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Observation of $^{95}Mo-^{14}N$ Spin-Spin Coupling in Multinuclear NMR Studies on $(\eta^5\text{-}C_5H_5)Mo(CO)_2(NO)$ and Related Compounds[1]

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One impetus for the rapid growth of ^{95}Mo NMR as a direct probe of molybdenum centers in the past few years[2] is the importance of molybdenum in many enzymatic reactions[3] and the future possibility of studying the molybdenum-containing cofactors[4,5] of enzymes by ^{95}Mo NMR. Important prerequisites for such future cofactor studies are chemical shift and coupling constant data from known molybdenum complexes. Especially pertinent to the cofactors for nitrogenases[5] and the cofactors for nitrate reductases[4] are ^{95}Mo NMR studies of molybdenum complexes of simple nitrogen ligands. Here, we report the first example of $^{95}Mo-^{14}N$ spin-spin coupling in a molybdenum compound.

Experimental Part

The procedure of Legzdins et al.[6] was used to prepare $(\eta^5\text{-}C_5H_5)Mo(CO)_2(NO)$, and the method of Atwood et al.[7] was used for $(\eta^5\text{-}C_5Me_5)Mo(CO)_2(NO)$. Both compounds were sublimed prior to the NMR measurements. $K[HB(3,5\text{-}Me_2Pz)_3Mo(CO)_3]$ and $K[HB(Pz)_3Mo(CO)_3]$ (where $HB(3,5\text{-}Me_2Pz)_3$ = hydrotris(3,5-dimethylpyrazolyl)borate and $HB(Pz)_3$ = hydrotris(pyrazolyl)borate) were prepared according to Trofimenko,[8] converted to their dicarbonylnitrosyl derivatives, and purified according to the procedure of McCleverty et al.[9]

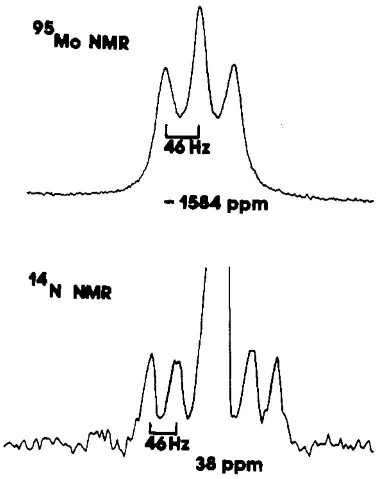

Figure 1. ^{95}Mo and ^{14}N NMR spectra of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(NO)$ in CH_3CN at 293 K showing $^{14}N-^{95}Mo$ spin-spin coupling.

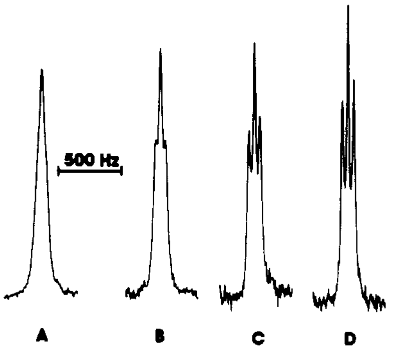

Figure 2. ^{95}Mo NMR spectra of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(NO)$ in CH_3CN at different temperatures: (A) T = 245 K; (B) T = 263 K; (C) T = 283 K; (D) T = 293 K.

All solvents were dried prior to use, and the NMR spectra were measured in sealed 10-mm NMR tubes under nitrogen or argon. Solution concentrations were usually 0.1 M; less soluble complexes were studied as saturated solutions. The NMR spectra were obtained by using a Bruker WM250 NMR spectrometer. For the ^{95}Mo NMR spectra a molybdenum probe (16.3 MHz) was used. A delay of 200 μs prior to acquisition was used to reduce the effects of probe ringing. A 2 M Na_2MoO_4 solution in H_2O at pH 11 was used as external standard.

For the ^{14}N (18.1 MHz) and ^{17}O (33.9 MHz) NMR spectra a 10-mm broad-band probe (9-36 MHz) was used. Nitromethane (neat) was used as external reference for ^{14}N, and H_2O was the external reference for ^{17}O.

