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Direct and Indirect Recording of ^{183}W NMR Spectra and Structure Determination of (Diene)$_3$M (M = W, Mo) Compounds in Solution

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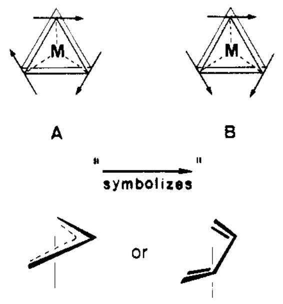
The ^{183}W NMR parameters $\delta(^{183}\mathrm{W})$, $^2J(\mathrm{W,H})$, $^1J(\mathrm{W,C})$, $T_1(^{183}\mathrm{W})$, and $\eta_{\mathrm{NOE}}(^{183}\mathrm{W,H})$ of tris(diene)tungsten compounds and tetrakis(allyl)tungsten and some ^{95}Mo NMR parameters of homologous molybdenum compounds have been determined. The most effective way of measuring ^{183}W NMR spectra is the indirect two-dimensional $^1\mathrm{H}\{^{183}\mathrm{W}\}$ technique via $J(\mathrm{W,H})$. Structure determination of tris(butadiene)tungsten (**1**), the two tris(isopropene)tungsten isomers **2a** (75%) and **2b** (25%), and tris(2,3-dimethylbutadiene)tungsten (**3**) in solution is based on ^{183}W, ^{13}C, and ^{1}H NMR spectroscopy. In **1**–**3** the dienes are in s-cis conformation and "in-phase" η^4 bonded to W yielding a trigonal prismatic surrounding at the metal. **1** and **3** have D_{3h} symmetry. **2b** has a C_3 symmetry axis. In **2a** asymmetry results from a different arrangement of the methyl substituents, of which one is below and two are above the plane, generated by W and the bisecting lines of the three inner isoprene carbon bonds. In the series **1**–**3** a reduction of W–olefin π bonding is evidenced by increasing $^1J(\mathrm{W,C_4})$, $^2J(\mathrm{W,H})$, $^2J(\mathrm{H,H})$, and $\delta(^{183}\mathrm{W})$ values.

Introduction

Various isomeric structures have to be considered when there are three open chain π-ligands like η^3-allyl or η^4-butadiene complexed to one transition-metal atom. The X-ray structure of tris(η^4-butadiene)molybdenum[2] and tris(2,3-dimethylbutadiene)tungsten (**3**)[3] showed that in the crystal the metal has a trigonal prismatic surrounding. The NMR spectra of tris(η^3-allyl)cobalt[4] and tris(η^3-allyl)rhodium[5] have also been interpreted in terms of a trigonal prismatic structure. For the allyl cobalt system in solution structures with both an "in-phase" (cf. A) and an "out-of-phase" arrangement (cf. B) of the open chain π-ligands have been found. Also for tris(η^4-butadiene)tungsten (**1**) and **3** two isomers might exist in solution, and for tris(η^4-isoprene)tungsten (**2**)[3] the situation might become still more complex. The most direct way for determining the number of isomers is to use ^{183}W NMR spectroscopy[6] because tungsten NMR spectra of mononuclear complexes are simple and the spectral dispersion is high.[7] However, the receptibility of the ^{183}W nucleus is low.[6,7] We have therefore examined various NMR parameters which are relevant for the recording technique of ^{183}W NMR spectra. In the first part of this paper the two-dimensional indirect $^1\mathrm{H}\{^{183}\mathrm{W}\}$ recording technique is introduced, by which ^{183}W parameters become accessible in the most effective manner. In the second part the solution structures of **1**–**3** as well of the molybdenum compounds (η^4-isoprene)$_3$Mo (**6**) and (η^4-2,3-dimethylbutadiene)$_3$Mo (**7**) are elucidated by using combination of ^{183}W, ^{95}Mo, ^{13}C, and ^{1}H NMR spectroscopy.



