Transition Metal (^{53}Cr, ^{59}Co, ^{91}Zr, and ^{95}Mo) and ^{14}N NMR Spectroscopy of Coordination Compounds Containing Nitrogen Donor Ligands in Low-Viscosity Fluids

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Keywords: High-pressure NMR / Low-viscosity solvents / NMR spectroscopy / Quadrupole nuclei / Supercritical fluids / Subcritical fluids / Transition-metal NMR

Appreciable decreases of the line widths of NMR resonances of the quadrupolar nuclei ^{14}N, ^{53}Cr, ^{59}Co, ^{91}Zr, and ^{95}Mo have been obtained in supercritical solvents and in low-viscosity liquefied gases. Several α-diimines $R^1N{=}C(R^2){-}C(R^2){=}NR^1$ and their coordination compounds have been studied. Regarding the solubility of two α-diimines and some Cr, Zr, and Mo complexes it appears that the addition of small amounts of a modifier (acetone, CH_2Cl_2, THF) results in enhanced solubility of compounds without detrimental effects on the line widths. The use of HP NMR tubes (with and without pressure sensor) is very appropriate for measurements of NMR spectra under high pressure in supercritical fluids and liquefied gases of low viscosity. In several cases it appeared that the use of liquefied gases is more straightforward than the use of supercritical fluids, and gives similar or better results in terms of reduction of line widths.

Introduction

Nuclear magnetic resonance in solution plays an essential role in structure elucidation in chemistry, particularly the characterization of organometallic and coordination compounds. The development of transition metal NMR spectroscopy has greatly increased the knowledge of the relation between chemical shift and structure[1,2] in metal-containing compounds, and can help in solving structures and elucidating reaction mechanisms involving transition metal complexes.[3] Unfortunately, approximately 75% of the metal nuclei have a nuclear spin $I > {}^1/_2$, i.e. these nuclei possess a nuclear quadrupole moment. Obtaining NMR spectra of such nuclei can be troublesome due to their short T_1 and T_2, caused by the (extremely) efficient quadrupolar relaxation mechanism, which results in broadened resonance lines.[4,5] Accordingly, the application of nitrogen NMR spectroscopy for the analysis of nitrogen-containing compounds is difficult due to the low natural abundance of ^{15}N (0.36%), and the quadrupole moment of ^{14}N.

If line widths of quadrupolar nuclei could be considerably reduced, their acquisition and analysis would be greatly facilitated.[6,7] The quadrupolar relaxation[4] of a nucleus with $I > {}^1/_2$ is given in Equation (1), where I denotes the nuclear spin, η_s is the asymmetry parameter of the complex, χ is the nuclear quadrupole coupling constant, and τ_c is the rotational correlation time of the molecule in solution.

$$\Delta\nu_{1/2} = \frac{1}{\pi T_1} = \frac{1}{\pi T_2} = \frac{3\pi}{10}\left(\frac{2I+3}{I^2(2I-1)}\right)\left(1+\frac{\eta_s}{3}\right)(\chi)^2\,\tau_c$$

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The expression for the rotational correlation time is presented in Equation (2), where V is the molecular volume, η_v is the bulk solvent viscosity, k is Boltzmann's constant, and T the temperature.

$$\tau_c = \frac{V\eta_v}{kT}$$

From Equation (1) and Equation (2) it appears that the quadrupolar relaxation rates can be reduced by employing solvents with a low bulk viscosity. For instance, supercritical fluids (SCFs) possess very low viscosities, which is one to two orders of magnitude lower than that of organic solvents,[6] enabling significant reductions of the line widths of quadrupolar broadened resonance lines.[7] Fortunately, the critical temperature and pressure of numerous compounds (see Table 1) are readily accessible by employing versatile yet simple devices like sapphire high-pressure NMR tubes in commercial NMR spectrometers.[8] This fact greatly facilitates the semi-routine acquisition of NMR spectra in supercritical fluids.

The recent and rapid growth in the use of SCFs as reaction media, particularly in catalysis involving transition metal compounds in homogeneous solution, is clearly evident.[9] A major problem is the low solvating power of these

Table 1. Critical values of solvents used in this study

Solvent[a]	T_c[b]	P_c[c]	ρ_c[d]
$CHCl_3$	536.4	54.7	0.667
Acetone	508.1	47.00	0.278
CO_2	304.14	73.75	0.468
CH_2F_2	351.6	58.30	0.545
CHF_3	299.3	48.58	0.526
$CClF_3$	302	38.7	0.581
SF_6	318.69	37.7	0.734

[a] Data taken from ref.[13] – [b] Critical temperature in K. – [c] Critical pressure in bar. – [d] Critical density in g/mL.

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fluids. Apolar compounds usually dissolve sufficiently in SCFs for catalysis and NMR spectroscopy (e.g. small organic molecules[6a,6c] or metal-carbonyl complexes[6b,6d]). For more polar compounds, there are several options: (i) modification with fluorinated anions[10] or with apolar side chains;[11] (ii) addition of small amounts of a co-solvent to a supercritical fluid;[12] (iii) application of polarizable SCFs, e.g., CHF_3, $CClF_3$, $CHClF_2$. In this study, we have taken recourse to the latter two options.