Results and Discussion

The ^{95}Mo NMR signal of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(NO)$ (**1**) occurs at −1567 ppm and is split into a triplet due to $^{95}Mo-^{14}N$ spin-spin coupling between the molybdenum atom and the nitrogen atom of the nitrosyl ligand. The coupling constant is 46 Hz in CH_3CN at room temperature (Table I and Figure 1). Cooling the sample, which causes an increase in the correlation time (τ_c), leads to the collapse of the triplet to a single line with a line width that is smaller than the overall width of the triplet (Figure 2). Heating the sample (decrease of τ_c) sharpens the triplet. Because of solvent limitations and decomposition of the complex at higher temperatures, a perfect 1:1:1 triplet could not be observed.

The collapse of the triplet with decreasing temperature follows the trend observed in spectra of protons coupled to ^{14}N

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[10] The ^{95}Mo, ^{14}N, and ^{17}O NMR spectra were measured at two fields, 5.872 T (Bruker WM 250) and 9.395 T (Bruker WM 400). The measurements on the WM 400 were carried out by Dr. C. Brevard at the Bruker facilities in Wissembourg, France.

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Table I. ^{95}Mo, ^{14}N, and ^{17}O NMR Data

compd	chem shift, ppm		^{95}Mo–^{14}N coupling, Hz	chem shift, ppm	
	^{95}Mo^a	^{14}N^b		C^{17}O^c	N^{17}O
$(\eta^5\text{-}C_5H_5)Mo(CO)_2(NO)$	−1584 (≤40)^{d,j}	38 (50)^e	46^d	423 (10)^d	448 (100)^d
$(\eta^5\text{-}C_5Me_5)Mo(CO)_2(NO)$	−1404 (≤40)^{d,j}	52 (60)^e	46^f	424 (10)^d	454 (120)^d
HB(3,5-Me$_2$Pz)$_3$Mo(CO)$_2$(NO)	−751 (60)^{g,j}	17 (130)^e	44^h		
HB(Pz)$_3$Mo(CO)$_2$(NO)	−672 (70)^{g,j}	18 (160)^e	i		

^{a} Relative to 2 M Na$_2$MoO$_4$ at pH 11; line width in Hz in parentheses. ^{b} Relative to nitromethane neat. ^{c} Relative to H$_2$O. ^{d} In CH$_3$CN at 293 K. ^{e} In CH$_2$Cl$_2$/CD$_2$Cl$_2$ at 293 K. ^{f} In CH$_3$CN at 343 K. ^{g} In CH$_3$CN/acetone at 293 K. ^{h} In DMF at 423 K. ^{i} Not yet resolved in DMF at 423 K. ^{j} Line width of the central peak at half-height.

as the rate of electric quadrupole relaxation of the ^{14}N nucleus is increased.[11-14] The line widths as estimated from peak intensities follow the expected 3:2:3 ratio for an intermediate rate of quadrupole relaxation of the ^{14}N nucleus.[15] Similar ^{95}Mo–^{14}N spin–spin coupling was observed in DMF, CH$_2$Cl$_2$, and benzene. In higher viscosity solvents, elevated temperatures were required to observe well-resolved triplets. The splittings are field independent,[10] further confirming their origin as spin–spin coupling.

If the $(\eta^5\text{-}C_5H_5)^-$ ligand of **1** is replaced by $(\eta^5\text{-}C_5Me_5)^-$, HB(3,5-Me$_2$Pz)$_3^-$, or HB(Pz)$_3^-$, then τ_c increases in the order $(\eta^5\text{-}C_5H_5)^- < (\eta^5\text{-}C_5Me_5)^- <$ HB (3,5-Me$_2$Pz)$_3^-$ < HB(Pz)$_3^-$, and elevated temperatures are required to resolve the ^{95}Mo–^{14}N coupling (Table I). The relative order of τ_c for the HB(3,5-Me$_2$Pz)$_3^-$ and HB(Pz)$_3^-$ complexes is the opposite of that expected from their molecular weights. The same relative order of τ_c is found from ^{11}B NMR on these two complexes. Different interactions of the complexes with the solvent are one possible explanation for this behavior. For the HB(Pz)$_3^-$ compound the triplet is just beginning to be resolved at 423 K in DMF.

