756 *Organometallics* **1990,** *9,* 756-761

Probing ^{187}Os NMR of Complexes Containing ^{187}Os in Natural Abundance via Indirect Heteronuclear 2D NMR Spectroscopy†

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Received August 22, 1989

A versatile approach for determination of osmium-187 NMR data of dilute solutions of complexes containing ^{187}Os in natural abundance is presented. In neutral $[(\eta^5\text{-cyclopentadienyl})(L)_2(R)]$Os and in cationic $[(\eta^5\text{-Cp})(\eta^2\text{-}CH_2{=}CH_2)(L)_2Os]^+$ complexes (L = Ph_3P, Ph_2MeP, $PhMe_2P$, Me_3P, $(OMe)_3P$, $(OPh)_3P$; $(L)_2$ = cycloocta-1,5-diene, $L^1 = Ph_3P$, $L^2 = \eta^2\text{-}CH_2{=}CHC_5H_{11}$; R = halogen, alkyl, aryl, hydrogen) $\delta(^{187}Os)$ and J(Os,X) have been determined by employing two-dimensional indirect (X,Os) spectroscopy (X = ^{1}H and ^{31}P). In these complexes $\delta(^{187}Os)$ spans a range of -2500 to -5500 ppm relative to $\delta(^{187}OsO_4) \equiv 0$. The shifts are strongly influenced by charge density effects and the average electronic excitation energy ΔE. From the combination of two 2D experiments, i.e., (^{1}H,^{187}Os) and (^{31}P,^{187}Os) (the latter conducted with selective decoupling of individual protons) the magnitude and signs of ^2J(Os,H), ^1J(Os,H), ^1J(Os,P), ^2J(P,H), and ^3J(P,H) were determined. ^1J(Os,P), ^1J(Os,H), and ^3J(P,H) via the metal are positive, while ^2J(Os,H) and ^2J(P,H) are negative. Longitudinal relaxation times $T_1(^{187}Os)$ have been determined indirectly from representative natural-abundance samples at $B_0 = 9.4$ T and $T = 300$ K by employing a one-dimensional pulse sequence in which a normal and a reverse DEPT scheme is incorporated. Identical $T_1(^{187}Os)$ values are obtained in two-nuclei {Os,X} spin systems for X = ^{1}H and X = ^{31}P. $T_1(^{187}Os)$ values lie between 0.5 and 13 s: $T_1(^{187}Os)$ steadily increases in going from complexes with L = Ph_3P ($T_1 \sim 1$ s) via L = Ph_2MeP (~ 2 s) to L = Me_3P ($T_1 \sim 6$ s). ^{187}Os NMR is a sensitive tool for characterization of complexes containing osmium in natural abundance.

Introduction

Osmium-187 is the most insensitive nucleus in NMR spectroscopy,[1] and for a long time the only known $\delta(^{187}Os)$ shift was that of the standard OsO_4[2] and of some μ-hydrogen-bridged binuclear osmium complexes.[3] On the other hand, there is extensive chemistry involving mononuclear and cluster compounds of osmium.[4] For investigations of the structure and fluxional processes in these molecules osmium-187 NMR data are of prime interest. However, until now only scalar spin-spin coupling constants of osmium coupled to some sensitive nuclei such as protons,[3,5-9] to carbon-13 in carbonyl clusters,[10,11] and in some cases also to phosphorus[12,13] were available. These couplings range from 14 to 210 Hz and were determined by observing the osmium satellites (in natural abundance) in the spectrum of the sensitive nucleus, i.e., ^{1}H, ^{31}P, or ^{13}C. It is, however, difficult to observe small coupling constants with conventional recording techniques since the satellites may be hidden under the parent signals. It also may occur that the satellites are broadened due to fast relaxation of the osmium-187 nucleus. Due to the low sensitivity of the ^{187}Os nucleus its relaxation behavior is more or less totally unknown. With the steady-state technique, $T_1(^{187}Os)$ in OsO_4 was estimated to lie between 1 and 26 s at $B_0 = 2.1$ T and $T = 300$ K.[2]

Recently it was shown that the indirect 2D recording scheme[14-16] is of great use not only in ^{13}C[15,17] and ^{15}N[14,16,18] NMR spectroscopy but also for determination of NMR parameters of low-γ spin-$^1/_2$ metal nuclei.[3,19-25] We have extended that scheme and introduced the indirect heteronuclear triple resonance spectroscopy.[22-25] In the following we apply that technique to the characterization of the osmium shift scale, the determination of the magnitude and sign of ^nJ(Os,X) (n = 1, 2 and X = ^{1}H, ^{31}P) and the longitudinal relaxation time T_1(Os) in complexes of the type $[(\eta^5\text{-cyclopentadienyl})(L)_2(R)]$Os and $[(\eta^5\text{-Cp})(\eta^2\text{-}CH_2{=}CH_2)(L)_2Os]^+$ (L = Ph_3P, Ph_2MeP, $PhMe_2P$, Me_3P, $(OMe)_3P$, $(OPh)_3P$, $(L)_2$ = cycloocta-1,5-diene, $L^1 = Ph_3P$, $L^2 = \eta^2\text{-}CH_2{=}CHC_5H_{11}$; R = halogen, alkyl, aryl, hydro-

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† Dedicated to Professor G. Wilke on the occasion of his 65th birthday.