We have studied a number of nitrogen donor ligands (α-diimines) and transition metal complexes in liquefied gases and supercritical fluids by ^{14}N and transition metal (^{59}Co, ^{91}Zr, ^{95}Mo, ^{53}Cr) NMR spectroscopy. Several of these low-viscosity (supercritical) solvents were used to try to reduce their resonance line width. The solubility of α-diimines in several supercritical solvents has also been assessed. The data have been compared to those in common organic solvents.

Results and Discussion

A. ^{14}N NMR Spectroscopy of α-Diimines

Solubility

The solubility of the α-diimine $Me_3CCH_2N{=}C(Me){-}C(Me){=}NCH_2CMe_3$ [*neo*Pe−DAB(Me)] has been determined in $CDCl_3$, CO_2, CHF_3, and $CClF_3$ at 293 K and 323 K by comparison of the relative integrals of the proton signal of the $CH_2C(CH_3)_3$ moiety in their ^1H NMR spectra in the respective solvents. The sample volume of the HP NMR tube[8] was reduced to 1.7 mL employing an aluminum plug inserted in the high pressure NMR tube in order to reduce convection in the HP NMR tube and to ensure proper thermostatization of the samples during NMR experiments. The relative solubilities, the line widths at half height $\Delta\nu_{1/2}(^{14}N)$ and the ^{14}N and ^1H chemical shifts have been compiled in Table 2.

In liquefied gases and supercritical fluids, saturated solutions of *neo*Pe-DAB(Me) were employed at concentrations ranging from 0.004 to 0.072 M. The maximum achievable concentration in the compressed gasses amounted to 0.072 M in CO_2(l) at 293 K and 55.5 bar; the concentration employed in $CDCl_3$ was 0.091 M. The solubilities at 293 K and at 323 K are graphically shown in Figure 1.

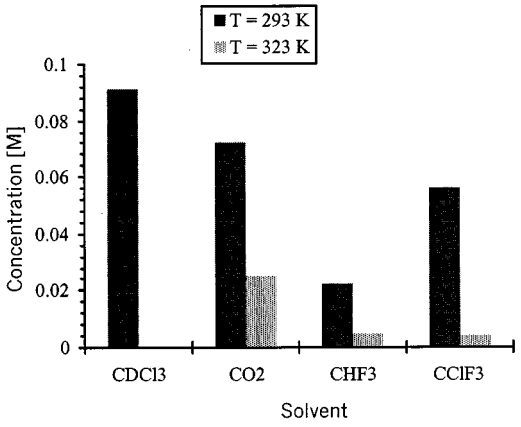

Figure 1. Solubility of $Me_3CCH_2N{=}C(Me){-}C(Me){=}NCH_2CMe_3$ [*neo*Pe-DAB(Me)] in various liquid and supercritical solvents

The solubility of *neo*Pe-DAB(Me) decreases by a factor of about 5 going from $CDCl_3$ to liquefied CHF_3 (293 K), but not very much for liquefied CO_2 or $CClF_3$. Its solubility is much lower (by a factor of between 4 and 20) in the supercritical state for the solvents studied (CO_2, $CClF_3$, CHF_3). This is the result of the low density of the SCFs compared to the density of the liquid state, which leads to a decrease of the solvent−solute interactions. The highest solubility of *neo*Pe-DAB(Me) in the series of pressurized gases studied was observed for CO_2 and $CClF_3$ in the liquid state. Its solubility in CHF_3, either in the liquid or supercritical state, is approximately a factor 4 or 5 lower than its solubility in liquid or supercritical CO_2. The higher solubility of *neo*Pe-DAB(Me) in liquid $CClF_3$ compared to liquid CHF_3 is due to the higher polarizability of the former. The higher solubility of *neo*Pe-DAB(Me) in CO_2 compared to CHF_3 is surprising as the dipole moment of the latter is higher than that of CO_2 [$\mu(CHF_3)$ = 1.65 Debye; $\mu(CHCl_3)$ = 1.01 Debye][13] and the polarizability of CHF_3

Table 2. Solubility and ^{14}N line width of *neo*Pe-DAB in several low-viscosity solvents

[a]	$CDCl_3$		CO_2		CHF_3		$CClF_3$	
T (K)	293	323	293	323	293	323	293	323
P[b]	nd	nd	55.5	97.9	40.3	67.0	31.2	48.6
ρ_c[c]	−	−	ld	0.67	ld	0.64	ld	0.66
Amount/mmol[d]	0.154	0.154	0.126	0.120	0.136	0.125	0.127	0.127
[*neo*Pe-DAB][e]	0.091	n.d.	0.072	0.025	0.022	0.005	0.056	0.004
$\delta(^1H)$[f]	0.95	0.97	−0.6	0.3	−0.4	0.4	−0.6	0.4
$\Delta\nu_{1/2}$[g]	1100±25	670±25	295±10	160±10	280±10	160±10	300±10	140±10
$F_{1/2}$[h]	1.6		1.8		1.8		2.1	
$\delta(^{14}N)$[i]	−40	−39	−41	−40	−42	−41	−41	−40