Experimental Section

Materials. The preparation of the tris(diene)tungsten compounds **1**–**3**, as well of tris(isoprene)molybdenum (**6**), tris(2,3-dimethylbutadiene)molybdenum (**7**), tetrakis(η^3-allyl)tungsten (**4**), and tetrakis(η^3-allyl)molybdenum (**5**), has been described earlier.[2,3,8,9] The NMR measurements were carried out by use of solutions of **1**–**7** in tetrahydrofuran-d_8 or toluene-d_8 in sealed 5-mm (^{1}H, ^{183}W) or 10-mm (^{13}C, ^{95}Mo, ^{183}W) sample tubes.

NMR Spectra. ^{183}W NMR experiments were performed on Bruker AM 400 and WH400 spectrometers, equipped with standard 10-mm probe heads optimized for the low-frequency range (^{57}Fe–^{109}Ag, AM400) and the high-frequency range (^{109}Ag–^{31}P, WH400), respectively. For the indirect detection mode of the ^{183}W NMR parameters the 90° pulse lengths were 22.5 μs (^{1}H) and 40 μs (^{183}W) (AM400) and 50 μs (^{1}H) and 50 μs (^{183}W) (WH400). For the normal direct detection scheme on the WH 400 the 90° (^{1}H) pulse via the decoupler is about 15% shorter (42.5 μs) whereas the 90° (^{183}W) pulse is about 10% longer (55 μs). In the ^{95}Mo NMR experiments (WH 400) the 90° (^{95}Mo) pulse was 51 μs. In all pulse experiments[10] the ^{1}H and the metal resonance carrier frequencies were set "on resonance", if possible.

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Table I. Selected ^{95}Mo and ^{183}W NMR Parameters of Tris(diene)metal and Tetrakis(η^3-allyl)metal Compounds at 9.4 T (for δ(M) Standards cf. Experimental Section)

		T, K	δ(M)	$\Delta\delta/\Delta T$	η = NOE$_{exp}$ − 1	T_1, s
$(\eta^4\text{-}C_4H_6)_3W$[a]	**1**	273	−3630			
$(\eta^4\text{-}2\text{-}MeC_4H_5)_3W$[b]	**2a** (75%)	253	−3277	0.37	0.12	5.4[f]
$(\eta^4\text{-}2\text{-}MeC_4H_5)_3W$[b]	**2b** (25%)	253	−3279	0.37	0.16	5.5[g]
$(\eta^4\text{-}2,3\text{-}Me_2C_4H_4)_3W$[a]	**3**	297	−3021			
$(\eta^3\text{-allyl})_4W$[b]	**4**	310	−3186	0.53	0	9.7[h]
$(\eta^3\text{-allyl})_4Mo$[b]	**5**	310	−1405[c]			
$(\eta^4\text{-}2\text{-}MeC_4H_5)_3Mo$[b]	**6a** (80%)	310	−1717[d]	0.28	0.13	0.3
$(\eta^4\text{-}2\text{-}MeC_4H_5)_3Mo$[b]	**6b** (20%)	310	−1723[e]	0.28	0.16	1.6
$(\eta^4\text{-}2,3\text{-}Me_2C_4H_4)_3Mo$[b]	**7**	310	−1641[e]			

[a] Solvent = THF-d_8. [b] Solvent = toluene-d_8. [c] $W_{1/2}$ = 17 Hz. [d] $W_{1/2} \sim$ 8 Hz. [e] $W_{1/2} \sim$ 2.5 Hz. The half-width, $W_{1/2}$, is given for the ^{1}H decoupled spectra. [f] T_1 = 10.7 s at 273 K. [g] T_1 = 9.5 s at T = 273 K. [h] T_1 = 6.6 s at T = 273 K.

T_1 measurements of **2**, **4**, and **6** were performed under proton decoupling using the inversion recovery pulse sequence.[11] The error limits for $T_1(^{183}W)$ and $T_1(^{95}Mo)$ as taken from regression analysis are smaller than ±15%. For **2** and **4** (**6**) $\eta(^1H,^{183}W)$ ($\eta(^1H,^{95}Mo)$) was determined by use of a recovery time between the excitation pulses in the order of 10 times T_1.

