minimum η_{CH}.

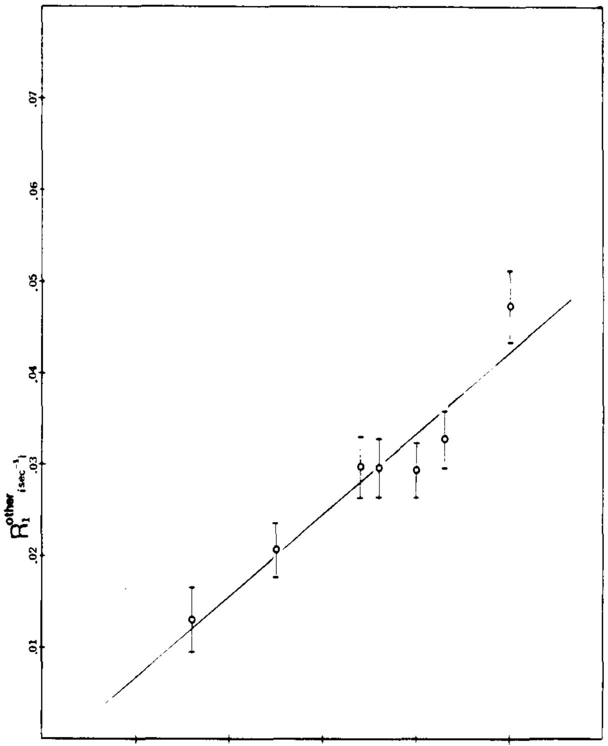

Figure 1. Plot of the nondipolar relaxation rate of the methyl carbon of $Os(CO)_4(CH_3)_2$ vs. $\sqrt{T}$. The line is the least-squares fit to the data, and the bars represent estimated uncertainties.

Table II. ^{13}C(Methyl) Relaxation Data at 67.8 MHz[a] (63.5 kG)

compd	T_1, s	η_{CH}	$T_1{}^{DD}$	$T_1{}^{other}$
$Os(CO)_4(CH_3)_2$	14.3	1.11	25.6	32.4
$CH_3Re(CO)_5$	8.06	0.79	20.3	13.4

[a] Temperature 34 °C.

As indicated by the fact that $R_1{}^{other}$ is much greater than $1/25\ s^{-1}$ at 38 °C (the maximum spin-rotation contribution found for organic methyls[12]) and decreases with increasing temperature, the spin-rotation contribution is minor. On the other hand, the fact that $R_1{}^{other}$ *decreases* markedly with increasing field suggests that scalar relaxation (as described by eq 12 in the Introduction) is important. The field dependence of the scalar contribution can be used to formulate a pair of simultaneous equations (eq 14 and 15) which describes the nondipolar relaxation in two different fields H_1 and H_2.

$$R_1{}^{other(H_1)} = R_1{}^{SC(H_1)} + R_1{}^{SR} \tag{14}$$

$$R_1{}^{other(H_2)} = (H_1/H_2)^2\ R_1{}^{SC(H_1)} + R_1{}^{SR} \tag{15}$$

Solving these equations using $R_1{}^{other}$ values obtained at 23.5 (Table I[21]) and 63.5 kG (Table II) yields the values of $T_1{}^{SR}$ = 22 s and $T_1{}^{SC}$ = 4.6 s in the former field at 34 °C. Scalar relaxation of the second kind is thus the dominant relaxation mechanism for the methyl carbon in $CH_3Re(CO)_5$.[22,23] The observation of field dependence of this type (i.e., $R^{other} \propto 1/H_0{}^2$), is, in the extreme narrowing limit, diagnostic for such a scalar contribution.

$J_{Re\text{-}^{13}C}$ can be estimated as 640 Hz from eq 12 using the estimated value of $T_1{}^Q$(Re) and the experimental value of $R_1{}^{SC}$. This value is reasonable in light of known M–C couplings (e.g., $J_{^{195}Pt\text{-}^{13}C}$ is 594 Hz in *cis*-$(CH_3)_2Pt(P(CH_3)_2Ph)_2$[24]) and is consistent with the fact that no Re–^{13}C coupling is observed (i.e., $2\pi J T_1{}^Q \approx 7.2 \times 10^{-3} \ll 1$).

