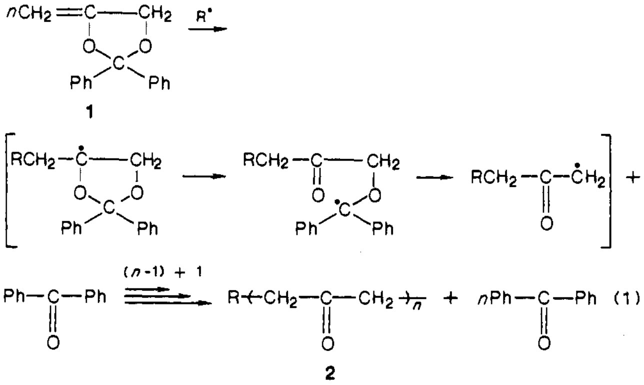
the radical ring-opening polymerization of unsaturated cyclic ethers or diketene,[10] have been reported; any of such obtained polymers contains undetermined structural units or no more than ketone moieties partially. We now report a novel synthesis of polyketone via the radical ring-opening polymerization of **1** accompanying the quantitative elimination of benzophenone.

Monomer **1**[11] was synthesized by the acetal formation as follows: benzophenone was allowed to react with 3-chloro-1,2-propanediol in benzene in the presence of *p*-toluenesulfonic acid (*p*-TsOH) with azeotropic removal of water for 6 h. The obtained chloro compound, 2,2-diphenyl-4-(chloromethyl)-1,3-dioxolane[12] was dehydrochlorinated with sodium methoxide in *N*,*N*-dimethylformamide (DMF) for 3 h at 50 °C. The polymerization of **1** was carried out at 120 °C in chlorobenzene in the presence of di-*tert*-butyl peroxide (DTBP) (3 mol %) as an initiator.[13] Since the reaction mixture solidified as the polymerization proceeded, the polymerization of **1** almost stopped after about 7 h. The detection of benzophenone from the soluble part in methylene chloride after the purification indicated that **1** was polymerized with the elimination of benzophenone. All the IR spectra of thus obtained polymers (**2a** (time, 0.5 h), **2b** (2 h), **2c** (4 h), **2d** (7 h), **2e** (11 h), **2f** (16 h)) showed absorption at 1693 cm^{-1} assigned to C=O group. All the ^{1}H NMR spectra showed only one signal at 2.62 ppm corresponding to methylene protons, and the ^{13}C NMR spectrum of polymer **2f** showed two signals at 206.84 and 35.37 ppm corresponding to the carbonyl carbon and the methylene carbon, respectively. To our notice, neither aromatic proton nor aromatic carbon was found in all the spectra. Moreover, the found value of elemental analysis of polymer **2f** agreed with the calculated value for $(C_3H_4O)_n$. These spectral data and the result of the elemental analysis indicated that **1** underwent the ring-opening reaction accompanying the quantitative elimination of benzophenone to form polyketone **2** as shown in eq 1.



Further confirmation of the polyketone structure was carried out by the chemical reaction of the obtained polymer with phenylhydrazine.[14]

$$2 + n\mathrm{H_2NNHPh} \xrightarrow[95\ ^\circ\mathrm{C},\ 6\ \mathrm{h}]{p\text{-TsOH}/p\text{-cresol}} -[\mathrm{CH_2C({=}NNHPh)CH_2}-]_n + n\mathrm{H_2O} \quad (2)$$

In the IR spectrum of the reaction product, the absorption of C=O group disappeared completely but the new absorptions at 1601 cm^{-1} assigned to C=N and the phenyl group were observed. These results strongly supported the structure of **2**.

Although the five-membered ring containing two oxygen atoms (dioxolane) has lower strain energy, that the reaction proceeded smoothly might be caused by the formation of a stable radical, diphenylmethyl radical, which cannot attack the olefin, and as a result the production of the ketone group (benzophenone). In other words, the predominant formation of a ketone group and diphenylmethyl radical is the driving force for the polymerization of **1**.

It is also expected that the ketone moieties can be easily incorporated into the backbone of vinyl polymers by a copolymerization method. In practice, it has been already found that the ketone moieties can be incorporated into the backbone of polystyrene. A report relating to the copolymerization of **1** with vinyl monomers will be presented subsequently.

