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The ^{19}F and ^{99}Tc NMR Spectrum of ax-$Tc_2(CO)_9(PF_3)$

CASEY C. GRIMM, RONALD J. CLARK* and RICHARD ROSANSKE

Department of Chemistry, Florida State University, Tallahassee, FL 32306, U.S.A.

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Although ^{99}Tc is the fourth most sensitive nucleus for NMR detection, only a few reports of ^{99}Tc NMR spectra exist [1–6]. Its high spin, $I = 9/2$ with resultant quadrupolar moment, and radioactive nature (low energy β emitter; $t_{1/2} = 2 \times 10^5$ y) have prevented extensive study of diamagnetic technetium compounds by NMR. Generally, one expects efficient relaxation via the quadrupolar moment which results in very short T_2s and consequently broad NMR signals. However, if the electronic distribution about the nucleus is symmetrical, a sharp ^{99}Tc NMR signal can be obtained. For example, the ^{99}Tc NMR spectrum of the tetrahedral pertechnetate ion TcO_4^- gives a line width at half height ($\nu_{1/2}$) of less than 2 Hz [5]. For symmetry less than O_h or T_d, a person's chemical intuition relative to symmetry and line widths can be misled. For instance, it has been shown [7] that the C_{3v} facial isomer of complexes like MoP_3C_3 (P = a phosphine and C = CO) is a pseudooctahedral complex and yields a much sharper molybdenum spectrum than the meridional isomer although many guess the opposite.

A recent report [8] of the ^{99}Tc NMR spectrum of $Tc_2(CO)_{10}$ and our independent discovery of the same characteristics, demonstrated that compounds of lower symmetry containing two technetium nuclei can produce a sharp signal ($\nu_{1/2}$ = 1.4 Hz). The Tc atoms are equivalent [9] but not symmetric along the metal–metal axes and neither possess local T_d or O_h symmetry. The compound, $Tc_2(CO)_{10}$, has D_{4d} symmetry with both of the metal atoms in the zero valent state. Neither of the corresponding spin 5/2 manganese or rhenium compounds gives sharp metal NMR spectra although their nuclear properties are somewhat different from those of technetium. It was the purpose of this investigation to see if the sharp technetium spectrum was an accident or has broader implications to technetium organometallic chemistry.

The forward and back metal–carbon electron donation in metal carbonyls is well known. Trifluorophosphine has been shown to possess bonding characteristics similar to those of carbon monoxide, and has been used as a probe to study the chemistry of metal carbonyls [10, 11]. If any ligand can preserve the electronic environment of the decacarbonyl, it is likely to be PF_3. In the case of the molybdenum compounds $Mo(CO)_{6-x}(PF_3)_x$, the substitution of PF_3 for CO causes only moderate broadening and little chemical shift in the molybdenum-95 spectra [12].

Preparation and isolation of the sample will be reported separately [13]. The data were obtained on an in-house-constructed 'SEMINOLE' NMR having a magnetic strength of 3.55 T. An aqueous solution of NH_4TcO_4 was employed as an external and secondary reference for the ^{99}Tc NMR. An internal standard of $Tc_2(CO)_{10}$ (−2480 ppm from TcO_4^-) was used as the primary reference for the technetium spectra. For ^{19}F, an external reference of $CFCl_3$ was used. The Tc resonance in TcO_4^- is found at 34 MHz, while the fluorine in $CFCl_3$ is found at 142 MHz. Spectra were obtained in $CHCl_3$.

Figure 1 gives the ^{19}F NMR spectra of ax-$Tc_2(CO)_9(PF_3)$ at: (a) 257 K; (b) 297 K; and (c) 337 K. The doublet results from $^1J_{F-P}$ coupling of 1280 Hz which is the characteristic splitting of P–F compounds. The peaks in each half are unusually broad with $\nu_{1/2}$ of 360 Hz at room temperature. The ^{19}F spectra of the analogous compounds $Mn_2(CO)_9(PF_3)$ and $Re_2(CO)_9(PF_3)$ have signals with $\nu_{1/2}$ of less than 5 Hz. An approximately equal mixture of $Re_2(CO)_{10-x}(PF_3)_x$ and $Tc_2(CO)_{10-x}(PF_3)_x$ compounds yields sharp ^{19}F signals for the rhenium compounds while only broad peaks are observed for the technetium compounds. This is a strong indication that the broadening of the ^{19}F NMR signal is due to the presence of the Tc nucleus rather than other prob-