The dipolar contribution exhibits the expected temperature dependence (Figure 3). In agreement with the above conclusions, the nondipolar contribution, dominated by scalar relaxation of the second kind, approximates the temperature dependence predicted by eq 12 (Figure 3).

Barriers to Methyl Rotation. Zens and Ellis[12] have noted an empirical relationship

$$V_0 = (T_1{}^{SR} - 25.6)/9.78 \tag{16}$$

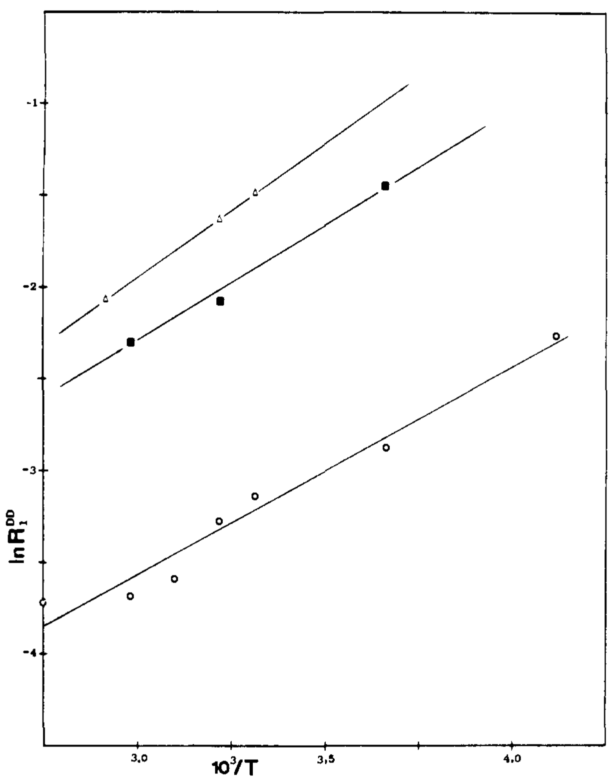

Figure 2. Plot of the logarithm of the dipolar relaxation rate of the methyl carbon in $Os(CO)_4(CH_3)_2$ (○), (π-C_5H_5)$Fe(CO)_2CH_3$ (■), and (π-C_5H_5)$Mo(CO)_3CH_3$ (△) vs. the reciprocal temperature. The lines are the least-squares fits to the data.

Table III. Methyl Rotational Barriers

compd	T_1^{SR}, s[a]	V_0, kcal/mol[b]
CH_3AuPPh_3	19 ± 3	−0.7 ± 0.3 ~ 0
$CH_3Re(CO)_5$	22 ± 20	−0.4 ± 2 ~ 0
$Os(CO)_4(CH_3)_2$	33.8 ± 4	0.84 ± 0.4
(π-C_5H_5)$_2Zr(CH_3)_2$	120 ± 20	>6[c]
(π-C_5H_5)$Fe(CO)_2CH_3$	150 ± 37	>6[c]
(π-C_5H_5)$Mo(CO)_3CH_3$	>500[d]	>6[c]

[a] Calculated from eq 2. [b] Calculated from eq 16. [c] The calculated values are out of the range of the correlation expressed by eq 16. [d] Calculated using η_{CH} = 1.97, the lower limit of the error spread.

between T_1^{SR} at 38 °C and the barrier to methyl rotation V_0 for organic compounds with barriers less than 6 kcal/mol. A V_0 from eq 16 is highly sensitive to temperature and uncertainty in T_1^{SR}. We regard the relationship as being only qualitatively useful for high barriers (where the uncertainty in T_1^{SR} is high, and where deviations from tetrahedral geometry about the methyl carbon are likely, rendering the parameters in eq 16 unreliable[25]), but anticipate reasonable quantitative agreement for low ones. We thus calculate the barriers in Table III; the agreement with our preliminary report is generally good. We attribute the differences (i.e., for $Os(CO)_4(CH_3)_2$) to concentration and viscosity effects (the original relaxation data were obtained for very concentrated solutions, while dilute solutions of labeled compounds were used in the present work) and experimental error: T_1^{SR} (and hence V_0) is difficult to measure accurately when the spin-rotation contribution to the total relaxation rate is small.