Polarization transfer experiments have been carried out for **3** on the AM400 spectrometer using the INEPT sequence without refocusing.[12] The preparation time was 2 s and the delay between the 90° and 180° pulses was chosen as 0.015 s. In total 26 270 scans were accumulated yielding for the spectrum presented in Figure 1a a measuring time of about 24 h.

For the indirect two-dimensional (2D) $^1H\{^{183}W\}$ spectra the ^{183}W frequency and the 90° phase cycling were generated via a PTS 160 synthesizer. Pulsing of the ^{183}W frequency was achieved with a BSV 3 unit.[13] The indirect 2D spectra[14] were carried out with pulse sequence 1.[15] An 8- or 16-step phase cycling was employed,

$$90(^1\mathrm{H})\ \frac{1}{2J(\mathrm{W,H})}\ 90(^{183}\mathrm{W})\ \frac{t_1}{2}\ 180(^1\mathrm{H})\ \frac{t_1}{2}\ 90(^{183}\mathrm{W})\ \mathrm{FID}(t_2,{}^1\mathrm{H}) \tag{1}$$

which rejects the protons at magnetically inactive tungsten (85.6%) and gives quadrature detection in F_1 dimension. $\delta(^{183}W)$, J(H,H) are displayed in $F_1(t_1)$ dimension whereas the $F_2(t_2)$ dimension contains $\delta(^1H)$, J(H,H), and $J(^{183}W,H)$. In practice distribution of 256 t_1 increments over a spectral width of 8000 Hz posed no problems for detection of the cross peaks. Thereby a spectral range of $\Delta\delta(^{183}W)$ of 500 ppm could be covered within 1 h of recording time. In order to check that the cross peaks are not folded and to determine $\delta(^{183}W)$ most exactly, the $^1H\{^{183}W\}$ experiment was repeated with a small spectral range in F_1 dimension and a changed carrier frequency. The 2D FIDs were processed in the usual manner, using trigonometric apodization functions in both dimensions and zero filling in the F_1 domain. For **2** direct 2D ^{183}W, ^{1}H correlated spectra as well as two-dimensional indirect $^1H\{^{183}W\}$ spectra were recorded.

Calculation of the ^{183}W shifts was carried out by determining the absolute ^{183}W frequencies of the cross peaks and relating them to that of W(CO)$_6$. The resonance frequency of a saturated solution of W(CO)$_6$ in tetrahydrofuran-d_8 at T = 310 K was 16.613 142 MHz. (Under these conditions the resonance frequency of Me$_4$Si is 400.134 660 3 MHz, yielding for W(CO)$_6$ Ξ = 4.151 888 MHz.) In Table I all $\delta(^{183}W)$ values are referenced to the standard $\delta(Na_2{}^{183}WO_4) \equiv 0$, taking into account $\delta(^{183}W(CO)_6) = -3484$. The ^{95}Mo NMR shifts are related to a saturated solution of K$_2$MoO$_4$ in D$_2$O as external standard. For this sample Ξ = 6.516 688 was measured at T = 310 K. All shifts in Table I are presented as δ values with $\delta(K_2{}^{95}MoO_4) \equiv 0$.

Proton and carbon spectra of **1**–**4** were recorded with the Bruker WH400 spectrometer in the conventional manner. Some ^{1}H and ^{13}C data of **1** and **4** have been reported earlier.[16] All ^{1}H and ^{13}C NMR shifts are presented as δ values referenced to internal Me$_4$Si. Two-dimensional ^{1}H, ^{13}C spectra using J(C,H) were recorded with the standard pulse sequence.[10,17] ^1J(C,C) coupling constants of **1**–**3** were obtained via the 1D INADEQUATE sequence[10,18] with an accuracy of ±0.5 Hz. In these measurements 128 phase cycles were employed.

