Journal of Organometallic Chemistry, 80 (1974) C31—C34

Preliminary communication

A ^{13}C NMR STUDY OF METAL CARBONYL DERIVATIVES HAVING QUADRUPOLAR NUCLEI (Mn, Co, Re AND Ir)

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(Received June 26th, 1974; by publisher September 9th, 1974)

Summary

The room and low temperature ^{13}C NMR spectra of $(PhC{\equiv}CPh)Co_2(CO)_6$, $C_6H_5CH_2Mn(CO)_6$, $Re_2(CO)_{10}$, $Re(CO)_5Br$ and $(\eta\text{-}C_5H_5)Ir(CO)_2$ have been studied. The application of "thermal decoupling" in the case of the first row metal carbonyl derivatives was found to be useful for clarification of the spectra.

Carbon-13 nuclear magnetic resonance has developed in recent years into a powerful tool for the structure elucidation of organo-transition metal compounds [1]. However, there is only a very limited amount of available data on organometallic compounds containing manganese [2—4], cobalt [5,6], and iridium [1,7]. The elements ^{55}Mn (I = 5/2), ^{59}Co(I = 7/2), ^{185}Re and ^{187}Re (I = 5/2) and ^{191}Ir and ^{193}Ir (I = 3/2) are of (or total to) nearly 100% natural abundance. These metals therefore possess quadrupole moments which can potentially broaden the ^{13}C NMR signals of metal-bonded carbon atoms. It has been demonstrated in ^{11}B NMR studies [8] that a resonance broadened by coupling to a quadrupolar nucleus can in certain cases be sharpened by sufficiently cooling the sample. We wish to report the results of a ^{13}C NMR study of some metal carbonyl derivatives in which this "thermal decoupling" technique was employed.

Figure 1 illustrates the room temperature and —67°C ^{13}C NMR spectra of $(PhC{\equiv}CPh)Co_2(CO)_6$. The peaks at 198.2 and 89.6 ppm in the 30° trace have a width at half height ($\delta\nu$) of 46 and 7 Hz respectively. Both of these signals are observably sharpened at the lower temperature. Even at —125°C, the peak at 198.2 ppm which is due to the carbonyl carbon atoms remains a single resonance suggesting (a) that the two types of carbonyl carbons expected for this molecule accidently have nearly the same chemical shift or (b) that the molecule is fluxional in solution. A single frequency off resonance spectrum of this compound demonstrated that only the signals at 128.1, 127.9 and 126.9 ppm (see Table 1) were proton-coupled phenyl

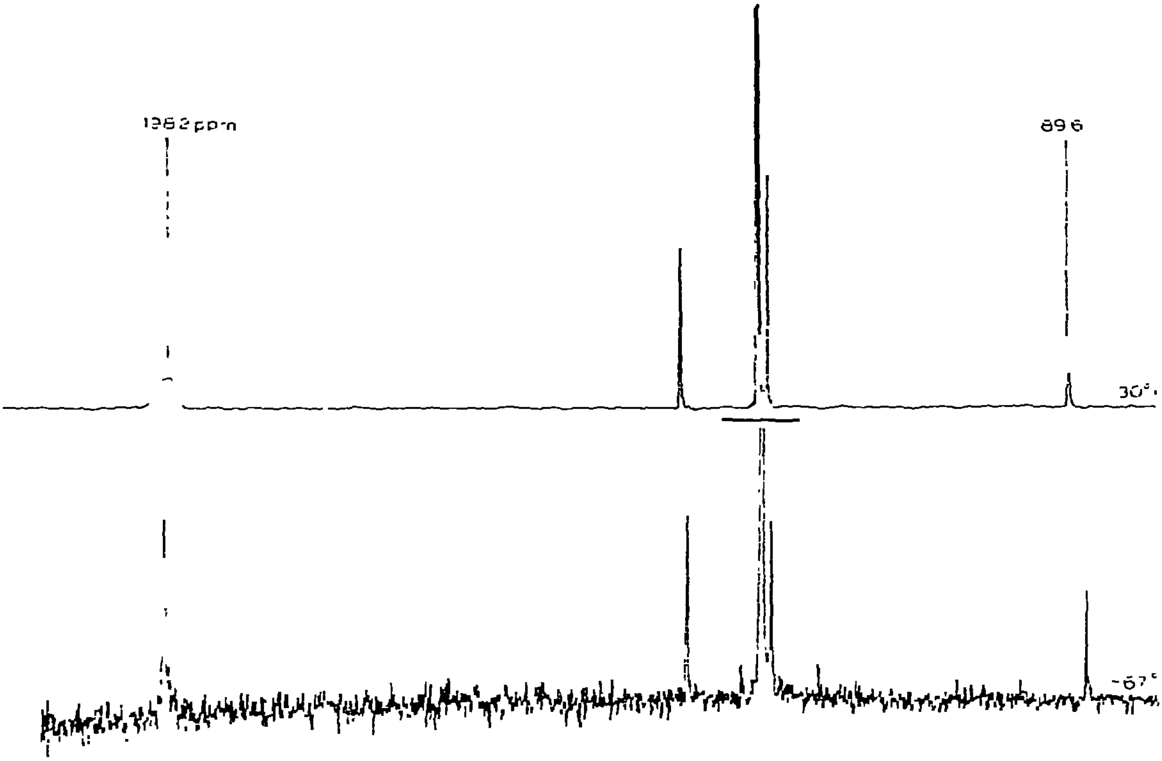

Fig. 1. The room temperature and −67°C ^{13}C NMR spectra of $(PhC{\equiv}CPh)Co_2(CO)_6$.