The ^{95}Mo chemical shifts become more deshielded in the order $(\eta^5\text{-}C_5H_5)^- < (\eta^5\text{-}C_5Me_5)^- <$ HB(3,5-Me$_2$Pz)$_3^-$ < HB(Pz)$_3^-$. Methylation of the $(\eta^5\text{-}C_5H_5)^-$ ligand causes deshielding whereas methylation of the HB(Pz)$_3^-$ ligand causes more shielding.

The ^{95}Mo–^{14}N spin–spin coupling of 46 Hz was also detected in the ^{14}N NMR spectrum of **1** by using Gaussian multiplication (Figure 1). A sextet of weak satellite peaks is expected in the ^{14}N spectrum from coupling to ^{95}Mo ($I = {}^5/_2$, 15.8% abundant), but the inner two components are obscured by the strong central line for ^{14}N bonded to the molybdenum isotopes with $I = 0$. This central line is broadened by coupling to ^{97}Mo ($I = {}^5/_2$, 9.46% abundant), which has a larger quadrupole moment than ^{95}Mo. The ^{15}N spectrum of **1** in CDCl$_3$ was reported earlier,[16] but no ^{15}N–^{95}Mo coupling was observed.

Replacement of the $(\eta^5\text{-}C_5H_5)^-$ group of **1** by $(\eta^5\text{-}C_5Me_5)^-$ causes a 14 ppm downfield shift of the ^{14}N resonance of the nitrosyl group. The nitrosyl groups of the HB(3,5-Me$_2$Pz)$_3^-$ and HB(Pz)$_3^-$ compounds have nearly identical resonances ~20 ppm upfield from **1** (Table I).[17,18]

The ^{17}O chemical shifts for the $(\eta^5\text{-}C_5H_5)^-$ and $(\eta^5\text{-}Me_5C_5)^-$ derivatives are also listed in Table I. No coupling between ^{17}O and ^{14}N was detected. Attempts to observe ^{95}Mo–^{13}C coupling as satellite peaks in the ^{13}C spectra were unsuccessful.

This is the first observation of ^{95}Mo–^{14}N spin–spin coupling. Previously, coupling of ^{95}Mo to ^{17}O,[19] ^{31}P,[2e,h,m,n] ^{19}F,[2n] and ^{13}C[20] has been reported. The observation of ^{95}Mo–^{14}N spin–spin coupling enhances the value of ^{95}Mo NMR as a tool for elucidating the structures of molybdenum compounds and the potential of ^{95}Mo NMR for investigating the binding of nitrogen-containing substrates to molybdenum centers.

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Registry No. 1, 12128-13-1; $(\eta^5\text{-}C_5Me_5)Mo(CO)_2(NO)$, 51213-19-5; HB(3,5-Me$_2$Pz)$_3$Mo(CO)$_2$(NO), 86272-24-4; HB(Pz)$_3$Mo(CO)$_2$(NO), 24981-46-2.

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Electrochemical Studies of Tetrakis(isocyanide) Rhodium(I) Dimers Containing Bis(diphenylphosphino)methane as the Bridging Ligand

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Dinuclear rhodium(I) isocyanide complexes have received a great deal of attention since Gray and co-workers[1] reported the hydrogen-generating properties of [Rh$_2$(bridge)$_4$][B(C$_6$H$_5$)$_4$]^2 (bridge = 1,3-diisocyanopropane). Structurally and electronically similar complexes containing the cation [Rh$_2$(RNC)$_4$(L$_2$)$_2$]$^{2+}$ (R = alkyl group; L$_2$ = bis(diphenylphosphino)methane (DPM) or bis(diphenylarsino)methane (DAM) have also been prepared,[2,3] but many of the properties of the DPM and DAM complexes have not been fully explored.

The generation of hydrogen from HCl solutions by the "bridge" complex results in the formation of mixed-oxidation-state oligomeric species.[4] Subsequent photolysis of these oligomers gives [Rh$_2$(bridge)$_4$Cl$_2$]$^{2+}$. This species is also obtained from the oxidative addition of Cl$_2$ to the parent "bridge"

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