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Preliminary communication

MOLYBDENUM-95 NMR SPECTRA OF SOME MOLYBDENUM CARBONYL AND RELATED COMPOUNDS

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Summary

Molybdenum-95 NMR spectra have been measured for a selection of molybdenum carbonyl compounds and $Mo(\sigma\text{-}C_5H_5)(\eta\text{-}C_5H_5)(NO)(S_2CNMe_2)$. A chemical shift range of more than 1500 ppm is found. The chemical shifts and linewidths are discussed.

At present ^{95}Mo NMR spectroscopy has attracted very little attention with only reports in the literature for a few compounds, namely $[MoO_nS_{4-n}]^{2-}$, $Mo(CO)_6$, and $[Mo(CN)_8]^{4-}$, when this work commenced [1—7]. While this work was in progress [8], a report appeared of ^{95}Mo NMR data for a variety of molybdenum carbonyl derivatives [9], and consequently emphasis was placed on examining different compounds.

The ^{95}Mo NMR spectra were measured at 28.88 MHz using a 10 mm broadband 12—50 MHz probe on a Bruker WH-400 NMR spectrometer. This probe was found to suffer from ringing and a delay of 500 μs was normally used between the pulse and data acquisition Na_2MoO_4 in basic D_2O was used as an external reference compound and the sign convention, that high frequency is positive, is used [10]. The ^{95}Mo NMR data are collected in Table 1.

The ^{95}Mo chemical shifts of the formally Mo^0 complexes cover a wide range from δ – 1033 ppm for *fac*-$Mo(CO)_3(py)_3$ to –1885 ppm for *fac*-$Mo(CO)_3(PCl_3)_3$ reflecting the dependence on the Ramsey equation [11]. As with cobalt(III) complexes [12], the dominant term will be the separation in energy between the occupied d_{xy}, d_{xz}, and d_{yz} orbitals and the empty antibonding d_{z^2} and $d_{x^2-y^2}$ orbitals. This energy gap will be large for *fac*-$Mo(CO)_3(PCl_3)_3$ where the π-acceptor PCl_3 ligands will stabilise the filled d_{xy}, d_{x^2}, and d_{y^2} orbitals. In contrast for *fac*-$Mo(CO)_3(py)_3$ the π-donor pyridine ligands will destabilise these orbitals and decrease the energy gap. As in the approximate Ramsey formalism [11,13],

TABLE 1

^{95}Mo NMR DATA FOR SOME MOLYBDENUM COMPLEXES

Compound	Solvent	$\delta(^{95}Mo)$ (ppm)	$\Delta\nu_{1/2}$ (Hz)
$Mo(CO)_6$	$CDCl_3$	−1857.2	3
$Mo(CO)_5PPh_3$	$CDCl_3$	−1740.1	40
		$(^1J(^{95}Mo, ^{31}P) = 146 \pm 12$ Hz)	—
$Mo(CO)_5AsPh_3$	$CDCl_3$	−1752.6	145
$Mo(CO)_5SbPh_3$	$CDCl_3$	−1861.8	240
$Mo(CO)_5py$ [a]	$CDCl_3$	−1387.4	68
$[Mo(CO)_5Br][NEt_4]$	CD_2Cl_2	−1540.0	125
$[Mo(CO)_5I][NBu^n{}_4]$	CD_2Cl_2	−1660.0	190
$Mo(CO)_5CNCMe_2Ph$	$CDCl_3$	−1752.2	130
$Mo(CO)_4$(norbornadiene)	$CDCl_3$	−1590.7	25
$Mo(CO)_3$(cycloheptatriene)	$CDCl_3$	−1675.3	18.5
$[Mo(CO)_3Cp]_2$	$CDCl_3$	−1855.7	180
fac-$Mo(CO)_3(py)_3$ [a]	$CDCl_3$	−1033.1	85
fac-$Mo(CO)_3(PCl_3)_3$	$CDCl_3$	−1884.7	3
		$(^1J(^{95}Mo, ^{31}P) = 251 \pm 3$ Hz)	
fac-$Mo(CO)_3(AsPh_3)_3$	$CDCl_3$	−1548.9	350
fac-$Mo(CO)_3(SbPh_3)_3$	$CDCl_3$	−1668.8	49
$Mo(CO)_2(C_7H_7)I$	$CDCl_3$	−1348.2	107
$[Mo(CO)_2(C_7H_7)(dppe)][PF_6]$ [b]	CD_2Cl_2	−1083.0	250
		$(^1J(^{95}Mo, ^{31}P) =$ ca. 160 Hz)	
$Mo(\eta\ C_5H_5)(\sigma\text{-}C_5H_5)(NO)(S_2CNMe_2)$	$CDCl_3$	−369.0	390

[a] py = pyridine. [b] dppe = 1,2-bis(diphenylphosphinoethane).

$$\delta = -A + \frac{B}{\Delta E}$$

where ΔE is the energy gap, a reduction in the energy gap results in the chemical shift becoming more positive, as is observed.

The behaviour of the linewidths is far from simple and there must be several factors operating. For $Mo(CO)_6$ and *fac*-$Mo(CO)_3L_3$, in the absence of vibrational distortions, there should be no quadrupole electric field gradient at the nucleus [14] and consequently sharp lines are observed for $Mo(CO)_6$, *fac*-$Mo(CO)_3(PCl_3)_3$, and $Mo(CO)_3(\eta\text{-}C_7H_8)$. The line broadening observed for *fac*-$Mo(CO)_3(py)_3$, *fac*-$Mo(CO)_3(AsPh_3)_3$, and *fac*-$Mo(CO)_3(SbPh_3)_3$ is probably due to other factors such as scalar coupling or loss of C_{3v} symmetry duets rotamers present.

These preliminary results clearly show that ^{95}Mo NMR spectroscopy to be a viable technique in organometallic chemistry. There are no sensitivity problems, but there are some indications that considerable linewidths can occur making signal detection on a ringing probe difficult. Considerable work is necessary to establish chemical shift and linewidth scales.

References

1 J. Kaufmann, J. Kronenbitter and A. Schwenk, Z. Physik. A, 274 (1975) 87.
2 R.R. Vold and R.L. Vold, J. Chem. Phys., 61 (1974) 4360.
3 R.R. Vold and R.L. Vold, J. Magn. Res., 19 (1975) 365.
4 O. Lutz, A. Nolle and P. Kroneck, Z. Naturforsch. A, 31 (1976) 454.
5 W.D. Kautt, H. Krüger, O. Lutz, H. Maier and A. Nolle, Z. Naturforsch. A, 31 (1976) 351.
6 O. Lutz, A. Nolle and P. Kroneck, Z. Naturforsch. A, 32 (1977) 505.
7 P. Kroneck, O. Lutz and A. Nolle, Z. Naturforsch. A, 35 (1980) 226.

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9 A.F. Masters, R.T.C. Brownlee, M.J. O'Connor, A.G. Wedd and J.D. Cotton, J. Organometal. Chem., 195 (1980) C17.

10 Recommendations for the Presentation of NMR Data for Publication in Chemical Journals, Pure Appl. Chem., 29 (1972) 627; 45 (1976) 217.

11 N.F. Ramsey, Phys. Rev., 78 (1950) 699.

12 See for example R.G. Kidd, in R.K. Harris and B.E. Mann (Eds.), NMR and the Periodic Table, Academic Press, London and New York, 1978, p. 241.

13 Note that the Ramsey equation is normally given in terms of shielding rather than chemical shift, with consequential sign changes.

14 A. Yamasaki, F. Yajima and S. Fujiwara, Inorg. Chim. Acta, 2 (1968) 39.