[a] The experiments were performed in the HP NMR cell described in ref.[8] − [b] Pressure in bar, nd not determined. − [c] Density of the supercritical fluid in g/ mL, ld density of the liquefied gas at its vapour pressure and 293 K. − [d] Amount of *neo*Pe-DAB(Me). − [e] Uncorrected relative integral of the $CH_2C(CH_3)_3$ proton signal, the integral of a 0.091 M $CDCl_3$ solution was arbitrarily calibrated at 1. − [f] Proton chemical shift of $CH_2C(CH_3)_3$ in ppm. − [g] ^{14}N NMR resonance line width at half height in Hz. − [h] Reduction factor $F_{1/2}$= $[\Delta\nu_{1/2}(293\ K)]/[\Delta\nu_{1/2}(323\ K)]$. − [i] ^{14}N chemical shift in ppm.

is slightly higher than that of CO_2 [$\alpha(CHF_3) = 2.80$ Å^3; $\alpha(CO_2) = 2.63$ Å^3].[14]

Chemical Shift

The ^{14}N chemical shifts of *neo*Pe-DAB(Me) vary between $\delta = -39$ and -42 (Table 2), the ^{14}N NMR resonances shift by 1 ppm upon heating the solutions from 293 K to 323 K. The change in ^{14}N chemical shift observed when heating liquefied gases is similar to the change observed when heating a $CDCl_3$ solution. In the case of the compressed gases, the effect of temperature on the chemical shift of the ^{14}N NMR resonance of *neo*Pe-DAB(Me) is not caused by a decrease of the fluid density, but is due to variations in the shielding tensor.

The variation in the ^1H chemical shift is more striking. The proton signals are shifted by approximately -1.5 ppm upon changing the solvent from $CDCl_3$ to the liquefied gases. In $CDCl_3$ no change is observed for the ^1H chemical shift, when heating the solution from 293 K to 323 K, whereas the chemical shift increases by 1 ppm in the case of the liquefied gases. This is explained by the variation of the diamagnetic volume susceptibility of the compressed gases changing from the liquid to the supercritical state.[15]

Line Widths

Line widths of the ^{14}N NMR resonances of *t*Bu-DAB and *neo*Pe-DAB(Me) in CO_2, $CClF_3$, CHF_3, SF_6, and acetone/[D_6]acetone (3:1) have been determined at various temperatures in the range 293−323 K. These data are graphically shown in Figure 2.

The reduction of the ^{14}N line widths in supercritical solvents compared to acetone and $CDCl_3$ is appreciable. [The ^{14}N line width of *neo*Pe-DAB(Me) has also been compared to $CDCl_3$ at 293 K; 1100 ± 25 Hz and at 323 K: 670 ± 20 Hz, see above, Table 2.] This clearly demonstrates the advantageous effect of the low-viscosity fluids on quadrupolar relaxation rates: Indeed much sharper lines are observed in the liquefied gases and supercritical fluids. Although the line widths of the ^{14}N resonances of *t*Bu-DAB (Figure 2, A) and *neo*Pe-DAB(Me) (Figure 2, B) are very different, the variation in line width for each compound spans a similar range, indicating that the values of τ_c in the various liquefied gases and SCFs are comparable. Furthermore, as expected, the observed ^{14}N NMR line widths are lower in the SCFs (at 323 K) than in the liquefied gases (at 293 K). Reduction factors[16] of the line widths of the ^{14}N NMR resonances in liquefied gases at 293 K and in the SCFs at 323 K relative to $CDCl_3$ at 293 K, as well as at 323 K, have been compiled in Table 3.

Not withstanding the fact that acetone has a much lower viscosity than chloroform, the line widths of the ^{14}N resonances in the liquefied gases and SCFs are considerably reduced with respect to acetone solutions. The line widths of the ^{14}N resonances observed in the liquefied gases range from 280 to 300 Hz, the line widths in the SCFs range from 140 to 160 Hz. This indicates similar viscosities of the solvents used (CO_2, $CClF_3$, CHF_3) for each of the domains (liquid and supercritical state, respectively).