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Table I. ^{187}Os NMR Parameters of $[(\eta^5\text{-Cp})(R)(L)_2]Os$ Complexes[a] at T = 300 K

no.	$(L)_2$	R	$\delta(^{187}Os)$	$\delta(^{31}P)$	$^nJ(Os,H)$, Hz	$^1J(Os,P)$, Hz
1	$(P(C_6H_5)_3)_2$	Cl	−2595	−2.11		313
2	$(P(C_6H_5)_3)_2$	Br	−3008	−4.08		312
3	$(P(C_6H_5)_3)_2$	I	−3530	−7.11		311
4	$(PMe(C_6H_5)_2)_2$	Br	−3393	−14.42		306
5	$(PMe_2(C_6H_5))_2$	Br	−3418	−32.84		303
6[b]	$(PMe_3)_2$	Br	−3506	−42.98		301
7[c]	$(PMe_3)(P(C_6H_5)_3)$	Br	−3324	−1.73, −11.25		317, 300
8[d]	$(P(OMe)_3)_2$	Br	−3816	109.4		467
9	$(P(OC_6H_5)_3)_2$	Br	−3904	89.3		492
10[d]	$(P(C_6H_5)_3)_2$	CH_3	−4431	5.98	6.0	316
11	$(PMe_3)_2$	CH_3	−4779	−44.26	5.4	310
12	$(PMe_3)_2$	C_2H_5	−4670	−43.35		315
13	$(PMe_3)_2$	CH_2CMe_3	−4669	−43.04		309
14	$(PMe_3)_2$	C_6H_5	−4349	−41.53		311
15[d]	$(P(C_6H_5)_3)_2$	H	−5186	22.92	73.7	316
16	$(PMe_3)_2$	H	−5272	−45.4	76.2	297
17[d]	$(P(C_6H_5)_3)$[f]	H	−5184	29.92	69.1	291
18^+[e,g]	$(P(C_6H_5)_3)_2$	$\eta^2\text{-}C_2H_4$	−4401	−7.03		266
19[h]	$(\eta^4\text{-}1,5\text{-COD})$	H	−4889		64.3	

[a] In C_6D_6 unless otherwise stated. [b] Acetone-d_6. [c] Toluene-d_8. [d] THF-d_8. [e] CD_2Cl_2. [f] The other ligand is $\eta^2\text{-}CH_2{=}CH(CH_2)C(CH_3)_3$. [g] BF_4^- as counteranion. [h] Cp ligand is permethylated.

gen). Moreover, it is shown that the osmium NMR parameters $\delta(^{187}Os)$, $J(Os,X)$, and $T_1(^{187}Os)$ are readily accessible even for dilute samples and are sensitive probes for the osmium environment, so that ^{187}Os NMR should become a useful tool in inorganic and organometallic chemistry involving osmium.

Experimental Section

Materials. Solvents and reagents were purified and dried by using standard techniques. Sample tubes (5 mm) were used containing dilute solutions (around 1 mM) of the complexes dissolved in perdeuterated solvents. The $[(\eta^5\text{-Cp})(L)_2(\text{halogen})]Os$ compounds 1,[26] 2,[27] 3,[28] 6,[29] 8, 9,[30] and the $[(\eta^5\text{-Cp})(L)_2(\text{hydrogen})]Os$ complexes 15[31] and 19[32] (cf. Table I) were synthesized according to methods previously reported. The syntheses of the compounds 4, 5, 7, 10–14, and 16–18 will be reported elsewhere.[33]

NMR Hardware. NMR spectra were run on a modified multinuclear Bruker WH 400 spectrometer, equipped with an Aspect 2000 computer. All spectra were recorded under temperature control (T = 300 K). The measurements were carried out at frequencies of 400.13 (^{1}H), 161.97 (^{31}P), and 9.13 (^{187}Os) MHz. The details of the recording conditions are described elsewhere.[23] A 5-mm reverse ^{1}H–^{31}P–X triple probe head was used. The outer X coil is tunable in the frequency range 9–41 MHz. In the experiments described here the 90° pulses were 8 μs (^{1}H), 29 μs (^{31}P), and 43 μs (^{187}Os). To avoid pulse break through in the indirect $T_1(^{187}Os)$ measurements via ^{31}P, the transmitter pulse was attenuated by 3 dB. In these experiments the 90° ^{31}P pulse was 34 μs.

NMR Procedure. Conventional 1D spectra were recorded by using standard procedures, and special spectral windows were chosen for acquisition of the relevant signals. Selected spectral parameters for these spectra are as follows: (a) 4K data points, spectral width 500 Hz, Lorentzian to Gaussian multiplication of the ^{1}H NMR FIDs before transformation; (b) 2K data points, spectral width 800 Hz, weighted with an exponential line broadening of 2 Hz in ^{31}P NMR spectroscopy.

The simulation of the [AA′BB′CX] spin system (A, B, C = ^{1}H, X = ^{13}C) of the isotopomer residue $^{13}C(^{12}C)_4H_5$ in complex 15 was carried out with the LAOCOON programm[34] including magnetic equivalence. After iteration the following parameters were obtained: $^1J(C,H)$ = 177.6, $^2J(C,H)$ = 6.4, $^3J(H,H)$ = 3.6, $^3J(C,H)$ = 7.2, $^4J(H,H)$ = 0.8 Hz. A first-order isotope shift of 1 Hz and a half line width of 1 Hz were employed. The ^{1}H and ^{31}P chemical shifts are reported as δ values relative to internal $SiMe_4$ and external 85% H_3PO_4, respectively. The ^{187}Os shifts were calculated via their absolute frequencies with the conversion factor 9.132340 MHz for $\delta(OsO_4)$ = 0 ppm (Ξ = 2.282343 MHz).[1] The errors are smaller than ±1 ppm for the osmium shifts and ±0.5 Hz for the coupling constants.