Results and Discussion

The ^{183}W chemical shifts together with some relevant ^{183}W NMR parameters of **1**–**4** are summarized in Table I. In addition selected ^{95}Mo NMR parameters of the homologous molybdenum compounds **5**–**7** are also presented. The maximum ^{1}H, ^{183}W (^{1}H,^{95}Mo) nuclear Overhauser effect (NOE) is NOE$_{max}$ = $1 + \gamma_H/2\gamma_W = 13(1 + \gamma_H/2\gamma_{Mo} = 8.7)$. The actual signal enhancement factors η = NOE$_{exp}$ − 1 in **2** and **4** (**6**), however, indicate that for the relaxation of the metal nuclei, dipole–dipole interaction of the ^{183}W (^{95}Mo) and ^{1}H nuclei is negligible. The temperature dependence of the T_1 values in **2** and **4** indicates that at lower temperatures the relaxation of the ^{183}W nucleus is governed by the chemical shift anisotropy (CSA) mechanism.[11] A similar behavior was recently found for the ^{195}Pt[19] and ^{103}Rh nucleus[20] in organometallic compounds. Consequently high magnetic fields not only improve the Boltzmann factor but also may shorten the recording times due to faster ^{183}W relaxation.

A quite different temperature dependence of the line width is observed for the ^{95}Mo NMR signals of **6a** and **6b**: for **6a** the half width ($W_{1/2}$ increases from 8 Hz (310 K) over 10 (273 K) to 21 Hz at 243 K; for **6b** $W_{1/2}$ is nearly constant ($W_{1/2} \sim$ 3 Hz) between this temperature interval. Apparently in **6a** the relaxation of the ^{95}Mo nucleus is dominated by the quadrupolar mechanism while in the more symmetrical minor component **6b** there is also significant relaxation via the spin–rotation mechanism.

Due to the low solubility of **3** conventional direct observation of its ^{183}W spectrum was critical. However, **3** exhibits a geminal $J(^{183}W,H_E)$ coupling. Since $1/^2J(W,H_E)$ is significantly smaller than $T_1(^{183}W)$, the INEPT polarization transfer technique was employed (cf. Figure 1). This sequence can yield a sensivity gain up to γ_H/γ_W =

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Table II. ^{13}C NMR Data for 1-3

		C_1	C_2	C_3	C_4	Me	$J(C_1-C_2)$, Hz	$J(C_2-C_3)$, Hz	$J(C_3-C_4)$, Hz	$J(C_2-Me)$, Hz
1[a]	δ	33.78	103.97	103.97	33.78		38.5		38.5	
	J(C,W), Hz	19.8			19.8					
	J(C,H), Hz	151	165	165	151					
2b[b]	δ	40.44	113.99	100.53	33.01	23.03	37.8	48.8	38.5	43.7
	J(C,W), Hz	25.4	6.6	5.6	21.4					
	J(C,H), Hz	149		162	150	126				
3[a]	δ	44.24	111.65	111.65	44.24	20.10	38.0		38.0	43.6
	J(C,W), Hz	25			25					
	J(C,H), Hz	147.0			147.0	126.0				
2a[b]	δ	33.91	118.40	100.03	40.02	23.12	38.6	48.5	38.4	43.5
	J(C,W), Hz	19.8	6.6	5.1	23.4					
	J(C,W), Hz	148.0		162.0	150.0	126				
	δ	40.47	115.16	103.56	33.53	22.94	38.2	48.4	38.5	43.5
	J(C,W), Hz	25.4	6.6	5.6	21.4					
	J(C,H), Hz	149		162	150	126.0				
	δ	33.48	116.97	100.74	40.04	22.90	38.5	48.6	38.4	43.6
	J(C,W), Hz	19.3	7.1	5.1	23.4					
	J(C,H), Hz	151		162	149	126				

[a] Solvent = THF-d_8, T = 310 K. [b] Solvent = toluol-d_8, T = 253 K. The ^{13}C shifts of row i are correlated to the ^1H shifts of column i in Table III.

24. In addition, the repetition time for the pulse sequence is governed by $T_1(^1H)$, which is shorter than $T_1(^{183}W)$.