TABLE 1

^{13}C NMR DATA OF SOME COBALT, MANGANESE, RHENIUM AND IRIDIUM CARBONYL COMPOUNDS

Compound	Solvent	Chemical shift [a] (ppm)	Assignment
$(PhC{\equiv}CPh)Co_2(CO)_6$ [b]	CH_2Cl_2	198.2	carbonyl carbons
		136.9	substituted phenyl carbon
		128.1	protonated phenyl carbons
		127.9	
		126.9	
		89.6	acetylene carbons
$C_6H_5CH_2Mn(CO)_5$ [c]	CH_2Cl_2	211.1	*cis* carbonyl carbons
		209.1	*trans* carbonyl carbons
		151.0	substituted phenyl carbon
		127.2	protonated phenyl carbons
		124.3, 121.7	
		8.7	methylene carbon
$Re_2(CO)_{10}$ [d]	THF	192.8	*cis* carbonyl carbons
		183.7	*trans* carbonyl carbons
$Re(CO)_5Br$ [e]	THF	179.3	*cis* carbonyl carbons
		177.9	*trans* carbonyl carbon
$(\eta\text{-}C_5H_5)Ir(CO)_2$ [e]	THF	173.8	carbonyl carbons
		84.6	cyclopentadienyl carbons

[a] TMS 0 ppm. [b] −67°C. [c] −87°C. [d] −60°C. [e] 30°C.

carbons. The two remaining signals at 136.9 and 89.6 ppm are the substituted phenyl carbon and the acetylene carbon resonances respectively. One can distinguish the acetylene carbon resonance because it is broadened by the quadrupolar cobalt nucleus at room temperature but not at −67° (see Fig.1).

Recently the ^{13}C NMR spectrum of $CH_3Mn(CO)_5$ was reported employing $Cr(acac)_3$ as a shiftless relaxation reagent [2]. The signal in the carbonyl region was a very broad, possibly unsymmetrical, peak which did not distinguish between the *cis* and *trans* carbonyl groups. In Fig.2 are given the room temperature and −87° C ^{13}C NMR spectra (carbonyl region only) of $C_6H_5CH_2Mn(CO)_5$. With the aid of thermal decoupling, the *cis* and *trans* carbonyl resonances are clearly resolved at the lower temperature. It is interesting to note that the *trans* carbonyl signal is upfield of the *cis* carbonyl signal, which is the reverse of what is usually observed for substituted metal carbonyl derivatives [9].

The ^{13}C NMR spectra of $Re_2(CO)_{10}$ and $Re(CO)_5Br$ are fairly well resolved even at room temperature although a slight increase in sharpness is obtained at lower temperatures. Again with these molecules the *trans* carbonyl resonances are upfield of the *cis* carbonyl signals. Recently it was reported [10] that the equatorial carbonyl resonance of $H_2Os(CO)_4$ is upfield of the axial signal. It appears then that covalent single bond substituents on metals may cause *trans* carbonyl resonances to occur at unusually high field.

The ^{13}C NMR data of several iridium compounds have been recently reported e.g. $Ir_4(CO)_8(Ph_2AsCH_3)_4$ [7] and $[(1,5\text{-cyclo-}C_8H_{12})IrCl]_2$ [1]. In these cases no line broadening problems were reported with the room temperature spectra. We have observed that both the cyclopentadienyl and carbonyl resonances of (η-C_5H_5)Ir(CO)$_2$ are sharp singlets at room temperature. These studies with rhenium and iridium compounds suggest that limited quadrupolar broadening difficulties may be encountered with the ^{13}C NMR spectra of compounds of these transition metals.

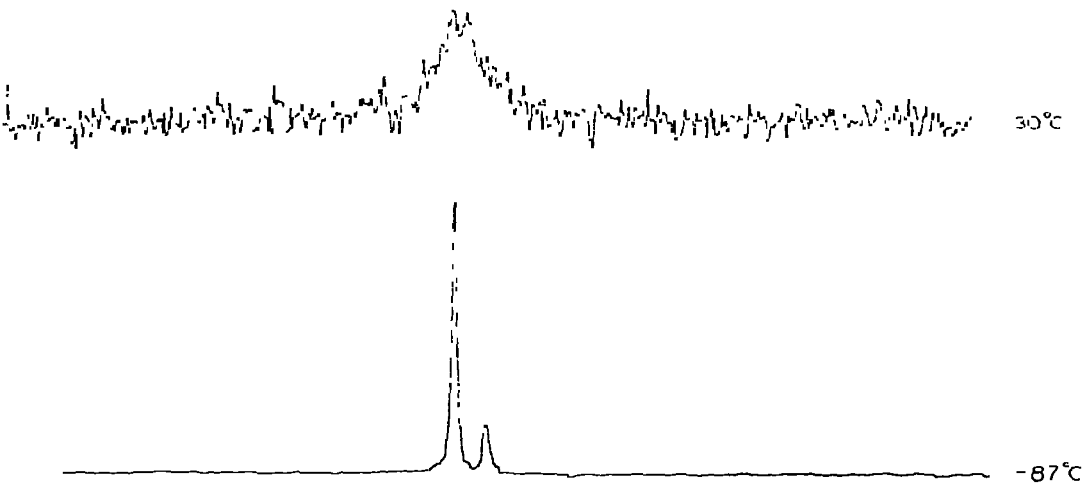

Fig.2. The room temperature and −87°C ^{13}C NMR spectra (carbonyl region only) of $C_6H_5CH_2Mn(CO)_5$.

Acknowledgement

The authors gratefully acknowledge the support of this research by the National Science Foundation through Grant GP 42757. We also thank Dr. Marvin Rausch for a sample of the (η-C_5H_5)Ir(CO)$_2$.

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