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(11) 2,2-Diphenyl-4-methylene-1,3-dioxolane (**1**): yield 59.4%; bp 82 °C (0.06 mmHg); mp 39.0–40.0 °C; IR (neat) 3063, 3032, 2886, 1686, 1068, 756 cm^{-1}; ^{1}H NMR (CDCl$_3$, 60 MHz) δ 7.93–7.13 (m, 10 H, Ar H's), 4.03–3.80, 4.70–4.30 (m, 4 H, C=CH$_2$, OCH$_2$).

(12) 2,2-Diphenyl-4-(chloromethyl)-1,3-dioxolane: yield 69.0%; bp 126 °C (0.07 mmHg); mp 42.0–43.0 °C; IR (neat) 3063, 3028, 2889, 1076, 1030, 752 cm^{-1}; ^{1}H NMR (CDCl$_3$, 60 MHz) δ 8.00–6.73 (m, 10 H, Ar H's), 4.60–3.13 (m, 5 H, CH$_2$Cl, OCH$_2$, OCH).

(13) Six sealed polymerization tubes (5 mL) containing **1** (2.00 g, 8.39 mmol), DTBP (36.8 mg, 0.252 mmol), and chlorobenzene (4.3 mL) were heated at 120 °C for 0.5, 2, 4, 7, 11, and 16 h, respectively. The resulting products were purified by dissolution in *p*-cresol, followed by precipitation in the mixture of methylene chloride and triethylamine (10:1). The precipitated materials were dried under reduced pressure at room temperature to give 0.035 g of **2a** (7.6%), 0.125 g of **2b** (26.9%), 0.246 g of **2c** (52.3%), 0.348 g of **2d** (75.5%), 0.365 g of **2e** (77.5%), and 0.371 g of **2f** (78.8%), respectively: [η] 0.63 dL/g at 30 °C in *m*-cresol (**2d**); IR (KBr) 2912, 1693, 1408, 1331, 1055 cm^{-1} (**2a–f**); ^{1}H NMR (Me$_2$SO-d_6, 140 °C, 100 MHz) δ 2.62 (s, 4 H, CH$_2$COCH$_2$) (**2a–2f**); ^{13}C NMR (Me$_2$SO-d_6, 140 °C, 25.00 MHz) δ 206.84 (CO), 35.37 (CH$_2$) (**2f**); Anal. Calcd. for $(C_3H_4O)_n$: C, 64.27; H, 7.19. Found: C, 64.64; H, 7.01 (**2f**).

(14) A solution of the polymer (24.3 mg) and phenylhydrazine (170 mg) in *p*-cresol (1.5 mL) was heated at 95 °C for 6 h in the presence of *p*-TsOH (0.075 g). After *p*-TsOH was destroyed by the addition of triethylamine (0.1 mL), the product was purified by precipitation in a mixture of ether and triethylamine (10:1). The precipitated polymer was dried under reduced pressure at room temperature to give 55.8 mg of polyimine (88.0%): IR (KBR) 2976, 2939, 1601, 1496, 1184, 694 cm^{-1}.

NMR Properties of the Complexes *trans*-$[M(\eta^2\text{-}H_2)(H)(PEt_2CH_2CH_2PEt_2)_2]^+$, M = Fe, Ru, Os; Intramolecular Exchange of Atoms between η^2-Dihydrogen and Hydride Ligands

Maria Bautista, Kelly A. Earl, Robert H. Morris,* and Andrea Sella

Department of Chemistry and the Scarborough Campus
University of Toronto, Toronto, Ontario M5S 1A1, Canada

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An important question arising from the recent discovery of several η^2-dihydrogen complexes[1-8] is under which conditions is the η^2-dihydrogen coordination mode, M(η^2-H$_2$), preferred over the classical, dihydride structure, M(H)$_2$?[9]

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$$M(\eta^2\text{-}H_2)L_n \rightleftharpoons M(H)_2L_n \qquad (1)$$