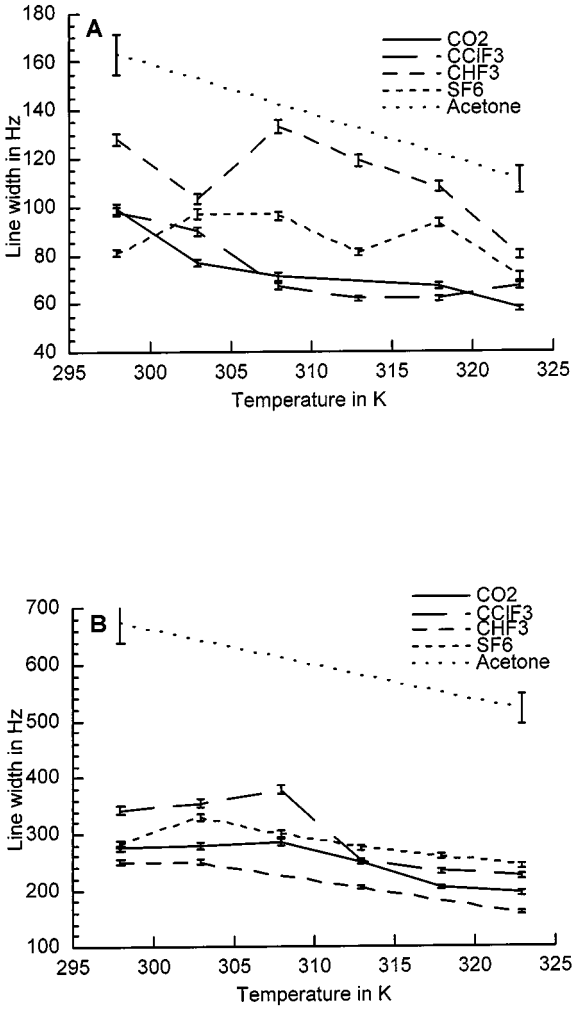

Figure 2. ^{14}N line widths at half height of (A) $Me_3CN{=}C(H){-}C(H){=}NCMe_3$ (*t*Bu-DAB) and (B) $Me_3CCH_2N{=}C(Me){-}C(Me){=}NCH_2CMe_3$ [*neo*Pe-DAB(Me)] in various compressed gasses and acetone; estimated error for the line widths (2%) indicated

Table 3. Reduction factors ($F_{1/2}$) of the ^{14}N line width for *neo*Pe-DAB(Me) in liquefied gases and supercritical fluids

$CDCl_3$[a]	CO_2		CHF_3		$CClF_3$	
T (K)	293	323	293	323	293	323
293	3.7	6.9	3.9	6.9	3.7	7.8
323	2.3	4.2	2.4	4.2	2.2	4.8

[a] Reduction factors [$F_{1/2} = \Delta\nu_{1/2}$(organic solvent)/$\Delta\nu_{1/2}$(compressed gas)] are reported relative to $CDCl_3$ at 293 K and 323 K.

Heating solutions in liquefied gases to above the critical temperature results in a reduction of the ^{14}N line width. The reduction factors associated with these changes range from 1.8 to 2.1. For $CDCl_3$ a reduction factor of 1.6 is observed when heating a solution from 293 K to 323 K. This indicates that the additional line narrowing resulting from the reduced viscosity of the supercritical fluid compared to the liquefied gas is small. The combined temper-

ature and viscosity effect of $CDCl_3$ is similar to that observed for the compressed gases. The fact that only a small viscosity effect is observed points to a significant "free rotor" contribution to the overall rotational correlation time, as has been described for tertiary amines.[17] For *neo*Pe-DAB(Me) the highest reduction of the ^{14}N resonance line width is found in supercritical $CClF_3$ (7.8 and 4.8 relative to $CDCl_3$ at 293 K and 323 K, respectively). The $F_{1/2}$ values found for supercritical CO_2 and CHF_3 are equal: 6.9 and 4.2 relative to $CDCl_3$ at 293 K and 323 K, respectively. This finding indicates that in CO_2 and CHF_3, the values of τ_c are similar under the conditions used.

In some cases the ^{14}N resonances were found to broaden upon heating the solutions from room temperature to the supercritical state, further heating resulted in a decrease of the ^{14}N line width. The initial (inhomogeneous) broadening of the ^{14}N resonances is attributed to the precipitation of solid material and convection.

Finally, we note that the reduction factors within a given solvent increase with temperature, as is seen for the ^{14}N resonances of *t*Bu-DAB and *neo*Pe-DAB(Me) (Table 2, Figure 2). When going from a liquefied gas at 298 K to the supercritical fluid at 323 K, the same or slightly larger reduction factors are observed when compared to the reduction factors for the acetone solutions in the same temperature range. This indicates that the reduced viscosity of the supercritical fluid compared to the liquefied gas contributes only slightly to the reduction of line widths.

B. Transition Metal and ^{14}N NMR Spectroscopy of Selected Coordination Compounds

^{59}Co NMR Spectroscopy

As an initial test of the appropriateness of our HP NMR system for transition metal NMR spectroscopy in SCFs, we have repeated an experiment performed by Rathke et al. in a static probe.[9a] The ^{59}Co NMR spectrum of $Co_2(CO)_8$ has been recorded in $[D_6]$benzene and CO_2(sc) and line widths of 10.4 kHz in $[D_6]$benzene at 296 K and 5.5 kHz in supercritical CO_2 at 310 K were observed. The ^{59}Co resonance recorded in supercritical CO_2 is well in agreement with the previously reported value of 5.1 kHz. The line width observed in $[D_6]$benzene is a factor of three smaller than the line width of 30 kHz reported previously.[9a] Possibly, the much larger line width in that case is due to poor homogeneity.