One- and two-dimensional indirect experiments were carried out using sequences (1)[15,16] and (2).[22] Typically in these experiments a repetition time of around 2 s was used.

$$90(H) - \frac{1}{2J} - 90(Os) - \frac{t_1}{2} - 180(H) - \frac{t_1}{2} - 90(Os) - FID(H) \quad (1)$$

$$BB(H) - 90(P) - \frac{1}{2J} - 90(Os) - \frac{t_1}{2} - 180(P) - \frac{t_1}{2} - 90(Os) - FID(P) \quad (2)$$

The F_2 dimension was digitized with 1K data points using the same spectral windows as for the 1D spectra. For generation of the F_1 dimension, 16–256 data points were chosen. Between 96 and 1400 transients were used for each t_1 increment. A sweep width of the osmium nucleus up to 50000 Hz was covered within one experiment. A second experiment with a spectral window of 1000 or 500 Hz was carried out to check that no folding in the F_1 dimension had occurred and to determine $\delta(^{187}Os)$ with higher accuracy. The interferograms in the t_1 dimension were zero filled to 512 points before Fourier transformation. Generally, the data

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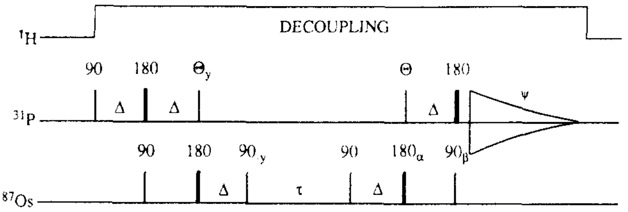


(3)

Phase Cycling

α	x	-x	y	-y				
β	y	y	y	y	-y	-y	-y	-y
ψ	x	x	-x	-x	-x	-x	x	x

Figure 1. Pulse sequence (3) and phase cycling for heteronuclear (^{31}P) indirect detection of T_1 of low-γ nuclei (^{187}Os). $\Delta = 1/[2J(Os,P)]$, τ denotes the variable delay, and Θ is the length of the polarizing pulse. For the two nuclei {Os,P} spin system Θ is 90°.

were processed by using (shifted) sine bell functions in both dimensions. The experiments where correlations via $^2J(Os,H)$ were used were performed with a digitalization of 2K data points in the F_2 dimension. The 2D data matrix was multiplied by a Gaussian function and $\pi/6$ shifted sine bell function in the F_2 and F_1 dimension, respectively, before Fourier transformation. All spectra are presented in magnitude mode.

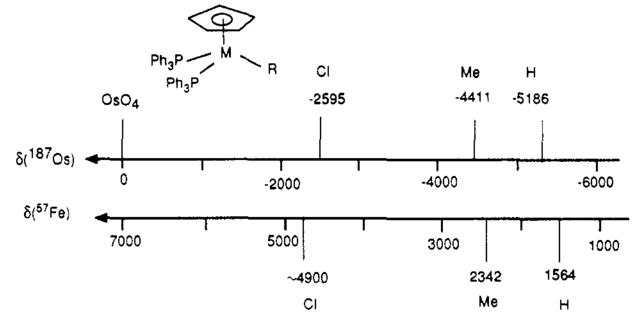
The spin-lattice relaxation times of ^1H and ^{31}P were measured by using the standard inversion recovery technique while $T_1(^{187}Os)$ was measured by using the pulse sequence[35,36] given in Figure 1. The repetition time was set to $1.5T_1$ of the sensitive nucleus. Waiting times up to $7T_1$ yielded no significant alteration in the determined $T_1(^{187}Os)$ values. Computed relaxation times were obtained by using a three-parameter fitting program for a monoexponential decaying function. They are estimated to be accurate to ±5% for ^1H and ^{31}P and to ±13% for ^{187}Os.

Results and Discussion

$\delta(^{187}Os)$ in $[(\eta^5\text{-Cp})(L)_2(R)]Os$. The osmium chemical shifts of complexes **1**–**19** listed in Table I were determined with either sequence (1) or (2). In these complexes $^1J(Os,P)$ is between 266 and 492 Hz and therefore appears as satellites in the conventional 1D $^{31}P\{^1H\}$ spectra. Although $^1J(Os,H)$ is smaller and the signal of the hydride can be split by further couplings to phosphorus or hydrogen (in **19**) it is straightforward to identify the osmium satellites in the proton spectra of **15**–**17** and **19**. In these complexes $^1J(Os,H)$ is around 70 Hz. Thus in addition to (^{31}P,^{187}Os) correlation experiments (^1H,^{187}Os) spectroscopy was also used for determination of $\delta(^{187}Os)$ of these complexes.