The calculated barriers are consistent with the dipolar relaxation results. In those compounds with low calculated barriers, fast methyl group rotation decreases τ_c and lengthens T_1^{DD}. On the other hand, when the barrier is high and methyl rotation is slow, τ_c is long and dipolar relaxation is efficient.

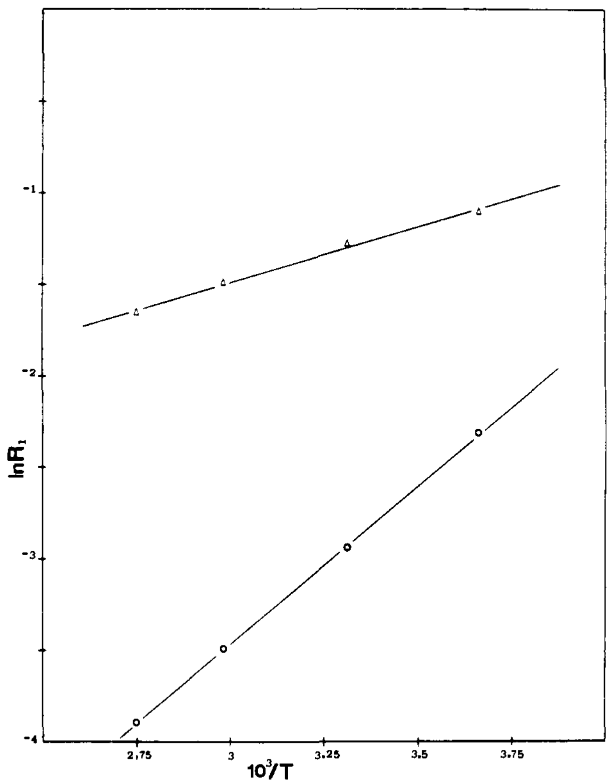

Figure 3. Plot of the logarithms of the dipolar (○) and nondipolar (△) relaxation rates of the methyl carbon in $CH_3Re(CO)_5$ vs. the reciprocal temperature. The lines are the least-squares fits to the data.

The calculated barriers are also consistent with the molecular geometries. The methyl groups in sterically uncrowded $CH_3Re(CO)_5$ and CH_3AuPPh_3 exhibit the expected negligible barriers, while $Os(CO)_4(CH_3)_2$ similarly has a low V_0. Furthermore, the methyl groups in $CH_3Re(CO)_5$ and $Os(CO)_4(CH_3)_2$ rotate against a background of exact or approximate fourfold symmetry; the resulting molecular potentials must be at least approximately 12-fold, with correspondingly shallow minima and low barriers. The high barriers in $CpFe(CO)_2CH_3$, $Cp_2Zr(CH_3)_2$, and $CpMo(CO)_3CH_3$ reflect the higher degree of steric crowding in these compounds, as well as the low symmetry of the environment of the methyl group and the resulting depth of the potential well in the most stable configuration.

^{13}C Relaxation of $Os_3(CO)_{10}(CH_3)(H)$. "$Os_3(CO)_{10}CH_4$" exists as an equilibrium mixture of methyl-bridged ($Os_3(CO)_{10}(CH_3)(H)$) and methylene-bridged ($Os_3(CO)_{10}(CH_2)(H)_2$) forms. To explain the NMR results for a partially deuterated sample, Shapley[26] has proposed a structure for the methyl-bridged isomer which involves an unsymmetrical Os-CH_2-H-Os bridge. The "methyl" must undergo fast (on the NMR time scale) reorientation since only one methyl ^1H signal, which does not broaden down to −100 °C, is seen. ^{13}C T_1 and η_{CH} measurements were performed in order to further investigate the nature of the bridging methyl group.