Further, we investigated the line widths of the ^{59}Co NMR resonances of $Co_4(CO)_{12}$ in $CDCl_3$ and CO_2. Due to its low solubility, the ^{59}Co NMR spectrum could only be recorded in liquid CO_2. The line widths for the apical ^{59}Co resonance of $Co_4(CO)_{12}$ are 4.0 kHz in $CDCl_3$ (296 K) and 3.6 kHz in CO_2 (296 K). The resonances of the cobalt atoms at the basal position were broader: 12.0 kHz in $CDCl_3$ (296 K) and 5.2 kHz in CO_2 (296 K). The variation in line width is the result of differences in the electric field gradient, experienced at the two sites of the cluster. This explanation is in agreement with previous reports concerning substituted cobalt clusters[18] and mixed cobalt−ruthenium clusters.[19] Upon changing from $CDCl_3$ solution to CO_2 solution, the reduction of the line width of the apical resonance is only 10%, whereas the line width of the basal resonance is reduced by more than a factor of two. The reduction of the rotational correlation time upon reducing the solvent viscosity from $CDCl_3$ to liquid CO_2 applies to the whole cluster, therefore one would expect the reduction factors of the line widths of the basal and apical ^{59}Co NMR resonances to be equal. However, it is documented that, due to differences in solvent polarity, the ratio of the line widths of the basal and the apical cobalt nuclei in various solvents varies between 1.9 in pentane and 3.2 in $CDCl_3$.[6] Here, we obtained a calculated ratio of 1.4 which, in agreement with the more apolar character of CO_2, is smaller but close to that observed for pentane.

^{53}Cr and ^{14}N NMR Spectroscopy

The application of supercritical solvents for the reduction of the resonance line width of quadrupolar transition metal nuclei has been further demonstrated for ^{53}Cr NMR spectroscopy. Two chromium isonitrile complexes $Cr(CO)_{6-x}(t\text{BuNC})_x$ (x = 1, 2) were studied by means of ^{14}N and ^{53}Cr NMR. The results have been compiled in Table 4.

Table 4. ^{14}N and ^{53}Cr NMR chemical shifts and line widths of two chromium isocyanide complexes of type $Cr(CO)_{6-x}(t\text{BuNC})_x$ in $[D_6]$acetone and CO_2

x[a]	Nucleus[b]	$[D_6]$Acetone[c]	CO_2(l)[c]	CO_2(sc)[d]	$F_{1/2}$[e]
1	^{14}N	2.5 Hz δ = −171.4	6 Hz δ = −176.1	5 Hz δ = −175.6	0.5
	^{53}Cr	90 Hz δ = 17.9	35 Hz δ = 15.7	35 Hz δ = 36.1	2.6
2	^{14}N	7 Hz δ = −174.5	7.5 Hz δ = −178.6	−	0.9
	^{53}Cr	44 Hz δ = 60.4	34 Hz δ = 52.4	−	1.3

[a] Number of *t*BuNC groups. − [b] Nucleus studied. − [c] Line width in Hz and chemical shift in ppm at T = 295 K. − [d] Line width in Hz and chemical shift in ppm at T = 343 K. − [e] Reduction factor [$F_{1/2} = \Delta\nu_{1/2}$(organic solvent)/$\Delta\nu_{1/2}$(compressed gas)].

The ^{14}N NMR resonances of the chromium complexes are sharp and broadened slightly with respect to uncoordinated *t*BuNC [$\Delta\nu_{1/2}(^{14}N)$ = 0.6 Hz[8]], indicating a small increase in the electric field gradient at the nitrogen atom upon coordination of the isocyanide group to the chromium center. The in this special case already very narrow ^{14}N line widths are found to increase slightly, changing from a $[D_6]$acetone solution to a liquid or supercritical CO_2 solution. This is most likely the result of inhomogeneous broadening as the experiment was performed on an unlocked and non-spinning sample. In addition, the precipitation of some solid material might have occurred in supercritical CO_2. The spectrum of $Cr(CO)_4(t\text{BuNC})_2$ could not be recorded in supercritical CO_2 due to its poor solubility in this medium.

The line widths of the chromium resonances for $Cr(CO)_{6-x}(t\text{BuNC})_x$ were found to decrease by a factor of

2.6 ($x = 1$) and 1.3 ($x = 2$) when changing the solvent from [D_6]acetone to supercritical ($x = 1$) and liquid ($x = 2$) CO_2. The reduction of the line widths of the already narrow ^{53}Cr resonances is relatively modest, especially when compared to ^{53}Cr line widths of many other chromium compounds[5c,20] and to the reduction of the ^{59}Co resonances described above.