In the osmium complexes **1**–**19** $\delta(^{187}Os)$ spans a range of −2500 to −5500 ppm relative to the standard OsO_4. By variation of the phosphine L or the one-electron ligand R, the factors that govern the metal shielding in these quasi-tetrahedral complexes can be elucidated. The halogen dependence of $\delta(^{187}Os)$ in complexes **1**–**3** is normal. If the halogen atom is replaced by a methyl group (**10**) or a hydrogen (**15**), the osmium nucleus becomes more shielded. Similarly, when the phenyl groups at the phosphorus ligand are replaced by methyl moieties, higher $\delta(^{187}Os)$ are observed (compare the shifts in **2** and **4**–**7**). These findings can be rationalized by the charge density dependence of the shielding term. On the other hand, in the series PMe_3, PPh_3, $P(OMe)_3$, and $P(OPh)_3$ the latter ligand is generally believed to have the lowest donor but highest acceptor power, and thus on the basis of charge density effects it should produce the lowest shielding of the metal. The osmium shielding in the series **2**, **6**, **8**, and **9**, however, is not in accord with this suggestion. Since the geometry in all these complexes is basically unchanged, it must by assumed that $\delta(^{187}Os)$ is largely governed by the $1/\Delta E$ dependence of the paramagnetic shielding term via the donor/acceptor ability of the phosphorus ligand.

Scheme I



To large extent the osmium shifts of **1**–**19** resemble those of the homologous iron complexes.[23] In Scheme I the shift scales of both nuclei are displayed for comparison. Since the chemical shift range is generally greater for the heavier nuclei,[37] it is remarkable that the osmium shift range $\Delta\delta$ in these complexes seems to be of similar size or even less than that of iron.[38] A similar trend has been found on comparison of the $\Delta\delta(^{59}Co)$ and $\Delta\delta(^{103}Rh)$ in $[(\eta^5Cp)(\eta^2\text{-olefin})_2]M$ complexes.[39]

$^nJ(Os,X)$ (n = 1, 2; X ^1H, ^{31}P). If the indirect 2D technique is to find an application as wide as possible, it is essential that it also works when small scalar couplings have to be employed. We have therefore examined the methyl compounds **10** and **11** for the presence of long-range $^nJ(Os,X)$ couplings. In Figure 2, trace a, the signal of the methyl protons of **11** is shown. This signal is a triplet due to the coupling with two equivalent phosphorus atoms. Even when resolution-enhancing apodization functions are used and the vertical display is enhanced by a factor of 32 (trace b), it is hard to identify the ^{187}Os satellites. Since the ^{187}Os shift of this compound is known from the 2D (^{31}P,^{187}Os) experiment, sequence (1) can be applied with on-resonance osmium pulses for determination of $^2J(Os,H)$. In this one-dimensional version of sequence (1) the evolution time t_1 is zero. In this experiment the parent signals with magnetically inactive osmium are suppressed, and thus $^2J(Os,H)$ can be directly obtained (c.f. trace c in Figure 2). In complexes **10** and **11** it was found that $^2J(Os,H) = 6.0$ and 5.4 Hz, respectively.

Of course, it also would be desirable to detect a $^2J(Os,H)$ coupling between osmium and the cyclopentadienyl protons. However, there are probably two reasons why we did not succeed in finding such a coupling. Firstly, it can be assumed that $J(Os,X)$ is governed by the Fermi contact term (evidence for this assumption will be given below) so that the coupling of osmium with the η^5-bonded ring protons can be expected to be even smaller than the above-mentioned $^2J(Os,H)$ coupling in **10** or **11**, where σ-bonds are involved. From our experiments we place 2 Hz as the upper limit for the coupling of osmium with the cyclopentadienyl protons: even with sequence (1) or (2) such small couplings are difficult to detect. Special pulse sequences using long-range couplings[40] were not used be-

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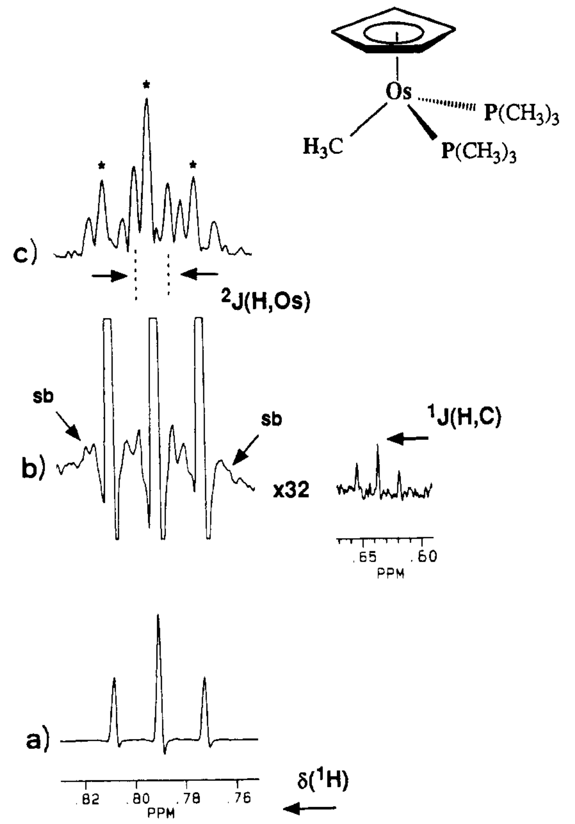


Figure 2. Expansion of the ^{1}H NMR spectrum in the region of the methyl protons in 11: (a) conventional 1D spectrum; (b) as in (a) but with resolution enhancement and expansion in the vertical; sb denotes spinning side bands. The ^{13}C satellite on the right-hand side is shown for comparison. (c) after employing sequence (1) with $t_1 = 0$ the parent signals (marked by asterisks) are suppressed, and the osmium satellite subspectrum can be directly identified.

cause they introduce extra delays that prolong the overall duration of the sequence and thus lead to loss of sensitivity due to relaxation in the evolution period. Second, the detection of a coupling between osmium and the cyclopentadienyl protons is hampered by the signals of the isotopomer containing the η^5-(^{13}C(^{12}C)$_4$H$_5$) moiety, which yields a {AA'BB'CX} (A, B, C = ^{1}H, X = ^{13}C) satellite subspectrum. Simulation of the proton part of this spin system indicates that the inner lines will overlap the wanted osmium lines (cf. Figure 3). Although in principle these lines are eliminated when sequence (1) is employed, in practice some residual signals are always present at the center of the parent multiplet that may cause difficulties when observing small osmium couplings in natural-abundance samples.

