Journal of Organometallic Chemistry, 195 (1980) C17—C20

Preliminary communication

MOLYBDENUM-95 NUCLEAR MAGNETIC RESONANCE. APPLICATIONS TO SUBSTITUTED CARBONYLS

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(Received June 5th, 1980)

Summary

Molybdenum-95 NMR spectra of a variety of substituted molybdenum carbonyl species are reported. The large chemical shift range permits easy resolution of substituent effects, both within similar ligands and in the number of carbonyls replaced. Molybdenum-95—phosphorus-31 spin—spin coupling is observed by this technique for the first time. The results are discussed in terms of general applications of the technique to molybdenum organometallic chemistry.

The influence of the metal on the solution properties of organometallic species is usually inferred indirectly via physical techniques such as infrared and ^1H nuclear magnetic resonance (NMR) spectroscopy. More recently, ^{13}C and ^{17}O NMR have augmented these techniques [1,2]. However, the appropriate metal NMR (e.g., ^{103}Rh [3], ^{195}Pt [4], ^{207}Pb [5]) is a most valuable direct probe for that metal in its organometallic chemistry.

This communication reports the direct observation of the ^{95}Mo NMR spectra [6] at natural abundance (15.8 atom %) of a representative series of substituted molybdenum carbonyl species. Although linewidths for this quadrupolar ($I = \frac{5}{2}$, $Q = 0.12 \times 10^{-24}$ cm^2) nucleus are acceptably narrow for these compounds, the relaxation rates allow rapid data accumulation (often limited only by machine parameters). The present results illustrate for the first time the potential of ^{95}Mo NMR in applications to the study of molybdenum organometallics.

Spectra were obtained on naturally abundant samples with a JEOL PFT-100 NMR spectrometer (using a specifically tuned probe) operating in the pulsed Fourier Transform mode at 6.5 MHz. Samples were measured at room temperature in dried degassed solvents where appropriate and signals are conventionally* referenced to external aqueous 2 *M* Na_2MoO_4 at pH 11, the Lamor frequency of which is taken to be 6.5137 MHz exactly. Digital resolution was 0.1 ppm (0.97 Hz) per data point. Concentrations were approximately 0.5 *M* where possible and 1000 transients usually gave an acceptable (>10/1) signal to noise ratio. Representative spectra are illustrated in Fig. 1.