The results are given in Table IV. It is clear that the slow tumbling of the Os_3 framework results in extremely effective dipole-dipole relaxation at both carbons. While this dominates contributions from other mechanisms which might have given more structural information, certain possibilities for the nature of the CH_3 bridge can be ruled out if we assume equal correlation times for the reorientation of the $Os_3(CO)_{10}(CH_3)(H)$ and $Os_3(CO)_{10}(CH_2)(H)_2$ molecules. For example, the methyl group cannot be undistorted (normal C-H distances) and fixed to the Os_3 frame, since in that case $T_1^{CH_3}$ would be equal to $\frac{2}{3}T_1^{CH_2}$ (the CH_2 is presumably fixed).[2b] Also, it cannot be

Table IV. ^{13}C Relaxation Data (25.1 MHz) for $Os_3(CO)_{10}(H)(^{13}CH_3) \rightleftarrows Os_3(CO)_{10}(H)_2(^{13}CH_2)$[a,b]

	CH_3	CH_2
δ (vs. Me_4Si)	−59.5	25.8
T_1, s	1.20	1.10
η_{CH}	1.99	1.99

[a] Probe temperature 32 °C. [b] CD_2Cl_2 solvent.

undistorted and undergoing free internal rotation, since the dipole-dipole interaction would then be controlled by an (internal rotation) angle averaged Hamiltonian[27] and $T_1^{CH_3}$ would equal $6T_1^{CH_2}$.

We can, however, make the qualitative conclusion that, since $T_1^{CH_3} \approx T_1^{CH_2}$ (i.e., dipolar relaxation per hydrogen at the methyl carbon is slightly less efficient than at the methylene carbon), the methyl must exhibit some combination of hindered internal motion and/or longer than normal C-H distances. This is consistent with the Shapley model.[28] It appears that in general dipolar relaxation will be extremely efficient in cluster compounds unless internal motions which shorten τ_c occur.

Conclusion

Methyl carbons bonded to transition metals will in general relax by C-H dipolar and internal spin-rotation mechanisms. The relative magnitudes of these contributions will be determined by the rate of overall molecular tumbling and the barrier to methyl rotation. Scalar relaxation of the second kind may be important when the metal is quadrupolar, and as in $CH_3Re(CO)_5$ may dominate the dipolar and spin-rotation contributions. Relaxation due to chemical shift anisotropy appears to be unimportant.

Experimental Section

Sample Preparation. $(\pi\text{-}C_5H_5)Fe(CO)_2CH_3$,[29] $(\pi\text{-}C_5H_5)Mo(CO)_3CH_3$,[29b,30] CH_3AuPPh_3,[31] and $CH_3Re(CO)_5$[32], all 90% ^{13}C(methyl) labeled, and 30% ^{13}C(methyl) labeled *cis*-$Os(CO)_4(CH_3)_2$[33] were prepared by previously published methods using appropriately enriched $^{13}CH_3I$. $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ (80% enriched) was prepared by the reaction[34] of $(\pi\text{-}C_5H_5)_2ZrCl_2$ with enriched methyllithium.[35] Solutions (4-6 × 10^{-1} M) of the compounds in toluene-d_8 or benzene-d_6 were sealed under vacuum in 5-mm NMR tubes. All samples were degassed by at least six freeze-pump-thaw cycles on a high-vacuum line, and the solvents were distilled from P_2O_5 before use. The ^{13}C(methyl) enriched $Os_3(CO)_{10}(CH_3)(H)$ sample was obtained from Professor John R. Shapley and an NMR sample was prepared as described above in CD_2Cl_2.

NMR Measurements. The ^{13}C T_1's were determined by the conventional $(180°\text{-}\tau\text{-}90°\text{-AT-PD})_n$ pulse sequence[9,36] on a Varian XL-100 (25.1 MHz) or a Brüker HX-270 (67.8 MHz)[37] spectrometer. The reported T_1's are averages of several measurements and are precise to ±5%. Each T_1 determination consisted of accumulating at least 50 transients at each of 8-15 τ values. Pulse delays were $1\text{-}2T_1$ or $>5T_1$.[38] The data from the former experiments were analyzed by exponential fitting using an iterative nonlinear least-squares procedure[39] which does not require long pulse delays, while for the latter experiments either the nonlinear method or the conventional least-squares procedure[9] was used. No evidence for nonexponential relaxation was found in any of the compounds studied.[5,40,41]

The η_{CH} values were determined by the gated decoupling technique[42] (with intervals of at least $10T_1$ between pulses[43]) and are considered precise to ±0.05. In each case the average of several measurements is reported. Short spectral widths (200 Hz) and 8K or 16K Fourier transforms were used to ensure adequate digitization and accurate integrals. Moderate decoupler power levels were used to avoid temperature variations due to radio-frequency heating of the sample.