The relative signs of J(Os,X) coupling constants were determined by combining two indirect 2D experiments based on sequence (1) or (2). In Figure 4 the (^{1}H,^{187}Os) correlation diagram involving complex 11 is illustrated. This experiment was performed by using sequence (1), knowing that ^2J(Os,H) is 5.4 Hz. In the contour diagram δ(^{187}Os) is displayed in the first dimension, while δ(^{1}H) and J(Os,H) are contained in the horizontal proton dimension (t_2 or F_2). In 11 the phosphorus nuclei couple to both the ^{1}H and the ^{187}Os nucleus, and consequently this coupling is contained in both dimensions. Since ^{31}P is not excited and the high-frequency proton peak correlates with the high-frequency osmium peak, it follows that ^3J(H,P) and ^1J(Os,P) possess the same sign. A similar experiment was carried out employing sequence (2). If in the (^{31}P,^{187}Os) correlation experiment the J(P,H) couplings within the phosphorus ligands are removed by selective continuous-wave (CW) decoupling of the aromatic protons in 10, the coupling with the methyl protons is conserved and these protons may be regarded as passive spins (cf. Figure 5). Then δ(^{31}P) together with ^1J(Os,P) are displayed in the F_2 dimension along with the (residual) coupling ^3J(P,H$_r$) of phosphorus with the protons of the Os methyl group. In the ^{31}P spectrum each satellite line due to ^1J(Os,P) is further split as a quartet. Besides δ(^{187}Os) the osmium dimension also contains ^2J(Os,H$_r$). When there is sufficient digital resolution, this coupling also can be determined from the F_1 projection of the 2D contour diagram. In our experiment the same value for J(Os,H$_r$) was obtained within the limits of error (±0.5 Hz) as in the 1D experiment. This confirms that the CW decoupling of the Ph$_3$P protons was highly selective and thus ^2J(Os,H$_r$) = ^2J(Os,H).

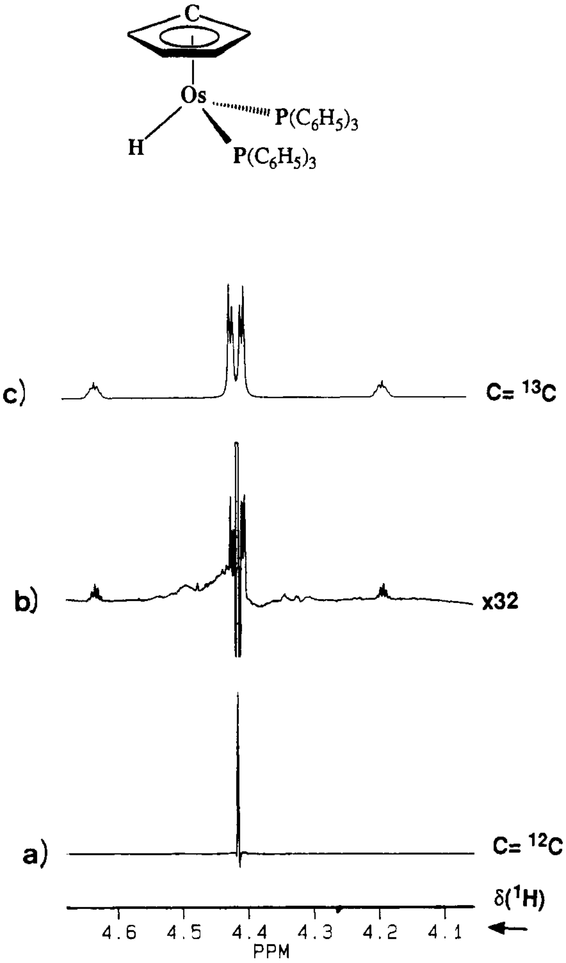
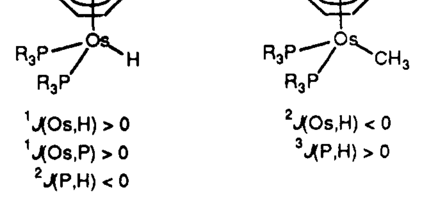


Figure 3. Conventional 400.13-MHz 1D spectra of 15 in the region of the cyclopentadienyl protons. (a) normal spectrum, (b) experimental spectrum illustrating the satellite subspectrum of the species containing the η^5-(^{13}C(^{12}C)$_4$H$_5$) ring, and (c) simulated spectrum of that isotopomer.



Again, from the position of the cross peaks, it follows that ^2J(Os,H) and ^3J(H,P) are of opposite sign. In total, both

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(40) Martin, G. A.; Zektzer, A. *Magn. Reson. Chem.* **1988**, *26*, 631. Bermel, W.; Wagner, K.; Griesinger, C. *J. Magn. Reson.* **1989**, *83*, 723.