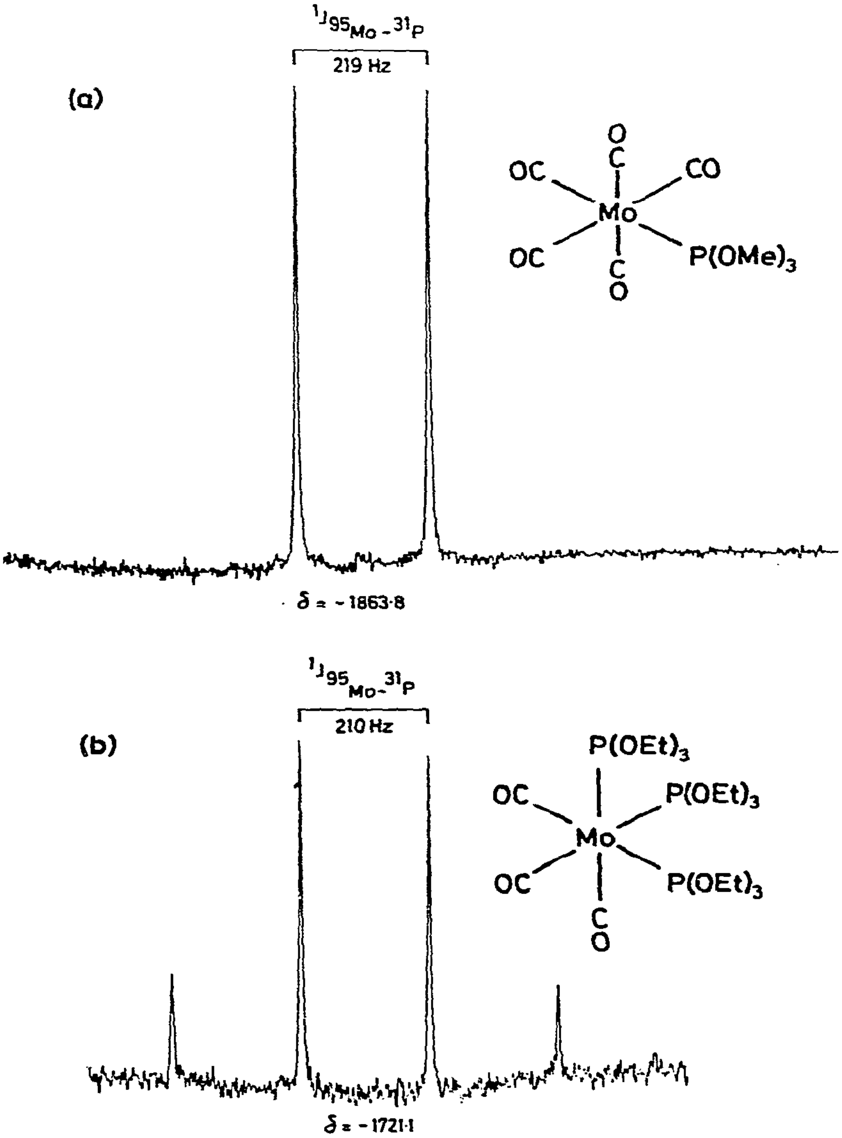

Fig. 1. ^{95}Mo NMR spectra of (a) $Mo(CO)_5[P(OMe)_3]$ (5113 transients) and (b) $Mo(CO)_3[P(OEt)_3]_3$ (3000 transients). Spectral parameters: 1.1 sec repetition time; 2000 Hz total spectral width; 4095 data points.

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*Chemical shifts are expressed as δ values in ppm. Positive values of δ represent a resonance at lower field than that of the standard [7]. This standard is used as it is easy to prepare, stable for several months, observed in a single transient, is approximately in the centre of the chemical shift range and gives a narrow signal.

Table 1 details the ^{95}Mo NMR spectra of the present series of substituted molybdenum carbonyls. Examples were chosen so that effects of simple variations in molecular parameters could be assessed, with a view to establishing a working chemical shift scale for the investigation of new compounds. Where possible, species studied previously using other nuclei have been included for comparison.

Specific points are: (i) Signals are narrow: the broader lines observed with the nitrogen-donor ligands may be due to nitrogen quadrupole effects. The combination of narrow signals and rapid accumulation offers the attractive potential of routine detection of reasonably low concentrations of individual organometallic species.

(ii) A very large chemical shift range is found for these related organometallic species*. This will allow subtle electronic effects at the molybdenum site to be observed. Thus, substituent effects, both within similar ligands, and in the number of $Mo(CO)_6$ carbonyls replaced are observed for several series of compounds (e.g. see Fig. 1).

(iii) A solvent dependence of the molybdenum resonance is observed for $Mo(CO)_6$ **. Similar solvent dependencies of the ^{13}C and ^{17}O NMR spectra have been noted [1,2].

(iv) Molybdenum—phosphorus spin—spin coupling is detected for $Mo(CO)_{6-n}(PR_3)_n$ species (Fig. 1). The coupling makes the assignments unambiguous and