The variation of coordination mode of dihydrogen within a group of metals is intriguing. When the 3d or 4d metal complex lies to the left of eq 1, the analogous 5d metal complex can lie to either side.[1a,b,2a,4b,5b] After our discovery of the η^2-dihydrogen complexes *trans*-$[M(H_2)(H)(dppe)_2]BF_4$, M = Fe (**1Fe**), M = Ru (**1Ru**), dppe = $PPh_2CH_2CH_2PPh_2$,[6] we set out to find a triad of complexes which included osmium. Here we report some properties of the new complexes $[M(\eta^2\text{-}H_2)(H)(depe)_2]BPh_4$, M = Fe (**2Fe**), Ru (**2Ru**), and Os (**2Os**), depe = 1,2-bis(diethylphosphino)ethane. A significant finding is that the H–H interaction is weakest and the M–H interactions in the H_2 ligand are strongest for **2Os**. Yet **2Os** exists, to the limits of detectability by ^{1}H and ^{31}P NMR, as an η^2-dihydrogen complex as opposed to $[OsH_3(depe)_2]^+$, the classical, seven-coordinate trihydride structure found for very similar 5d metal complexes $[OsH_3(PPh_3)_4]^+$[10] and $ReH_3(dppe)_2$.[11,12] The H_2 ligand in **2Ru** has the strongest H–H interaction and is the most labile and the one in **2Fe** has intermediate properties. A similar periodic ordering has been noted for the thermal stability of complexes $M(CO)_5(H_2)$.[2a] Also of significance is the small kinetic isotope effect for the intramolecular exchange $[Os(\eta^2\text{-}X_2)(Y)L_n]^+ \rightleftharpoons [Os(\eta^2\text{-}XY)(X)L_n]^+$, where X or Y are H or D.

The new complexes **2**[13] were prepared by reacting the precursor complexes *trans*-$M(H)(Cl)(depe)_2$[14] with sodium tetraphenylborate in acetone under 1 atm of hydrogen gas at 22 °C for 1 h. This reaction was based on the preparation of analogous dinitrogen complexes *trans*-$[M(N_2)(H)(depe)_2]BPh_4$, M = Fe, Ru, Os.[15] It substantiates the ideas that a binding site for dinitrogen is also a binding site for dihydrogen and that when the force constant of the dinitrogen ligand in a d^6 metal complex is greater than 17.5 mdyn/Å (2060 cm^{-1}) then eq 1 will lie to the left for the corresponding dihydrogen adduct.[16] The complexes are yellow (**2Fe**) or white (**2Ru**, **2Os**) oxygen-sensitive solids which are soluble and stable to loss of H_2 in THF or acetone under Ar at 22 °C. Solutions of complex **2Fe** react with N_2 to give *trans*-$[Fe(N_2)H(depe)_2]^+$ whereas solutions of **2Os** are stable under N_2.

The NMR spectra of the complexes in acetone-d_6 (CD_2Cl_2 for **1Fe**) below 223 K are similar and are consistent with an octahedral structure in which the η^2-H_2 ligand is trans to the terminal hydride as observed in the crystal structure for **1Fe**.[6] In the high-field region of the ^{1}H NMR spectra for each case there is a broad singlet with a very short apparent T_1 value[17] at 210 K (7 ms for **1Fe**, 12 ms for **2Fe**, 11 ms for **1Ru**, 11 ms for **2Ru**, 52 ms for **2Os**) which is characteristic of an η^2-H_2 ligand[5] and a quintet with a much longer T_1 value (146 ms for **1Fe**, 302 ms for **2Fe**, 280 ms for **1Ru**, 270 ms for **2Ru**, 260 ms for **2Os**) associated with the terminal hydride. The T_1 values decrease and the η^2-H_2 and H resonances broaden as the temperature is lowered below 210 K. The temperature dependences of T_1 for these resonances for complex **1Ru** in acetone-d_6 in the range 203–303 K where intramolecular exchange of H ligands is slow on the NMR time scale (as demonstrated by a spin saturation transfer study) are $\ln(T_1) = 0.58 - 1179/T$ for the η^2-H_2 resonance and $\ln(T_1) = 1.40 - 746/T$ for HRu.