To demonstrate the advantageous effect of the use of modifiers, the ^{53}Cr NMR spectrum of a 0.05 M solution of $(CO)_5Cr{=}C(NH_2)(Ph)$ was recorded in CO_2(sc) (critical density: 0.48 g/mL) with the addition of 5% (v/v) [D_6]acetone. This resulted in a ^{53}Cr NMR line width of 432 Hz ±5 Hz at δ = 170 (T = 323 K) after 14 h measuring time. This signal was found to be slightly broadened with respect to the signal recorded in the same mixture at 293 K, which had a line width of 402 ±5 Hz at δ = 169. The addition of a small amount of [D_6]acetone was used to dissolve the otherwise insoluble (in CO_2) chromium complex. Importantly, at the same sample concentration (0.05 M) no signal could be observed in pure [D_6]acetone after 14 h. A line width of $\Delta\nu_{1/2}$ = 1150 Hz at δ = 159 was reported for a highly concentrated sample (0.4 M in [D_6]acetone).[20] The signal observed by us for a 0.05 M sample after 48 h at 298 K in [D_6]acetone had a line width of 1340 Hz at δ = 151, thus a reduction factor $F_{1/2}$ = 3.3 applies.

^{95}Mo and ^{14}N NMR Spectroscopy

Complexes of type $Mo(CO)_4$(R-DAB) [R = *t*Bu, *c*Hex; R-DAB = R−N=C(H)−C(H)=N−R] are virtually insoluble in liquid and supercritical CO_2. The addition of a small amount of a modifier ([D_6]acetone) increases the solubility of these complexes in the low-viscosity liquid and supercritical fluid mixtures to such an extent that their ^{14}N and ^{95}Mo NMR spectra can be recorded. The results for $Mo(CO)_4$(R-DAB) complexes, which readily dissolve in [D_6]acetone and moderately so in CO_2/[D_6]acetone mixtures, have been compiled in Table 5 and Table 6.

Table 5. ^{14}N and ^{95}Mo line widths and chemical shifts of $Mo(CO)_4$(*t*Bu-DAB) in [D_6]acetone and CO_2/[D_6]acetone mixtures (critical density 0.48 ±0.02 g/mL)

R = *t*Bu % [D_6]acetone[a]	Nuc	T = 297 K $\Delta\nu_{1/2}$[b]	δ≅[c]	T = 323 K $\Delta\nu_{1/2}$[b]	δ[c]
7% (0.5 mL)	^{14}N	525	−31.6	390	−28.6
	^{95}Mo	54	−1178	33	−1171.1
11% (0.75 mL)	^{14}N	423	−33.7	428	−30.8
	^{95}Mo	27	1182.0	27	−1173.6
14% (1.00 mL)	^{14}N	494	−33.8	417	−32.1
	^{95}Mo	53	−1189.8	43	−1174.9
100%	^{14}N	669	−33.6	542	−31.2
	^{95}Mo	38	−1204.0	38	−1186.4

[a] Amount of acetone v/v in the supercritical state; volume of the HP NMR tube: 6.9 mL. − [b] Line width in Hz. − [c] Chemical shift in ppm.

In the CO_2/[D_6]acetone mixtures, the line width of the ^{14}N and ^{95}Mo resonances decreases relative to the line width observed in [D_6]acetone, and decreases slightly with decreasing acetone concentration in the CO_2. This was expected, based on the concomitant decrease of the viscosity of the mixture. The line width of the ^{14}N resonance of $Mo(CO)_4$(*t*Bu-DAB) is lower than that of $Mo(CO)_4$(*c*Hex-DAB), and is found at higher frequencies. The smallest line width for $Mo(CO)_4$(*t*Bu-DAB) was 390 Hz, observed in supercritical CO_2/7% [D_6]acetone, for $Mo(CO)_4$(*c*Hex-DAB) 417 Hz in supercritical CO_2/11% [D_6]acetone. Only modest reduction factors are thus obtained for these compounds. A solution of (*t*Bu-DAB)$Mo(CO)_4$ in liquid CCl_2F_2 at 323 K resulted in a ^{14}N line width of 450 Hz. The same compound measured in a $CClF_3/CH_2Cl_2$ (89:11; v/v) mixture at 323 K resulted in a ^{14}N-resonance line-width of 370 Hz, the complex was insoluble in pure $CClF_3$.

Table 6. ^{14}N and ^{95}Mo line widths and chemical shifts of $Mo(CO)_4$(*c*Hex-DAB) in [D_6]acetone and CO_2/[D_6]acetone mixtures (critical density 0.48 ±0.02 g/mL)

R = *c*Hex % [D_6]acetone[a]	Nuc	T = 297 K $\Delta\nu_{1/2}$[b]	δ≅[c]	T = 323 K $\Delta\nu_{1/2}$[b]	δ[c]
7% (0.5 mL)	^{14}N	nd[d]	nd[d]	555	−39.1
	^{95}Mo	nd[d]	nd[d]	38	−1185.9
11% (0.75 mL)	^{14}N	450	−37.0	417	−40.1
	^{95}Mo	30	1199	38	−1188.7
14% (1.00 mL)	^{14}N	745	−43.9	488	−42.2
	^{95}Mo	86	−1208	26	−1191.6
100%	^{14}N	919	−39.3	605	−38.3
	^{95}Mo	43	−1225.9	38	−1204.9

[a] Amount of acetone v/v in the supercritical state; volume of the tube 6.9 mL. − [b] Line width in Hz. − [c] Chemical shift in ppm. − [d] Not determined due to low solubility.