A still faster detection of the ^{183}W spectrum of **3** was achieved when two-dimensional indirect recording techniques[14,15] were applied. This procedure has been used for observation of low-γ nuclei like ^{15}N,[14,15] ^{187}Os,[21] and ^{57}Fe.[22] The first example for a two-dimensional $^1H\{^{183}W\}$ spectrum as recorded with pulse sequence 1 is depicted in Figure 1b.[23] The $\delta(^{183}W)$ value resulting from this recording technique is of course identical with that obtained from the INEPT spectrum. However, the recording time for the two-dimensional $^1H\{^{183}W\}$ spectrum was reduced by more than an order of magnitude. This seems reasonable, because via the indirect observation, the sensivity gain is $(\gamma_H/\gamma_W)^3$ as opposed to (γ_H/γ_W) via the direct observation involving polarization transfer techniques and it has been estimated[24] that 2D spectra do not require significant longer recording times than 1D spectra. It might be argued that the success of the 2D indirect measurement is dependent on the proper choice of the spectral window in the tungsten dimension; however, the same is true for the 1D polarization transfer experiments. On the other hand the indirect detection techniques seem to be less sensitive to missetting of the tungsten carrier frequency, because the modulation of the satellites can be easily monitored by ^1H NMR spectroscopy even if the carrier is far away from resonance.[25]

The ^{183}W chemical shifts of **1**–**4** (**5**–**7**) lie in the region typical for W(0) (Mo(0)) compounds.[7,23] The temperature coefficient for $\delta(^{183}W)$ ($\delta(^{95}Mo)$) is relatively small and its sign is as expected from the temperature dependence of the paramagnetic shielding term.[26] Electron-donating substituents at the complexed carbon skeleton like methyl groups at C_2 or C_3 of the diene moiety produce a deshielding of the ^{183}W (^{95}Mo) nucleus. Similar observations have been made for $\delta(^{91}Zr)$ in Zr(II)[27] and for $\delta(^{49}Ti)$ in Ti(IV)[28] π-compounds. The opposite behavior is found in

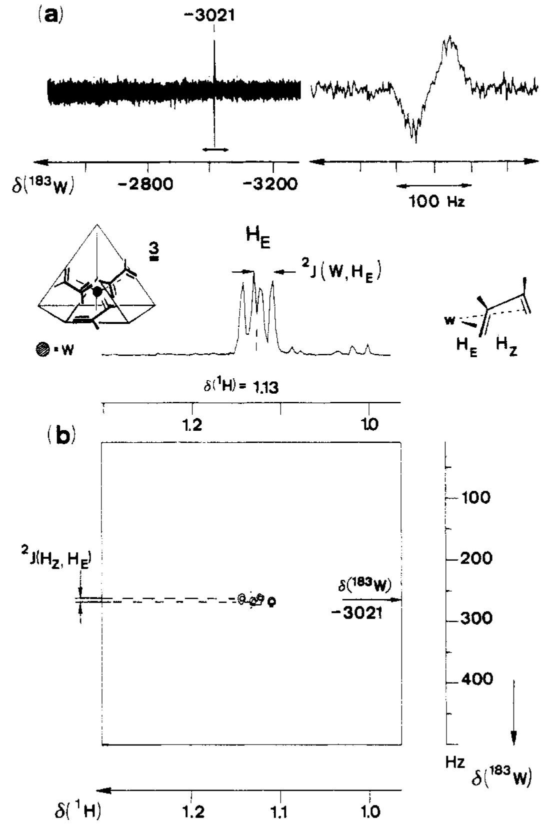

Figure 1. ^{183}W NMR spectra of tris(2,3-dimethylbutadiene)tungsten (**3**) dissolved in toluene-d_8. (a) 16.62 MHz ^{183}W unrefocused INEPT spectrum and its expansion using the protons as polarization transfer source. The ^2J(W,H) couplings (cf. expansion) can be extracted more readily from the 400-MHz ^1H spectrum. (b) Expansion of the two-dimensional indirect $^1H\{^{183}W\}$ spectrum of **3**. The $F_2(^1H)$ dimension presents $\delta(H_E)$, $^2J(H_E,H_Z)$, and $^2J(^{183}W,H_E)$ (cf. projection) whereas the $F_1(^{183}W)$ dimension yields $\delta(^{183}W)$.