The temperature-dependent, high-field, ^{1}H NMR spectra for solutions of **2Fe** and **2Os** (Figure 1)[18] are explained by an intramolecular exchange process $M(\eta^2\text{-}H_2)(H^*)L_n \rightleftharpoons M(\eta^2\text{-}HH^*)(H)L_n$ which has been observed for $[Fe(H_2)(H)(dppe)_2]^+$ (**1Fe**)[6] and $[Ir(H_2)(H)(C_{13}H_8N)(PR_3)_2]^+$, R = Ph, Cy.[5a,d] The spectra have been accurately simulated by use of the program DNMR-4[19] and a model where two protons in an A_2X_4 spin system with a short T_2 value interchange with one proton in a BX_4 spin system with a long T_2 value and where the T_2 values decrease with temperature. The spectra of **2Os** have two features not displayed by those of **2Fe** and **1Fe**.[6] First, the chemical shift of the η^2-H_2 ligand but not the terminal hydride has an unexplained, linear dependence on temperature.[13] Second, a coupling $^{2}J(H,P)$ of 9.7 Hz is resolved in the fast-exchange spectra which results from the averaging (1:2) of the terminal hydride coupling of 17.5 Hz (J_{BX}) with a $^{2}J(\eta^2\text{-}H_2,P)$ coupling of 5.8 Hz (J_{AX}). This is the first evidence for $^{2}J(\eta^2\text{-}H_2,P)$ coupling since the η^2-H_2 peaks of all known complexes are too broad at low temperatures to resolve couplings of this magnitude.[1,5,6] Incorporating these features into the simulation gives excellent matches with observed spectra. Simulations for **2Fe** indicate values for J_{AX} of 5 Hz and J_{BX} of 47 Hz. The spectra for **2Ru** are invariant over the range 200–310 K apart from a broadening of the η^2-H_2 resonance as the temperature is lowered as mentioned above. The $\Delta G^{\ddagger}$ values at 300 K for the exchange of the hydrogen atoms in the complexes decrease as **1Ru**, **2Ru** (>15 kcal/mol) > **1Fe** (14.2 ± 0.2) > **2Fe** (13.0 ± 0.2) > **2Os** (12.6 ± 0.2). This ordering differs from those observed for the classical hydride complexes $MH_2(PR_3)_4$ where the barriers were relatively insensitive to ligand variation but decreased as Os > Ru > Fe.[20]

The time for replacement of half of the metal-ligated hydrogens in the complexes by deuteria from D_2 gas in acetone at 22 °C increases as **1Ru**, **2Ru** (<5 min) < **1Fe**, **2Fe** (~2 h) < **2Os** (~180 h). There is no H/D exchange with any phosphine protons. The large $^{1}J(H,D)$ couplings characteristic of η^2-HD complexes[1d] have been resolved for isotopomers *trans*-$[M(HD)(D)L_2]^+$ derived from **1Ru** (32.9 ± 0.2 Hz, 293 K),[6] **2Ru** (32.0 ± 0.3 Hz, 293 K), **1Fe** (30 ± 1 Hz, 200 K), and **2Fe** (28 ± 1 Hz, 200 K).[21] Simulations of the line shapes of the η^2-HD resonances are consistent with the idea that the Os complex[21] has an unresolved coupling $^{2}J(H,P) \sim 6$ Hz for the HD or H_2 ligand whereas for Ru, $^{2}J(H,P) \sim 1$ Hz. Rates of exchange have been estimated for the process $[Os(HD)(D)(depe)_2]^+ \rightleftharpoons [Os(D_2)(H)(depe)_2]^+$ from temperature-dependent spectra. The kinetic isotope effect obtained in this way is $k_{OsH_3}/k_{OsHD_2} = 1.4 \pm 0.2$ at 248 K. This value falls in the range $k_H/k_D \sim 1$–2 observed for the dissociative addition of dihydrogen to transition metals.[22] An undetected fluxional, seven-coordinate, trihydride intermediate produced as in eq 1 is

