A Shiftless Relaxation Reagent for Carbon-13 Magnetic Resonance of Organometallic Carbonyl Compounds

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Summary The addition of small amounts of tris(acetylacetonato)chromium(III) to solutions of several metal carbonyls decreases their T_1 relaxation times without causing chemical shifts, enabling ^{13}C n.m.r. spectra to be obtained using Fourier Transform techniques.

Carbon-13 nuclear magnetic resonance is useful in the study of the bonding, structure, and chemical dynamics of organometallic carbonyls in solution.[1] Fourier transform (FT) methods[2] have made such studies routine for molecules containing carbon bonded to hydrogen, but they have seldom been used to obtain ^{13}C n.m.r. spectra of metal bonded carbonyls.[3] This is because metal bonded carbonyls have long T_1 relaxation times. Very small flip angles and long pauses between successive pulses in the FT technique are required to obtain a free induction decay (fid). We now describe an experimental technique which overcomes the relaxation problem.

The presence of paramagnetic metal ions in solution substantially decreases the T_1 relaxation time of solvent protons.[4] La Mar has recently used this to undermine the Overhauser effect in ^{13}C n.m.r. spectra of organic molecules.[5] The difficulty with using many metal ions is that in addition to reduced T_1 values, a chemical shift (contact shift) of resonances is observed.[4,5] To apply FT methods to the ^{13}C n.m.r. of carbonyls, what is required is a reagent that: (i) is soluble, stable, and kinetically inert in organic solvents, (ii) reduces T_1 relaxation times, (iii) does not cause contact shifts, and (iv) does not unduly broaden resonances by seriously affecting T_2 values. The metal ions Mn^{II}, Fe^{III}, Cr^{III}, and Gd^{III} satisfy requirement (ii).[5] Many metal complexes of these metal ions are soluble in organic solvents, but Cr^{III} is unusual in being relatively inert to substitution and oxidation or reduction reactions.[6]

Tris(acetylacetonato)chromium(III) $[Cr(acac)_3]$ is soluble, stable, and kinetically inert in organic solvents. The organic ligand prevents close approach to the metal of other solute resonances, satisfying requirements (iii), (iv), while still decreasing solute T_1 values.

We have used this reagent to obtain ^{13}C n.m.r. spectra of metal carbonyls, the data being recorded on a Brüker HFX-10 n.m.r. spectrometer.[7] Resonances of $Fe(CO)_5$ and a plot of integrated intensities *vs.* concentration of $[Cr(acac)_3]$ added to CH_2Cl_2 solutions initially 1·0M in $Fe(CO)_5$ with 20% v/v C_6F_6 added as an ^{19}F lock, 10% v/v CS_2, and 5% Me_4Si (present as internal chemical shift references) are shown in Figure 1. Spectra were obtained at identical instrument conditions using 120 μs pulse widths and 0·4 s time between pulses and crossed coil detection. At this pulse width the signal from $Fe(CO)_5$ in the absence of Cr^{III} was at maximum intensity. Addition of Cr^{III} causes a forty-fold increase in intensity. This translates to more than two orders of magnitude decrease in time needed to obtain the ^{13}C n.m.r. spectrum. Also, little line broadening is observed for concentrations of $[Cr(acac)_3]$ below 0·1M. No contact shift was detected within the limits of the experiment (±0·1 p.p.m.).

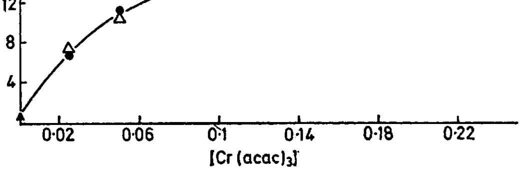

Figure 1. *^{13}C n.m.r. spectra* (a) *and integrated intensities* (b) *of* $Fe(CO)_5$ *obtained in the presence and absence of* $Cr(acac)_3$. ●, △ *refer to two identical but independent experiments.*

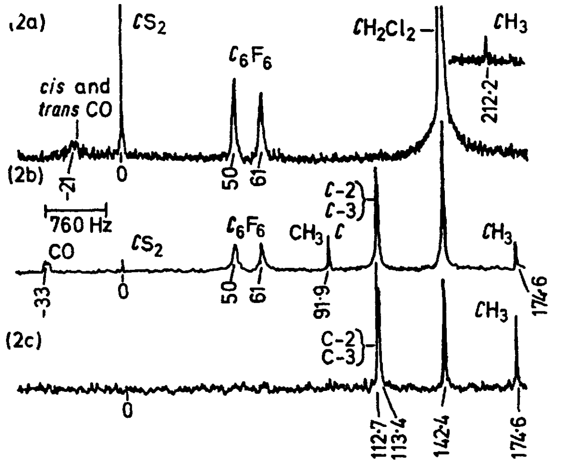

FIGURE 2. ^{13}C *n.m.r. spectra of* (a) $MeMn(CO)_5$ *and* (b,c) (π-MeC_5H_4)$Mn(CO)_3$. *Spectrum* 2a,b *obtained with addition of* 0·05M-$Cr(acac)_3$, 2c *obtained at same instrument conditions with no* $Cr(acac)_3$ *added. Spectra are proton decoupled.*

The shiftless relaxation reagent has also been used to obtain by FT methods the first reported ^{13}C n.m.r. spectra of two manganese carbonyls, though other attempts have been reported.[8] The ^{13}C n.m.r. spectrum of $MeMn(CO)_5$ (Figure 2a) has two signals with intensity ratio 5:1 corresponding to five carbonyl and one methyl resonance. Spectra in Figure 2b,c are from 25% (π-MeC_5H_4)$Mn(CO)_3$ in CH_2Cl_2 solution. No $Cr(acac)_3$ was present in the solution used to obtain Figure 2c, but 2b was measured using a solution 0·05M in the chromium complex. Neither the cyclopentadiene C-1 nor the carbonyl resonance is detected in Figure 2c. In the absence of the relaxation reagent, these resonances saturate. An added effect of the reagent is to ensure that upon signal integration, accurate intensity ratios may be obtained, since the Overhauser effect has been undermined.[5] The large line widths observed for the metal bonded carbonyls probably results from coupling to $I = 5/2$ metal nuclear moment.

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[1] O. A. Gansow and B. Y. Kimura, *J. Amer. Chem. Soc.*, in the press; B. E. Mann, *Chem. Comm.*, 1971, 976, 1173.

[2] R. E. Ernst and W. A. Anderson, *Rev. Sci. Instr.*, 1966, **37**, 93.

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

[4] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, 1962, **37**, 307; A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York, 1967, ch. 13; N. Bloembergen and L. O. Morgan, *J. Chem. Phys.*, 1961, **34**, 841.

[5] G. La Mar, *Chem. Phys. Letters*, 1971, **10**, 230; *J. Amer. Chem. Soc.*, 1971, **93**, 1040; R. Freeman, K. G. R. Pachler, and G. N. La Mar, *J. Chem. Phys.*, 1971, **55**, 4586.

[6] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, 1967, ch. 4.

[7] O. A. Gansow, J. Killough, and A. R. Burke, *J. Amer. Chem. Soc.*, 1971, **93**, 4297.

[8] P. Lauterbur and R. B. King, *J. Amer. Chem. Soc.*, 1965, **87**, 3266.