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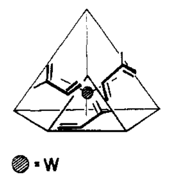
Table III. ^{1}H NMR Data of 1–3

	1^a	2b^b	3^a	2a^b		
δ, ppm						
1Z	0.35	−0.25	−0.33	0.38	−0.24	0.39
1E	1.42	1.10	1.13	1.00	1.15	1.03
3	4.68	4.46		4.41	4.50	4.34
4Z	0.35	0.38	−0.33	−0.24	0.38	−0.27
4E	1.42	1.26	1.13	1.43	1.22	1.37
Me		1.88	1.74	1.86	1.85	1.88
J(H,H), Hz						
1Z–1E	−4.46	5.2	5.2	5.2	5.0	5.3
1Z–3	−1.57	1.6		1.4	1.7	1.7
1E–3	1.44	1.9		2.0	2.0	1.9
3–4Z	8.09	7.7		7.0	7.2	7.3
3–4E	7.61	7.7		7.6	7.8	7.7
4Z–4E	−4.46	4.7	5.2	4.7	4.9	4.8
J(W,H), Hz						
W,1E	c	6.6	8.5	6.4	6.5	6.4
W,4E		7.0	8.5	7.0	6.8	7.0

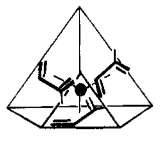
^{a} Solvent = THF-d_8; T = 300 K, for calculation of J(H,H) cf. ref 16. ^{b} T = 253 K, J(W,4Z) and J(W,4E) ∼ 2 Hz. For 2a the ^{1}H shifts of column i are correlated to the ^{13}C shifts of row i in Table II. ^{c} J(W,H) around 5 Hz.

(η^5-Cp)(η^2-olefin)$_2$Co compounds upon substitution of the cyclopentadienyl ligand.[4] The deshielding of the ^{183}W (^{95}Mo) nucleus in the series **1**–**3** (**6**–**7**) may be interpreted with a decrease in π-bonding, which in fact seems to be strongly affected by the methyl substituents (vide infra). Apparently, small changes in the W diene bonding produce larger changes in δ(^{183}W) than charge density effects of substituents at the carbon skeleton.

The metal shifts of the tetrakis(η^3-allyl)tungsten and molybdenum compounds **4** and **5** lie close to those of the (diene)$_3$M compound, in which the formal oxidation state of the metal is zero. This is in good agreement with the chemical behavior of these complexes[9] and corresponds also to what has been observed for other (η^3-allyl)$_n$M compounds (n = 2, M = Pt;[19b] n = 3, M = Co,[4] M = Rh[20]). The (η^4-diene)$_3$W compounds are isoelectronic with (η^3-allyl)$_3$Co and (η^3-allyl)$_3$Rh. However, in **1**–**3** the diene ligands are complexed "in-phase" and there are no indications for the presence of an isomer with an "out-of-phase" arrangement of the dienes. This is based on the ^{183}W, ^{13}C, and ^{1}H NMR data of **1**–**3** (cf. Table I–III). In particular, in the ^{183}W spectrum of **2** only two signals are found. Their signal separation is less than 33 Hz (cf. Figure 2). (Note that δ(^{195}Pt) for the two (η^3-allyl)$_2$Pt isomers differs by 297 ppm[19b].) A further argument in favor of structures **2a** and **2b** results from the ^2J(W,H$_E$) couplings, all of which are of similar size in **2b** and **2a** (note that ^2J(W,H$_Z$) ≃ 2 Hz and ^2J(W,H$_3$) ≃ 0 Hz).