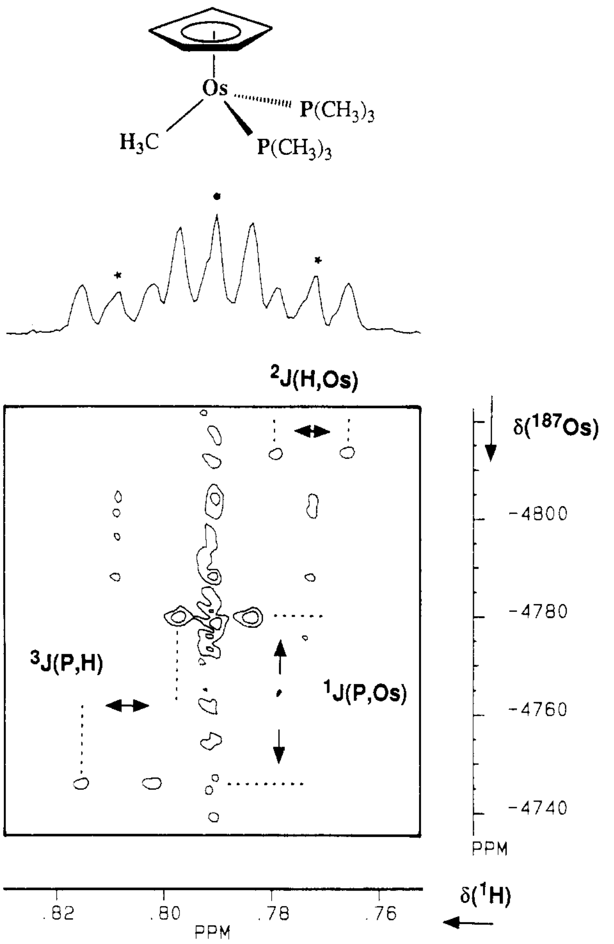

Figure 4. Indirect 2D (^{1}H,^{187}Os) spectrum of **11** in the region of the methyl protons recorded at 400.13 MHz. In the F_1 dimension $\delta(^{187}$Os) and J(P,Os,P) are displayed, while in the F_2 dimension $\delta(^{1}$H), J(P,H), and J(Os,H) are found. Incompletely suppressed parent signals in the horizontal projection are marked by asterisks.

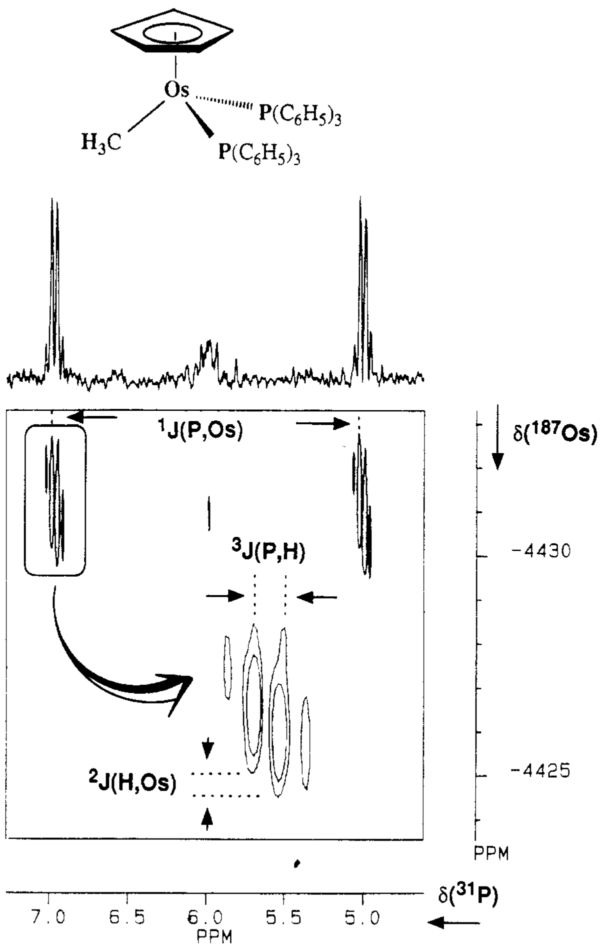

Figure 5. Indirect 2D (^{31}P,^{187}Os) spectrum of **10** recorded at 162 MHz with selective CW decoupling of the protons of Ph$_3$P. In the F_1 dimension $\delta(^{187}$Os) and ^{2}J(Os,H) are displayed, whereas in the F_2 dimension $\delta(^{31}$P) and also ^{1}J(Os,P) and ^{3}J(P,H) are contained.

experiments yield that ^{1}J(Os,P) and ^{3}J(P,H) are positive while ^{2}J(Os,H) is negative. A similar series of experiments were performed on the hydride complexes **15**–**17**. From the position of the cross peaks in the (^{1}H,^{187}Os) and (^{31}P,^{187}Os) correlation diagrams (via ^{1}J(Os,H) and ^{1}J(Os,P), respectively) it was confirmed that ^{1}J(Os,P) and ^{1}J(Os,H) are positive while ^{2}J(P,H) is negative.