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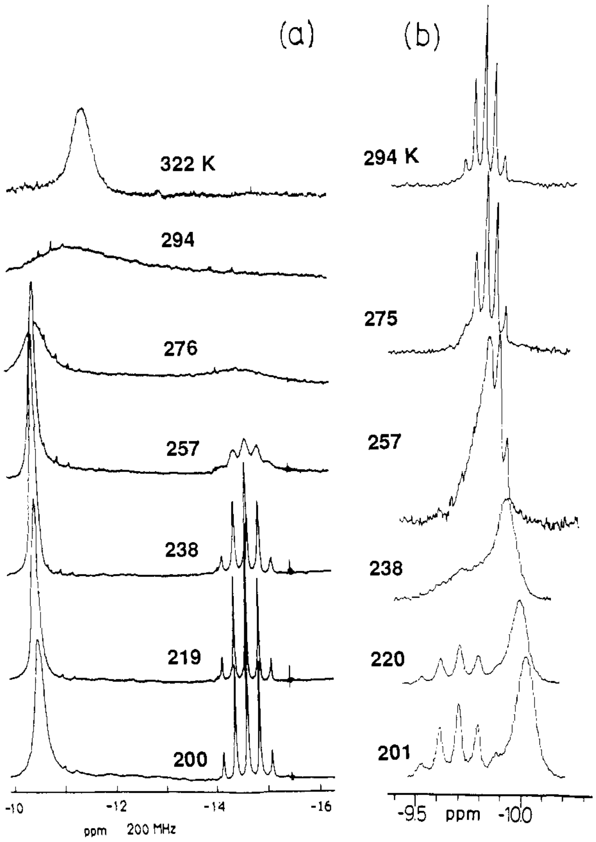

Figure 1. ^1H NMR spectra at 200 MHz as a function of temperature for the complexes **2Fe** (a) and **2Os** (b).

an attractive explanation for the hydrogen exchange process and the ordering of $\Delta G^\ddagger$ values for complexes **1** and **2**. However, a process involving isomerization of the octahedral complexes to bring exchanging groups cis to each other as in the complexes $[Ir(H_2)(H)(C_{13}H_8N)(PR_3)_2]^+$[5a] cannot be ruled out considering that the rate of exchange is sensitive to the nature of the phosphine ligand.

The trends in the barriers to intramolecular exchange of hydrogens, in the susceptibilities to H_2 loss, in the T_1 values, and in the couplings $^1J(H,D)$ and $^2J(\eta^2\text{-}H_2,P)$ all indicate that H-H interactions decrease in the order **1Ru** > **2Ru** > **1Fe** > **2Fe** > **2Os**. The M-H_2 interactions increase as the H-H interactions decrease. A combination of two factors could explain these trends. First, there is a general increase in metal-ligand bond strength down the group. Second, there is an increase in $d\pi \rightarrow \sigma^*$ back-donation in the order Ru < Os < Fe, dppe < depe as judged by $\nu(N_2)$ frequencies of corresponding dinitrogen complexes $[M(N_2)(H)(depe)_2]^+$[15] and $[Fe(N_2)H(dppe)_2]^+$.[23]

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Supplementary Material Available: Spectral and analytical data, table of activation parameters and rates, and figures of observed and simulated ^1H NMR spectra for complexes **1Fe**, **2Fe**, **2Os**, and HD_2 isotopomers of **2Os** (7 pages). Ordering information is given on any current masthead page.

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Suicidal Inactivation of Iron Porphyrin Catalysts during Alk-1-ene Oxidation: Isolation of a New Type of *N*-Alkylporphyrins

Isabelle Artaud, Luc Devocelle, Jean-Paul Battioni,
Jean-Pierre Girault, and Daniel Mansuy*

Laboratoire de Chimie et Biochimie
Pharmacologiques et Toxicologiques
UA 400, 45 rue des Saints-Pères
75270 Paris Cêdex 06, France

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Presently, two model systems using an iron porphyrin catalyst and an iodosylarene as oxidant have been reported to mimic the suicidal inactivation of cytochrome P-450 with formation of *N*-alkylporphyrins[1] during oxidation of terminal alkenes.[2,3] Upon oxidation of alk-1-enes by the Fe(TDCPP)(Cl)[4]–C_6F_5IO system,[2] the *N*-alkylporphyrins isolated after acidic treatment had a *N*-CH_2CHOHR structure identical with that issued from experiments in vivo[1] (A_2 in Scheme I). *N*-alkylporphyrins were also formed upon oxidation of the alkenes reported to give green pigments in vivo, by the Fe(TPP or TpClPP)(Cl)[4]–PhIO system.[3]