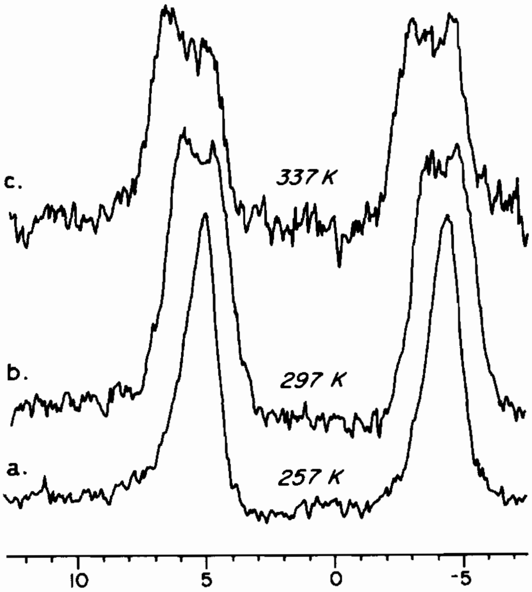

Fig. 1. The ^{19}F NMR spectrum of ax-$Tc_2(CO)_9(PF_3)$ in $CFCl_3$: (a) 257 K; (b) 297 K; (c) 337 K.

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*Author to whom correspondence should be addressed.

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lems such as paramagnetic impurities. Previous studies have reported only a weak interaction between Tc and F even when directly bonded [4].

The compounds were variously examined as raw samples, after filtration, after vacuum distillation, and after gas chromatographic separation. Broadness appears not to be attributable to sample conditions. In our previous experience with the fluorine or hydrogen spectra of PF_3 complexes of spin 5/2 metals like cobalt and manganese, H–F coupling occurs across the metal nuclei without coupling to it nor broadening caused by it. Line widths of only a few Hz were found. The fluorine spectra of the PF_3 complexes with quadrupolar metals are generally quite similar to those found with metals that do not have a quadrupole. The only time we see broad fluorine spectra is when several equivalent PF_3 groups exist resulting in second order broadening or, occasionally, when some stereochemically non-rigid process occurs as found with five-coordinate complexes. The broadening in the present case has the characteristics of neither.

The width of the fluorine line is presumably related to the coupling with technetium as it is found to be temperature dependent. The fluorine could couple to the immediate technetium to yield a ten line pattern which in turn could perhaps be split further by coupling to the far technetium (now chemically inequivalent) yielding the unresolved broad pattern. A related temperature phenomenon has been reported previously for a ^{13}C signal when attached directly to a quadrupolar nucleus [14, 15]. In our case, the $\nu_{1/2}$ drops from over 400 Hz at the elevated temperature to 360 Hz at room temperature to less than 200 Hz at the lower temperature (Fig. 1).

The ^{99}Tc NMR spectra are shown in Fig. 2 for ax-$Tc_2(CO)_9(PF_3)$ at three different temperatures: (a) 257 K; (b) 297 K; (c) 337 K. The sharp signal at 0 ppm is the internal reference $Tc_2(CO)_{10}$. The broad peak downfield at 19 ppm results from the unsubstituted Tc atom in the $(CO)_5Tc–Tc(CO)_4(PF_3)$ compound. The doublet upfield, centered about −130 ppm, is the substituted Tc split by the adjacent ^{31}P nucleus. The large $^1J_{Tc-P}$ coupling of 1750 Hz reflects the strong interaction between the two nuclei.

Cooling the sample sharpens and enhances the signal of the unsubstituted Tc, while substantially broadening the substituted Tc. Conversely, heating the sample sharpens the substituted Tc signal, and the signal of the unsubstituted Tc begins to resolve into a doublet. The $^2J_{Tc'-P}$ is small and is of the order of 40 Hz. The $^2J_{Tc-F}$ coupling is not resolved and can not be determined from the present data. However its existence is shown by the thermal decoupling of the ^{19}F spectrum as the signal sharpens at lower temperatures, which apparently does not affect the $^1J_{F-P}$ coupling.