2b



2a

On the basis of ^2J(W,H$_E$) and the two-dimensional indirect ^{1}H{^{183}W} shift correlation diagram (cf. Figure 2), the assignment of the four equal-intensity isoprene units in complexes **2a** and **2b** was achieved. The connectivity of the protons within each individual isoprene group was obtained via the J(H,H) couplings. The assignments of the carbon signals were taken from a two-dimensional ^{13}C, ^{1}H correlation diagram.

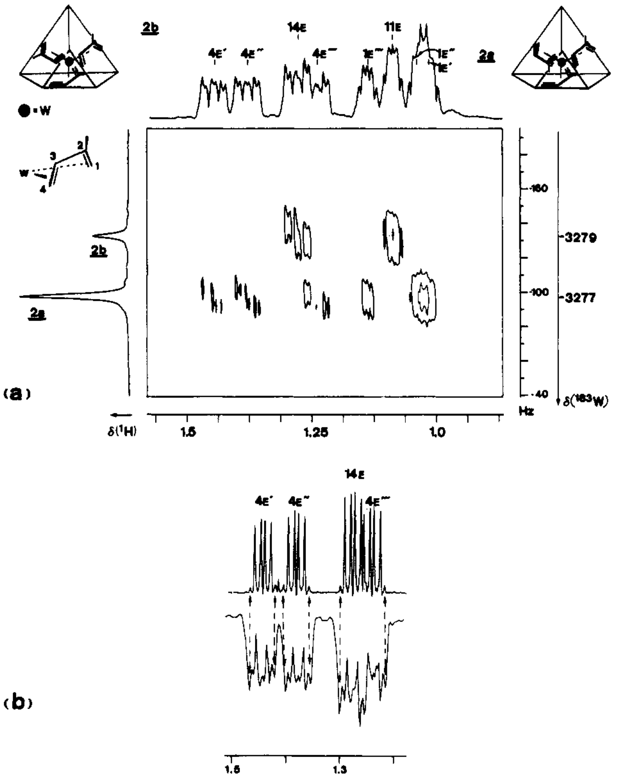


Figure 2. ^{1}H and ^{183}W NMR spectra of tris(isoprene)tungsten (**2a** (75%) and **2b** (25%)) at 9.4 T and 253 K. (a) Expansion of the 2D indirect ^{1}H{^{183}W} spectrum, yielding the assignment of the syn protons (H$_{1E}$ and H$_{4E}$) of **2a** and **2b**. The projection (F_2 dimension, horizontal trace) illustrates the ^{183}W satellites of the H$_{1E}$ and H$_{4E}$ protons. The ^{183}W spectrum in the vertical axis (F_1) stems from a conventional 1D measurement. (b) Comparison of the conventional ^{1}H spectrum of the four H$_{4E}$ protons (absorption) and of the corresponding ^{183}W satellite spectrum with total suppression of the parent signals (85.6%) with magnetically inactive tungsten (emission).

The coordination shifts $\Delta\delta$ = δ(complex) − δ(free ligand) for the protons and carbon atoms of dienes show the usual trend.[16] The ^1J(C$_1$,C$_2$) and ^1J(C$_2$,C$_3$) couplings of **2** differ markedly and indicate that there is more double bond character in the inner than in the outer diene bond. This is in line with X-ray studies[3] which showed that the bond length alteration in **3** is opposite that in free butadiene. In the series **1**–**3** ^2J(H,H), ^2J(W,H$_E$), ^1J(W,C$_4$), and δ(^{183}W) increase indicating decreasing π-character in the bonding between W and the terminal diene carbon atoms.

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From our findings we conclude that at high magnetic fields the T_1 values of small organotungsten compounds lie in the order of seconds, thus enabling various types of modern one- and two-dimensional NMR pulse experiments to be carried out. Provided that there is a scalar coupling between ^{183}W and both a high γ and a high abundant nucleus (of a few hertz), the two-dimensional indirect ^{1}H-{^{183}W} spectroscopy seems to be the most effective recording technique for determining $\delta(^{183}W)$. In the tris(diene)metal compounds **1**–**3** (**6**–**7**) the metal NMR shifts differ significantly. Together with the improved recording conditions it is therefore expected that ^{183}W NMR spectroscopy will become of wider use in organotungsten chemistry.