This paper reports the isolation and structure determination of the *N*-alkylporphyrins formed by the latter system and shows that they derive from the binding of a pyrrole nitrogen to the more substituted carbon of the $RCH{=}CH_2$ alkene and not to the less substituted carbon as in the case of cytochrome P-450[1] or in the former model system.[2]

Upon reaction of but-1-ene in CH_2Cl_2 with Fe(TpClPP)(Cl)[4] (10 mM) and PhIO (35 equiv) at -10 °C, the starting catalyst was progressively transformed into a new complex **1** exhibiting a Soret peak at 447 nm and not well-defined bands around 570 and 674 nm.[3] After acidic demetalation,[3] a green porphyrin **2** exhibiting a UV-visible spectrum typical of *N*-alkylporphyrins[3] was obtained (60% yield based on the starting catalyst). Despite its great instability (as complex **1**), **2** could be studied by mass and ^1H NMR spectroscopy. From its mass spectrum (field desorption), which exhibits a molecular peak at *m/e* 838 corresponding to $TpClPPH_2 + C_4H_6O_2$ and two fragments at *m/e* 794 (M - CO_2) and 752 ($TpClPPH_2$), and its ^1H NMR spectrum,[5] which exhibits four signals for this chain at δ -1.2 (3 H), -2.13 (1 H), -2.66 (1 H), and -3.93 (1 H), the most probable structure for the *N*-alkyl chain was $N\text{-}CH(COOH)CH_2CH_3$. The latter structure was established by two sets of experiments. First, treatment of **2** by $CF_3SO_3CH_3$ in C_6H_6 led to the corresponding methyl ester **3**, the structure of which was definitely proved by comparison of its ^1H NMR and mass spectrum characteristics[6] with those of an authentic sample prepared by reaction of the diazo ester $N_2C(COOCH_3)C_2H_5$ with Zn(TpClPP) and demetalation of the obtained Zn-*N*-alkylporphyrin, according to a procedure described previously for other $N\text{-}CH(COOCH_3)R$ porphyrins[7]

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(4) TDCPP, TPP, and TpClPP are respectively used for the dianion of *meso*-tetrakis(2,6-dichlorophenyl)-, *meso*-tetraphenyl-, and *meso*-tetrakis-(parachlorophenyl)porphyrin.

(5) ^1H NMR of **2** ($Me_2SO\text{-}d_6$): *N*-alkyl chain $N\text{-}CH_c(COOH)\text{-}CH_aH_bCH_3$, H_c (-3.93), H_b (-2.66), H_a (-2.13) assigned thanks to double irradiation and 2D NMR (COSY 90) experiments. Porphyrin signals: pyrrole H, 8.93 (2 H, s), 8.74 and 8.49 (2 H), 8.6 and 8.56 (2 H), 7.57 and 7,49 (2 H) (3 AB systems, J = 4 Hz); ortho H, 8,15-8.42 (8 H, m); meta H, 8.08 (4 H, d, J = 8.5 Hz), 7,98 (4 H, d, J = 8.5 Hz).

(6) **3**: *N*-$[CH_c(COOCH_3)CH_aH_bCH_3]$TpClPPH; mass spectrum, *m/e* 853 (100, MH^+), 753 (92, $TpClPPH_2$ + **1**); ^1H NMR ($Me_2SO\text{-}d_6$) 1.97 (OCH_3,s), -1.21 (3 H, t, 7.5), -1.78 (H_a, m, $J_{H_aH_b}$ = 15 Hz), -2.36 (H_b, m), -3.96 (H_c, dd, $J_{H_cH_a}$ = 8, $J_{H_cH_b}$ = 3.5); meta H 7.96 (4 H, d, J = 8 Hz), 8.04 (4 H, d, J = 8 Hz); ortho H, 8,11-8.40 (8 H); pyrrole H: 8.93 (2 H, s), 8.72 and 8.5 (2 H), 8.62 and 8.57 (2 H), 7.64 and 7.54 (2 H) (3 AB systems, J = 4.5 Hz).

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