This is the first example of Tc coupling to a nucleus to which it is not directly bonded. Of continuing interest is the thermal decoupling of fluorine in the ^{99}Tc spectrum. For the substituted nucleus, cooling results in the collapse of the signal, while for the unsubstituted Tc nucleus, cooling sharpens the signal. Substantially unanswered is the fundamental question of whether the sharp spectrum of $Tc_2(CO)_{10}$ is an accident or will be reflected in the NMR of other organometallic compounds. The extensive coupling complicates the determination of the natural line width.

The fluorine and technetium spectra of the diaxial diphosphine complex are even broader than the monophosphine. The two technetium atoms are equivalent, but even further possibilities for second order coupling exist. Further progress in the study demands better methods for the isolation of the individual complexes plus some decoupling experiments.

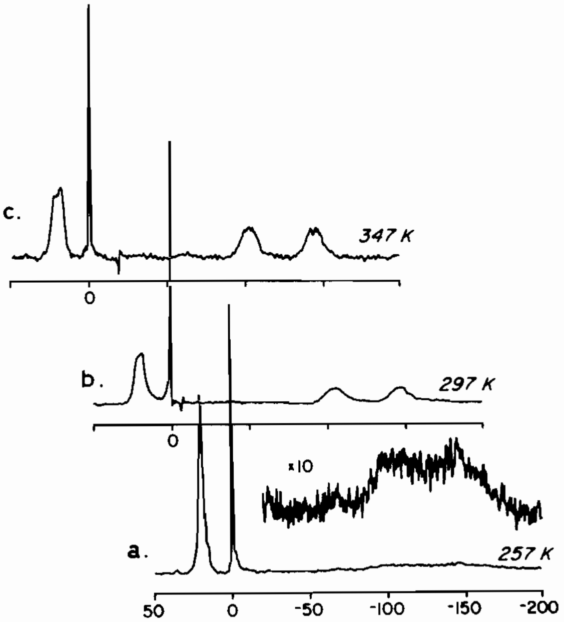

Fig. 2. The ^{99}Tc NMR spectrum of ax-$Tc_2(CO)_9(PF_3)$ in $CFCl_3$: (a) 257 K; (b) 297 K; (c) 337 K.

References

1 K. J. Franklin, C. J. L. Lock, B. G. Sayer and G. L. Schrobilgen, *J. Am. Chem. Soc., 104* (1982) 5303.
2 R. G. Kidd, *J. Magn. Reson., 45* (1981) 88.
3 M. J. Buckingham, G. E. Hawkes and J. R. Thornback, *Inorg. Chim. Acta, 56* (1981) L41.
4 D. W. Webster, D. H. White, F. W. Miller and R. T. Dean, *Inorg. Chem., 23* (1984) 1501.
5 J. L. Vanderheyden, A. R. Ketring, K. Libson, M. J. Heeg, L. Roecker, P. Motz, R. Whittle, R. C. Elder and E. Deutsch, *Inorg. Chem., 23* (1984) 3184.
6 A. Davison, J. F. Kronauge, A. G. Jones, R. M. Pearlstein and J. R. Thornback, *Inorg. Chem., 27* (1988) 3245.

7 K. A. Valiev and M. M. Zaripov, *Eh. Strukt. Khim.*, *7* (1966) 494; G. T. Andrews, I. J. Colquhoun, W. McFarlane and S. O. Grim, *J. Chem. Soc., Dalton Trans.*, (1982) 2353.

8 M. Findeisen, L. Kaden, B. Lorenz, S. Rummel and M. Wahren, *Inorg. Chim. Acta, 128* (1987) L15.

9 M. R. Churchill, K. N. Amoh and H. J. Wasserman, *Inorg. Chem., 20* (1981) 1609.

10 R. J. Clark and M. A. Busch, *Acc. Chem. Res.*, *6* (1973) 246.

11 R. F. Nixon, *Adv. Inorg. Chem. Radiochem.*, *29* (1985) 41.

12 J. T. Bailey, R. J. Clark and G. C. Levy, *Inorg. Chem.*, *21* (1982) 2085.

13 C. C. Grimm and R. J. Clark, *Inorg. Chim. Acta,* to be submitted.

14 H. Baell, C. H. Bushweller, W. J. Dewkett and M. Grace, *J. Am. Chem. Soc.*, *92* (1970) 3484.

15 L. J. Todd and J. R. Wilkinson, *J. Organomet. Chem.*, *80* (1974) C31.