The signs of the coupling constants are identical with those found in the homologous iron complexes.[23] The magnitudes of the couplings are best compared by using the reduced coupling constants $^{n}K(\mathrm{M,X}) = (1/h)(2\pi/\gamma_{\mathrm{M}})(2\pi/\gamma_{\mathrm{X}})^{n}J(\mathrm{M,X})$.[37] In **1**–**7** and **10**–**17** ^{1}J(Os,P) is around 300 Hz while in the corresponding iron complexes ^{1}J(Fe,P) is around 60 Hz. The ratio of the reduced coupling constants ^{1}K(Os,P)/^{1}K(Fe,P) is 7.2. This agrees well with the ratio of the respective metal s-electron densities of Os/Fe at the nucleus, which lies around 7.4.[41] With phosphite ligands ^{1}K(Os,P)/^{1}K(Fe,P) is 6.8, while for metal–hydride coupling ^{1}K(Os,H)/^{1}K(Fe,H) is around 11, still of the right order of magnitude. From these findings it is concluded that J(Os,H) and J(Os,P) are dominated by the Fermi contact term.

T_1(^{187}Os). With the help of sequence (3) T_1(^{187}Os) has been determined in selected complexes. The results are listed in Table II along with the relaxation times of phosphorus, the cyclopentadienyl protons, and the hydride (in **15**–**17**, **19**). If we neglect (or decouple) the passive phosphorus nuclei, the hydride complexes exhibit simple {Os,H} spin systems of two nuclei. According to theoretical arguments and experiments on enriched samples containing ^{13}C,^{1}H$_n$ fragments, sequence (3)[35,36,42] for the inverse T_1 measurement produces reliable results for two-nuclei spin systems (n = 1).[35,36,43] Such a situation is found in

Table II. T_1(^{187}Os) of Selected Compounds Together with T_1(^{31}P) and T_1(^{1}H) of Characteristic Sites (s)

no.	T_1(^{187}Os)[a]	T_1(^{31}P)	T_1(^{1}H)[d]	T_1(^{1}H)[e]
1	0.5 ± 0.07	0.88 ± 0.02		2.14 ± 0.07
2	0.6 ± 0.12	1.12 ± 0.08		2.68 ± 0.06
5	2.0 ± 0.30	4.11 ± 0.13		8.48 ± 0.07
6	6.7 ± 0.54	8.55 ± 0.15		14.70 ± 0.13
13	12.3 ± 1.65	7.08 ± 0.20		13.50 ± 0.43
14	6.3 ± 0.71	7.52 ± 0.13		13.20 ± 0.40
15	1.6 ± 0.21[b,c]	1.14 ± 0.04	0.64 ± 0.03	3.84 ± 0.09
17	2.2 ± 0.26[a,b]	2.01 ± 0.02	1.40 ± 0.02	5.79 ± 0.07
19	5.6 ± 0.59[b]		3.56 ± 0.03	

[a] Detected by observation of ^{31}P using sequence (3). [b] Detected by observation of ^{1}H. [c] 0.9 ± 0.1 when detected via ^{31}P({Os,P$_2$}). [d] Hydride signal. [e] Cyclopentadienyl protons.

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(41) Pyjkkö, P.; Wiesenfeld, L. *Mol. Phys.* **1981**, *43*, 557.

(42) Indirect T_1(^{13}C) determination via a 2D ^{1}H NMR pulse sequence using samples with ^{13}C in natural abundance; cf.: Nirmala, N. R.; Wagner, G. *J. Am. Chem. Soc.* **1988**, *110*, 7557.

(43) Using sequence (3), we have determined T_1(^{13}C) of CHCl$_3$ containing ^{13}C atoms in natural abundance as a test sample ({^{13}C,^{1}H} spin system). This experiment yielded T_1 = 21.6 ± 0.41 s, while using the inversion recovery sequence and direct ^{13}C observation yielded T_1 = 23.1 ± 1.14 s. A similar comparison was made for P(OCH$_3$)$_3$ [{^{13}C,^{1}H$_3$} spin system). Indirect detection gave T_1(^{13}C) = 6.8s while direct detection of T_1(^{13}C) yielded 15.0 s.

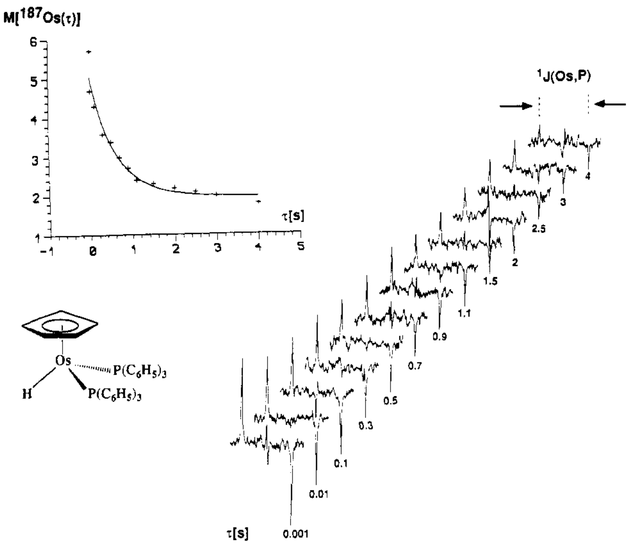

Figure 6. Indirect determination of $T_1(^{187}Os)$ by detection of the ^{31}P signal in **15** via application of sequence (3): variation of the intensity of the osmium satellites in the ^{31}P spectrum as a function of τ; data fitted to a monoexponential decaying function.

complex **17**, which yields either an {Os,H} or an {Os,P} two-nuclei spin system if we neglect (or decouple) the passive phosphorus nuclei or the protons, respectively. In **17** T_1(Os) can be determined indirectly by two independent experiments. Within the limits of error both experiments yield $T_1(^{187}Os) = 2.2$ s.