TABLE 1

^{95}Mo NMR PARAMETERS

Compound[a]	Solvent	δ (Mo) (ppm)	$\Delta\nu_{1/2}$ (Hz)
(tol)$Mo(CO)_3$	CH_2Cl_2	−2034.0	5
(mes)$Mo(CO)_3$	CH_2Cl_2	−1907.1	8
$Mo(CO)_5[P(OMe)_3]$	neat	−1863.8	5
		(^1J(Mo—P) 219 Hz)	
$Mo(CO)_6$	CH_2Cl_2	−1856.7	4
	C_6H_6	−1858.1	
$Mo(CO)_5[P(OEt)_3]$	neat	−1853.5	9
		(^1J(Mo—P) 215 Hz)	
$Mo(CO)_3[P(OEt)_3]_3$	CH_2Cl_2	−1721.1	4
		(^1J(Mo—P) 210 Hz)	
(cht)$Mo(CO)_3$	CH_2Cl_2	−1684.0	13
cp$Mo(CO)_3(CH_2C_6H_5)$	MeCN	−1598.8	31
cp$Mo(CO)_3(CH_2C_6H_4$-m-$CF_3)$	MeCN	−1579.0	37
$Mo(CO)_4(N_2$-pr)	DMF	−1310.6	88
$Mo(CO)_4$(bipy)	DMF	−1189.6	110
$Mo(CO)_3$(dien)	DMF	−1087.5	67

[a] Abbreviations used in this communication: tol = toluene, C_7H_8; cp = cyclopentadienide anion, $C_5H_5^-$; N_2-pr = 1,2-propanediamine, $C_3H_{10}N_2$; bipy = 2,2′-bipyridyl, $C_{10}H_8N_2$; dien = diethylenetriamine, $C_4H_{13}N_3$; Me = methyl; Et = ethyl; MeCN = acetonitrile, DMF = dimethylformamide.

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*The present report is part of a survey aimed at establishing a detailed ^{95}Mo NMR chemical shift scale. ^{95}Mo NMR resonances reported to date cover some 30 kHz (4600 ppm) e.g., [(tol)$Mo(CO)_3$], δ (Mo) −2034.0, $[MoS_4]^{2-}$, δ (Mo) 2259 [8].

**A solution of $Mo(CO)_6$ in tetrahydrofuran was previously used [6] to determine δ (Mo). In our hands, such solutions when fresh give a value of δ (Mo) upfield of that reported in ref. 6. On standing, the resonance shifts to the value of ref. 6, before sample decomposition.

represents the first chemical applications of spin coupling in ^{95}Mo NMR spectra. Such coupling has been observed previously [9] via ^{31}P NMR, but broad ^{31}P NMR signals ($\Delta\nu_{1/2}$ approx. 20 Hz) and consequent uncertainties in the values of ^{1}J(Mo—P) result from the similar magnetic moments of molybdenum-95 and -97 (both with $I = \frac{5}{2}$). In terms of linewidths, resolution and spectrum simplicity (two or four peaks in the ^{95}Mo NMR spectra as opposed to seven in the ^{31}P NMR spectra) ^{95}Mo NMR clearly offers advantages over ^{31}P NMR in these and like cases.

Studies directed towards the establishment of a detailed chemical shift scale are continuing.

Acknowledgements

We thank the Australian Wool Corporation and the Australian Research Grants Committee for financial support, Mr. S.F. Gheller for experimental assistance and Dr. C.J. Hawkins for a gift of $Mo(CO)_4(N_2\text{-pr})$.

References

1 L.J. Todd and J.R. Wilkinson, J. Organometal. Chem., 77 (1975) 1 and ref. therein.
2 J.P. Hickey, J.R. Wilkinson and L.J. Todd, J. Organometal. Chem., 179 (1979) 159.
3 D.S. Gill, O.A. Gansow, F.J. Bennis and K.C. Ott, J. Magn. Res., 35 (1979) 459.
4 J.D. Kennedy, W. McFarlane, R.J. Puddephatt and P.J. Thompson, J. Chem. Soc. Dalton, (1976) 874.
5 R.H. Cox, J. Magn. Res., 33 (1979) 61.
6 O. Lutz, A. Nolle and P. Kroneck, Z. Naturforsch. A, 31 (1976) 454.
7 IUPAC Commission on Molecular Structure and Spectroscopy. Pure and Appl. Chem., 45 (1976) 217.
8 O. Lutz, A. Nolle and P. Kroneck, Z. Naturforsch. A, 32 (1977) 505.
9 D.S. Milbrath, J.G. Verkade and R.J. Clark, Inorg. Nucl. Chem. Lett., 12 (1976) 921.