High-Pressure NMR Studies of CO Exchange with Cobalt Carbonyl Species†

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Exchange of free CO in solution with $Co_2(CO)_8$ has been studied by ^{13}C magnetization transfer techniques by using a novel high-pressure (sapphire) NMR tube. Rates for CO dissociation were found to be independent of pressure over the pressure and temperature range studied and provide the activation parameters $\Delta H^\ddagger = 25.5$ kcal/mol and $\Delta S^\ddagger = 22$ eu. Results obtained for dissociation in $CH_3CO{-}Co(CO)_4$ suggest stabilization of the coordinatively unsaturated intermediate, possibly by acyl oxygen coordination. Slower scrambling of the acyl CO is also observed and found to be markedly inhibited by higher concentrations of free CO. These results provide the ratio of rates for deinsertion and reassociation in $CH_3CO{-}Co(CO)_3$.

Introduction

The reactions of organometallic complexes with gases such as H_2 and CO have been of longstanding academic and industrial interest, and of these reactions, cobalt-catalyzed hydroformylation provides a prominent example. Spectroscopic studies in this area have been hampered by the general lack of availability of a cell capable of withstanding the pressures that are required to obtain reasonable concentrations of gas dissolved in solution. While high-pressure IR cells have been fruitfully utilized[1] in this way, the inherent advantages of NMR have remained largely unexploited because of the demands associated with construction and operation of high-pressure NMR probes.[2,3]

We have recently developed a high-pressure NMR tube, which is convenient to use, is relatively inexpensive and is suitable for use in commercial spectrometers without probe or hardware modification. In contrast to high-pressure IR cells, which require their own temperature control mechanism, this tube can directly take advantage of the full variable-temperature capabilities of NMR spectrometers (e.g., −100 to +150 °C). Finally, the new tube permits for pressurized samples the general advantage of NMR—namely, a direct basis for the determination of concentrations and the identification of chemical species.

While details of construction and performance of this high-pressure NMR tube have been presented elsewhere,[4] a brief description is included here. The tube consists of a single crystal of sapphire that was grown to the required dimensions (5-mm o.d. with 0.8-mm wall) and is sealed by means of a nonmagnetic titanium alloy valve. The tubes spin, provide routine resolution of approximately 1 Hz, and appear to offer a reasonable margin of safety in operation up to 2000 psi.

Caution: Although the burst pressure was found, in *one* test, to be in excess of 10 000 psi, it is impossible to specify a safe upper pressure limit with any accuracy. The detailed history of a given tube may eventually affect its performance. Pressurized tubes should always be transported behind an appropriate safety shield, and direct operator exposure to the tube must be avoided. Being single crystalline in nature, the tubes may be sensitive to vibrations such as occur in an ultrasonic cleaning bath.

The availability of these high-pressure tubes facilitates the systematic variation of dissolved gas concentrations in kinetic studies and also provides a means for stabilizing labile transition-metal carbonyl species. Both of these considerations apply to the current study that presents the details of our ^{13}C NMR investigations of CO exchange involving $Co_2(CO)_8$ and the model acyl $CH_3CO{-}Co(CO)_4$. The exchange processes involved are fundamental in the context of providing coordinatively unsaturated intermediates for the oxidative addition of H_2 or for reaction with other species.

Results

Exchange Involving $Co_2(CO)_8$. At pressures between 100 and 1100 psig of ^{13}CO, cyclohexane-d_{12} solutions of $Co_2(CO)_8$ reveal ^{13}C NMR spectra containing separate peaks for free CO and universally enriched $Co_2(CO)_8$ as the only species observable (see Figure 1). Since intramolecular exchange of the CO groups in $Co_2(CO)_8$ is very rapid,[5,6] all the coordinated CO's are treated as being equivalent. Although the use of ^{13}C-enriched CO is not

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† Contribution No. 3670.

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