The ^{95}Mo resonances are found at lower frequencies for (*t*Bu-DAB)$Mo(CO)_4$ than for the (*c*Hex-DAB)$Mo(CO)_4$ complex. Raising the temperature of the solutions of the complexes (R-DAB)$Mo(CO)_4$ (R = *t*Bu, *c*Hex) results in an increase of both the ^{14}N and ^{95}Mo chemical shifts. The chemical shifts of the ^{14}N and ^{95}Mo resonances are found to be lowest in the solutions containing a low percentage of [D_6]acetone. Increasing the amount of acetone results in a shift to higher ppm values. These findings are in agreement with a decrease of the metal-centered excitation energy ΔE_{av} at higher temperatures and higher solvent polarity, resulting in a high frequency shift.[5c,21]

Only very small reductions of the line widths (or none at all) of the already narrow ^{95}Mo NMR resonance were observed when changing from [D_6]acetone to low-viscosity CO_2/[D_6]acetone mixtures. This might be due to the coupling of the ^{14}N to the ^{95}Mo, resulting in broadened signals due to unresolved coupling. However, at low viscosity and high temperatures, no resolved couplings between ^{14}N and ^{95}Mo could be observed. Further studies at various magnetic field strengths may shed light on this conjecture.

^{91}Zr NMR Spectroscopy

The generally polar Zr^{IV} compounds are insoluble in liquid or supercritical CO_2, but these complexes can be solubilized in the apolar CO_2 by the addition of a small amount of THF (CO_2/THF = 93:7; v/v), similar to the cases described above. The solubility of Cp_2ZrCl_2 in CO_2/THF mixtures can be increased to such levels that it is possible to

observe the ^{91}Zr resonance in the supercritical mixture at 323 K. The line width of Cp_2ZrCl_2 is reduced from 375 Hz in THF at 296 K to 210 Hz in the supercritical mixture.[22a] However, the acquisition of the ^{91}Zr resonance in the CO_2/THF mixture took 14 h, whereas the ^{91}Zr signal can be acquired in 10 min in pure THF solution. Many ^{91}Zr resonances reported[5b][22b] are much broader, however. For such Zr species there may be an advantage of measuring ^{91}Zr NMR in CO_2/THF mixtures.

Conclusions

The employed HP NMR tubes with[8] and without[23] a pressure sensor are very appropriate and safe to use for measurements of NMR spectra under high pressure in supercritical fluids and liquefied gases of low viscosity. It has been shown that in order to increase the solubility of poorly soluble compounds in liquid or supercritical CO_2, small amounts of a modifier (an organic solvent) may be added, which further enables better shimming and acquisition in the locked mode.

The ^{14}N line widths follow the trend of the solvent viscosities, and are thus considerably reduced (by a factor of up to 7 or 8), even when compared to the line width observed in low-viscosity organic solvents like $CDCl_3$ and acetone. In view of the low solvating power of low-density SCFs, the use of liquefied gases, i.e. liquid CO_2 and $CClF_3$, might be preferred for the reduction of quadrupolar broadened NMR lines, since these combine a relatively high solvating power with large reduction factors. Moreover, the experimental procedure for NMR spectroscopy in liquefied gases is more straightforward than in SCFs and fewer problems with phase separation and precipitation of solid material are expected during NMR experiments.

NMR of quadrupolar transition metal ions in low-viscosity liquefied gases or in supercritical solvents with and without the addition of modifiers results in some cases in an appreciable decrease of their resonance line widths. Enhanced solubilities without detrimental effects on the line widths can easily be achieved by the addition of small amounts of a modifier (acetone, CH_2Cl_2, THF).

Experimental Section

General: All spectra were recorded with a Bruker DRX300 NMR spectrometer, employing a 10-mm broadband probe (^{103}Rh-^{91}Zr)-{^1H}. The solubility experiments were carried out in a 10-mm o.d., 8-mm i.d. sapphire HP NMR tube with pressure sensor as described previously.[8] The HP NMR tube was modified with an aluminum plug to reduce the sample volume to 1.7 mL. Some experiments were performed in a modified HP NMR tube similar to the one described by Roe.[23a] The volume of this 10-mm o.d., 8-mm i.d. tube is 6.0 mL.[23b] – The complexes $Co_4(CO)_{12}$,[24] $(t\text{BuNC})_x\text{Cr}(CO)_{6-x}$ (x = 1,2)[25] (R-DAB)Mo(CO)$_4$ (R = *t*Bu, *c*Hex, DAB = diazabutadiene;[26] and Cp_2ZrBr_2)[27] were synthesized according to literature procedures. A sample of $(CO)_5Cr{=}C(NH_2)(Ph)$ was kindly provided by Prof. Dr. K.-H. Dötz (Universität Bonn). Cp_2ZrCl_2 was obtained from Alfa and used as received.