Complex **19** also yields a simple two-nucleus {Os,H} spin system, and therefore the indirect determination of $T_1(^{187}Os)$ should lead to the correct results. In the proton satellite spectrum of complexes **15**–**17** the phosphorus nuclei may be regarded as passive spins when sequence (3) is applied (X = ^{1}H) to the hydride signal. Since phosphorus is not excited, the lines in the multiplet due to J(P,H) act like signals with different chemical shifts and therefore do not affect the indirect determination of T_1(Os). The situation becomes more complex when the relaxation time of e.g. **15** is determined via ^{31}P with decoupling of the protons. If we focus on the isotopomers with magnetically active osmium, then we deal with a three-nuclei spin system {Os,P$_2$}. Since sequence (3) starts with DEPT polarization transfer, zero- and double-quantum coherences are generated. Even with homogeneity-spoiling pulses, the zero-magnetization components cannot be destroyed in the variable time τ, and thus these terms will be transferred back to observable phosphorus magnetization by the subsequent reverse DEPT scheme with which sequence (3) finishes. In principle such a situation should produce a deviation from a pure single-exponential decay of T_1. However, in all our indirect T_1 measurements involving sequence (3) and {Os,P$_2$} spin systems the intensity of the satellites could be fitted to a monoexponential decaying function without any problems (cf. Figure 6). On the other hand, it was found that the indirect determination of $T_1(^{187}Os)$ produces values that are too short when applied to three-nuclei spin systems.[43] For example, in **15** $T_1(^{187}Os)$ was obtained as 1.6 and 0.9 s by detection via ^{1}H or ^{31}P, respectively. Since all the complexes **1**, **2**, **5**, **6**, **13**, and **14** yield {Os,P$_2$} spin systems and the T_1(Os) values were determined via ^{31}P, it can be assumed that the real T_1(Os) values are somewhat longer than those listed in Table II. Here our major goal, however, is to find the trends that determine T_1(Os) in these complexes, and for that purpose the achieved accuracy is sufficient.

At $T = 300$ K and $B_0 = 9.4$ T, and $T_1(^{187}Os)$ values in **1**–**19** lie between 0.5 and 13 s. Apparently relative short T_1 values around 0.6 s are obtained when the phosphorus ligand is Ph$_3$P. If this ligand is replaced by Me$_3$P, the values of $T_1(^{187}Os)$ are found around 6.5 s. Replacement of two phenyls by methyl groups within the phosphorus ligand produces intermediate $T_1(^{187}Os)$ values (**5**). It is interesting to note that, like $T_1(^{187}Os)$, both $T_1(^{31}P)$ and $T_1(^1H)$ also increase qualitatively in a similar manner in going from complexes **1** and **2** via **5** to **6** and **14**. At the same time $T_1(^1H)$ experiments show that the relaxation times of the residual signals of the deuterated solvent are more or less the same in all samples investigated. Thus it can be ruled out that the differences in $T_1(^1H)$ within a series of complexes are caused, for example, by different degrees of paramagnetic impurity. Conventional wisdom tells that homonuclear dipole–dipole interaction is the dominant relaxation pathway for the proton nuclei. The rather short $T_1(^1H)$ values for the cyclopentadienyl protons in **1** and **2** are therefore best rationalized by the plausible assumption that those complexes involving the bulky Ph$_3$P ligand possess a long correlation time τ_c. Consequently complexes with less sterically demanding ligands should have shorter τ_c values and thus produce longer $T_1(^1H)$ values. There is good evidence for assuming that the ^{31}P nucleus relaxes via heteronuclear dipole–dipole interaction[44] and thus the argumentation based on τ_c here also may help to rationalize the parallels in the $T_1(^1H)$ and $T_1(^{31}P)$ data (cf. Table II). For the relaxation of osmium also the spin rotation (SR) and the chemical shift anisotropy (CSA) mechanism have to be considered[39] in addition to dipole–dipole interaction. Since T_1 due to the spin rotation (SR) mechanism is proportional to τ_c and because relaxation via dipole–dipole interaction is insignificant for other heavy-metal spin-$^1/_2$ nuclei, the data in Table II show that in these complexes the osmium nucleus relaxes mainly via the CSA mechanism. At the same time, the T_1 values in **13** and **14** indicate that in certain cases the SR mechanism may also contribute to the relaxation of the osmium nucleus.

Conclusion

We have shown that ^{187}Os NMR parameters ($\delta(^{187}Os)$; ^nJ(X,Os), $n = 1, 2$; T_1) of dilute solutions of complexes containing ^{187}Os in natural abundance are readily accessible by using a combination of one- and two-dimensional indirect (X,Os) spectroscopy. These osmium NMR data are suitable probes for characterization of Os complexes in inorganic and organometallic chemistry. Moreover, since even at $B_0 = 9.4$ T the Os relaxation times are between 0.1 and 10 s and J(Os,X) may become large for e.g. X = ^{1}H, ^{13}C, and ^{31}P, it appears that the indirect 2D (X,Os) spectroscopy will become attractive in other areas, such as for X = ^{13}C at the investigation of Os carbonyl complexes and clusters.

Acknowledgment. F.L.O. thanks the Alexander von Humboldt Stiftung for the grant of a post doctoral fellowship.

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(44) Pregosin, P. S. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; New York, VCH Publishers: 1987; pp 465ff.