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Preliminary communication

Phosphorus–phosphorus coupling constants in *cis*- and *trans*-isomers of bis(trifluorophosphine)chromium tetracarbonyl

T.R. JOHNSON, R.M. LYNDEN-BELL and J.F. NIXON
Chemical Laboratory, University of Sussex, Brighton BN1 9QJ, Sussex (Great Britain)

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Jenkins and Shaw[1] have observed that phosphorus–phosphorus coupling constants (^2J(PMP')) in second and third row transition metal complexes containing identical phosphines are much larger when the phosphine ligands occupy *trans*-positions than when they are *cis*-, and this has been widely used as an aid to assigning stereochemistry[2,3,4].

In complexes containing dimethylphenylphosphine for example the proton NMR spectrum usually shows a deceptively simple "triplet" pattern in the strongly coupled system because ^2J(PMP') is much larger than ^2J(PCH). Spectra of this type have often been discussed in terms of the concept of "virtual" coupling. In *cis*-complexes ^2J(PMP') is usually rather small and the spectrum appears as a doublet, although two recent reports of metal carbonyl complexes of $P(OCH_2)_3CR$ ligands indicate that ^2J(PMP') can sometimes be large enough in *cis*-compounds to give a "virtually coupled" spectrum[5,6].

We describe here ^{19}F and ^{31}P NMR studies on a mixture of *cis*- and *trans*-bis(trifluorophosphine)chromium tetracarbonyl made by PF_3 displacement of norbornadiene from the norbornadienechromium tetracarbonyl complex which show conclusively than ^2J(PMP') is much larger in the *cis*-isomer than in the *trans*-isomer.

$$C_7H_8Cr(CO)_4 + 2PF_3 \rightarrow \textit{cis-} + \textit{trans-}(PF_3)_2Cr(CO)_4 + C_7H_8$$

Figure 1 shows the ^{19}F NMR spectrum of the *cis–trans*-mixture which are both $X_3AA'X_3'$ spin systems (X = fluorine, A = phosphorus) and the individual spectra are easily identifiable on account of their different fluorine chemical shifts (about 1.3 ppm). As discussed elsewhere[7,8] analysis of the spectra is facilitated because ^2J(PMP') << J(PF) and the resulting spin-coupling parameters are summarised in Table 1. ^1J(PF) and ^3J(PMPF) have *opposite* signs in agreement with our studies on *cis*-tetracarbonylmolybdenum fluorophosphine complexes[7] and it is interesting to note that the *trans*-isomer has much larger values for ^3J(PMPF) and ^4J(FPMPF) than the *cis*-analogue. The ^{31}P NMR spectrum of the mixture also clearly shows the presence of the two isomers and confirms that ^2J(PMP') (*cis*) > ^2J(PMP') (*trans*).

These results suggest that care should be taken when stereochemical assignments

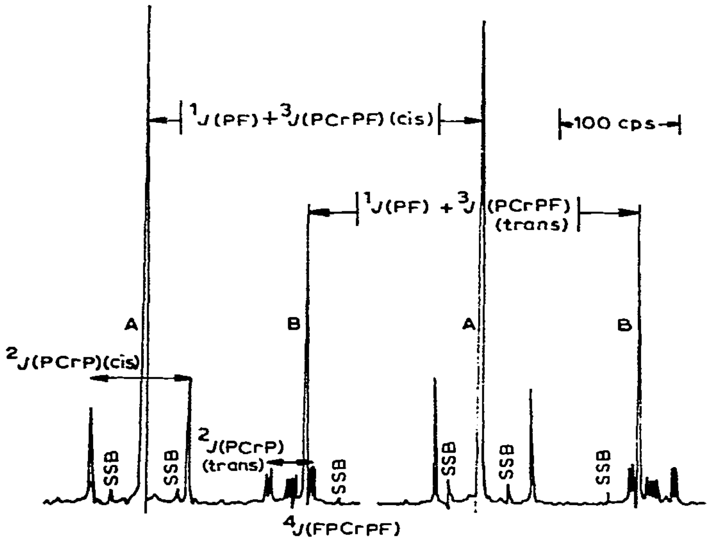

Fig.1.94.1 Mcps. ^{19}F NMR spectrum of a mixture of *cis*- and *trans*-Cr(CO)$_4$(PF$_3$)$_2$. A is the *cis*-isomer and B is the *trans*-isomer. The more extensive fine structure associated with the *trans*-isomer result from the larger values of ^3J(PCrPF) and ^4J(FPCrPF') coupling constants compared with those of the *cis*-isomer.
SSB = spinning band.

TABLE 1

NMR PARAMETERS FOR *cis*- AND *trans*-(PF$_3$)$_2$Cr(CO)$_4$

Isomer	Φ(F)[a]	δ(P)[b]	^1J(PF) (Hz)	^3J(PMPF) (Hz)	^4J(FPMPF) (Hz)	^2J(PMP') (Hz)
cis-[c]	-0.2	-173.2	(−)1312	(+) 2.5	≈0	77.0
trans-	+1.1	-177.8	(−)1318	(+)11.5	2.6	34.0

[a] In ppm (rel. CCl$_3$F). [b] In ppm (rel. H$_3$PO$_4$). [c] Prof. J.G. Verkade has independently studied this isomer (personal communication).

are made based entirely on NMR spectroscopic data, particularly in the case of chromium derivatives[9,10]. A further complication exists because ^2J(PMP') (*cis*) and ^2J(PMP') (*trans*) have opposite signs[11,12] and this aspect will be discussed in greater detail elsewhere[12].

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