Sample Preparation: The NMR samples were prepared by charging the HP NMR tube described previously[8] with the appropriate α-diimine, typically 50 mg. The HP NMR tube was flushed three times with the appropriate gas (to suppress the N_2 signal) and filled with the liquefied gas using either the hand driven pump for CO_2, or by condensation of the solvent gas with liquid nitrogen for $CClF_3$, CHF_3, and SF_6. The critical density used varied between ρ_c and ρ_c + 0.1 g/mL. – For the determinations of the solubility in liquefied gases, the HP NMR tube was charged with the appropriate amount of *neo*Pe-DAB(Me). The concentration of *neo*Pe-DAB(Me) amounted to 0.091 M in $CDCl_3$. In other solvents, saturated solutions were obtained with concentrations varying between 0.004 M and 0.071 M (see Table 2). Prior to dissolution of the α-diimines, the tube was flushed three times with the solvent gas. The gas was introduced using the methods described previously,[8] after warming to room temperature the excess solvent was carefully evaporated until the desired level was reached. For the determinations of the solubility in supercritical fluids, the aluminum plug was placed in the HP NMR tube after introduction of the desired compound. The tube was charged with the appropriate liquefied gas and the density of the supercritical state was determined by weight. All of the solutions studied were supercritical at 323 K, except for $CDCl_3$. – Samples for NMR experiments (determinations of line widths) were also prepared as described above[8] for the experiments with diimines. For NMR of metal complexes: A sample of (*t*Bu-DAB)Mo(CO)$_4$ (0.23 g, 0.6 mmol) was dissolved in the appropriate amount of [D_6]acetone (see Table 5 and Table 6), the HP NMR tube was filled with CO_2 employing a hand driven pump;[8] similarly, solutions of (*c*Hex-DAB)Mo(CO)$_4$ were prepared by dissolving a 0.10 g sample (0.25 mmol) in the appropriate amount of [D_6]acetone and filling the HP NMR tube with CO_2. A solution of (*t*Bu-DAB)Mo(CO)$_4$ in CCl_2F_2 was prepared by condensing CCl_2F_2 in an HP NMR tube containing a 0.10 g sample of the complex (0.26 mmol). Similarly $CClF_3$ was condensed in an HP NMR tube containing a solution of 0.10 g (*t*Bu-DAB)Mo(CO)$_4$ (0.26 mmol) in 0.5 mL CH_2Cl_2. A 0.05 M solution of $(CO)_5Cr{=}C(NH_2)(Ph)$ was prepared in CO_2/acetone, 95:5 (v/v). The samples of other metal compounds were prepared as concentrated solutions.

NMR Experiments: All spectra were recorded in the unlocked and non-spinning mode, except for the spectra recorded in $CDCl_3$ or acetone, these were recorded in the locked mode. The NMR experiments at 293 K were performed by cooling the samples with a stream of cold nitrogen using the spectrometers variable-temperature unit. The ^1H NMR spectra were recorded using the decoupler coil of the 10-mm broadband probe. A total of 20 transients were recorded for every spectrum. For each spectrum 32k complex points were sampled over a spectral width of 7585 Hz. An acquisition time of 2.2 s, a pre-acquisition delay of 10 s, and pulse duration of 5 μs were used (ca. 30). Before integration of the ^1H signals, the base line was corrected for small offsets using the spectrometer software in the automatic mode. In the proton spectrum, typically line widths of 2–3 Hz at half-height were found. The ^{14}N NMR spectra were recorded using the broad-band observe coil of the 10-mm broad band probe. An *anti*-ring sequence was used to reduce probe ringing. The number of transients recorded for the ^{14}N NMR experiments was 2000, and 4096 complex points were sampled over a spectral width of 10823 Hz, resulting in an acquisition time of 0.2 s, a pre-acquisition delay of 5 ms and a π/2 pulse duration of 27 μs were used. – The ^{95}Mo π/2 pulse duration was 34 μs, ^{53}Cr

$\pi/2$ pulse duration was 32 μs, and an *anti*-ring sequence was used to reduce rolling base lines. An exponential multiplication one tenth of the natural line width was applied prior to Fourier transformation. The ^{14}N resonances are reported relative to $MeNO_2$, ^{95}Mo relative to 2 M MoO_4Na_2 in D_2O, ^{59}Co relative to a saturated $K_3Co(CN)_6$ solution in D_2O, ^{53}Cr relative to a $Cr(CO)_6$ solution in $CDCl_3$ and ^{91}Zr relative to Cp_2ZrBr_2 in $CDCl_3$.[22b]

Acknowledgments

The authors wish to thank Ing. J. M. Ernsting for skillful technical assistance with the NMR spectrometer and H. Luyten for the construction and maintenance of the high-pressure NMR tube. We thank the Council for Chemical Sciences of the Netherlands Organization for Scientific Research (CW-NWO) and the John van Geuns Foundation for financial support with acquiring the spectrometer and probe.

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Received July 17, 2000
[I00283]