The low stability and solubility of CH_3AuPPh_3 required that η_{CH} be determined by the dynamic nuclear Overhauser enhancement (DNOE) method.[44] The two-parameter (S_0, η) fitting procedure was employed, using the separately determined T_1.

The temperatures for the T_1 and η_{CH} measurements were controlled by the XL-100 temperature control module. The probe temperature was measured before and after each run with a calibrated thermocouple or an NMR thermometer (Wilmad Glass Co.), and the variation in all cases was less than ±0.5 °C.

As a check of the accuracy of the results, ^{13}C(methyl) T_1 and η_{CH} for $^{13}CH_3I$[45] and toluene[12] were measured and found to be in agreement with literature values. Also, the XL-100 T_1 and η_{CH} results for $^{13}CH_3Re(CO)_5$ were verified by separate measurements on a Brüker HX-90.[46] Finally, the decay of the magnetization of solvent was monitored and measurements were made on duplicate tubes to ensure that there were no effects due to adventitious paramagnetic impurities.

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Metal Ion Complexes of α-Amido Acids. 1. Structure and Magnetic Properties of the Nickel and Cobalt Hippurates. Pseudo-One-Dimensional Magnetic Systems

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Abstract: The Ni(II) and Co(II) hippurates, $M(hipp)_2(H_2O)_3{\cdot}2H_2O$, have been studied at 298 K by single-crystal X-ray diffraction and UV-visible spectroscopy, and magnetic susceptibility measurements down to 2.2 K have been obtained. The compounds are essentially isostructural and crystallize as linear chains with canted metal octahedra bridged by the oxygen atom of a water molecule. The space group is $C2/c$ with four formula weights per unit cell. The structural properties of the Ni(II) and Co(II) hippurates, respectively, are (1) for Ni, $a = 40.833$ (10) Å, $b = 6.928$ (1) Å, $c = 7.884$ (2) Å, $\beta = 91.92$ (1)°, $R = 0.130$ for 392 reflections; for Co, $a = 40.823$ (7) Å, $b = 6.903$ (1) Å, $c = 7.992$ (2) Å, $\beta = 91.88$ (1), $R = 0.090$ for 715 reflections; (2) the intrachain M–M′ distances (3.942 Å, Ni; 3.966 Å, Co); (3) the interchain M–M* distances along the b axis (6.928 Å, Ni; 6.903 Å, Co); (4) along the a axis, the M–M* distance is about 20 Å in both compounds; (5) the M–O2 (bridging water molecule) distances (2.12 Å, Ni; 2.22 Å, Co); (6) the M–O2–M′ angle (137.2°, Ni; 128.3°, Co); (7) the canting angle, ϕ, made by the canted octahedra with the crystallographic axis (21.4°, Ni; 25.9°, Co). The Ni(II) hippurate complex exhibits a visible spectrum typical of high-spin octahedral Ni(II) complexes; however, the splitting in the visible spectrum of the Co(II) hippurate complex is indicative of the lower site symmetry (C_{2h}) of these compounds. Magnetic susceptibility studies show the Ni(II) hippurate to be an antiferromagnet with $T_c{}^c \simeq 34$ K and $J = -12.9$ cm^{-1}; the Co(II) hippurate is a metamagnet with $T_c{}^c \simeq 15$ K and $T_c{}^b \simeq 3.1$ K. The crystallographic and magnetic susceptibility data indicate that an anisotropic superexchange occurs along the chain (c axis) and that interchain exchange is restricted to dipolar interactions along the b axis. Thus, the nickel and cobalt hippurates constitute pseudo-one-dimensional materials characterized by layers of chains being separated by about 20 Å along the a axis. Since magnetic ordering is not expected between these layers, the nickel and cobalt hippurates represent the first examples of psuedo-one-dimensional magnetic materials in which three-dimensional magnetic ordering is not predicted to occur until $T \rightarrow 0$ K.

Introduction

An earlier communication from our laboratory[2a] reported the initial characterization of a unique cobalt(II) hippurate complex which exhibited a metamagnetic transition at low temperature. The structure was described as a canted, oxygen-bridged linear chain. The structural parameters for this molecule and the analogous nickel(II) complex have now been refined and their respective magnetic properties examined. These molecules represent the first examples of a series of α-amido acid complexes of first-row transition-metal ions

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