Notes

The Existence and Stability of Mononuclear and Binuclear Organopalladium Hydroxo Complexes, $[(R_3P)_2Pd(R')(OH)]$ and $[(R_3P)_2Pd_2(R')_2(\mu\text{-}OH)_2]$

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*Summary: Adding excess phosphines (Cy_3P, i-Pr_3P) to binuclear hydroxo complexes of palladium, $[(Cy_3P)_2Pd_2(Ph)_2(\mu\text{-}OH)_2]$ and $[(i\text{-}Pr_3P)_2Pd_2(Ph)_2(\mu\text{-}OH)_2]$, in hexane resulted in precipitation of the first mononuclear σ-phenylpalladium hydroxides, $[(Cy_3P)_2Pd(Ph)(OH)]$ (**1**) and $[(i\text{-}Pr_3P)_2Pd(Ph)(OH)]$ (**2**), respectively. Both **1** and **2** were isolated, characterized, and found to be stable in the solid state. In solution, however, they reversibly lost one of the two phosphine ligands, converting back to the binuclear hydroxides. Equilibrium between $[L_2Pd_2(R)_2(\mu\text{-}OH)_2]$ and $[L_2Pd(R)(OH)]$ ($L = Ph_3P$, Cy_3P, i-Pr_3P, and R = Ph, Me) was studied by variable-temperature ^{31}P NMR spectroscopy, and the corresponding K_{eq} and ΔG were calculated. The free energy values obtained at 333−235 K were in the range of +19 to −16 kJ/mol.*

Introduction

In recent years, there has been considerable interest in the chemistry of late transition metal hydroxo complexes, due to their remarkable reactivity and unusual catalytic and structural properties.[1−3] Various hydroxo compounds of the metals of the nickel triad have been reported, including organometallic complexes, which are of special interest because of their relevance to catalysis. A number of binuclear Ni,[4] Pd,[5] and Pt[6] organometallics with bridging hydroxo ligands have been synthesized and characterized. At the same time, mononuclear hydroxides, $[L_2M(R)(OH)]$, where L = tertiary phosphine and R = σ-organic ligand, are common only when M = Pt.[7] Their palladium congeners, $[L_2Pd(R)(OH)]$, are rare. Twenty years ago, Yoshida et al.[4b] described the synthesis of two hydroxo organopalladium complexes having perfluorinated and perchlorinated organic ligands, i.e., $[(Ph_3P)_2Pd(C_6F_5)(OH)]$ and $[(Ph_3P)_2Pd(CCl{=}CCl_2)(OH)]$. Analogous palladium complexes with conventional σ-organic ligands have not been reported, although the formation of $[(Ph_3P)_2Pd(Ph)(OH)]$ has been proposed in reactions of $[(Ph_3P)_2Pd(Ph)(I)]$ with KOH,[8] $[Bu_4N]^+OH^-$,[9] or $AgBF_4$, followed by hydrolysis.[9] However, this hydroxo complex was not isolated or reliably characterized in solution.

In this note, we report our preliminary results on the synthesis, isolation, and characterization of the first mononuclear σ-phenylpalladium hydroxides stabilized with bulky, electron-rich tertiary phosphines, $[L_2Pd(Ph)(OH)]$, where $L = Cy_3P$ and *i*-Pr_3P. We also communicate here our studies of the equilibrium between $[L_2Pd(R)(OH)]$ and $[L_2Pd_2(R)_2(\mu\text{-}OH)_2]$, where $L = Ph_3P$, Cy_3P, *i*-Pr_3P, and R = Ph, Me.

Results and Discussion

Adding tricyclohexylphosphine to solutions of $[(Cy_3P)_2Pd_2(Ph)_2(\mu\text{-}OH)_2]$[5d,8] in benzene, toluene, or hexane caused noticeable changes in the ^{31}P NMR spectrum of the samples. The intensity of the resonances at 38.0 and 36.3 ppm (6:1 due to the *trans* and *cis* isomers, respectively)[5d,8] diminished, and two new singlets arose at 10.2 and 22.2 ppm. The former was obviously due to the free phosphine, whereas the latter could be assigned to the new *mononuclear* hydroxo complex, $[(Cy_3P)_2Pd(Ph)(OH)]$. It was noticed that, as more phosphine was added, the new resonances at 10.2 and 22.2 ppm intensified in abundance and the peaks of the dimer became smaller. Similar observations were made when triisopropylphosphine was added to a hexane solution of $[(i\text{-}Pr_3P)_2Pd_2(Ph)_2(\mu\text{-}OH)_2]$. It is noteworthy that the triisopropylphosphine palladium hydroxo dimer is a new compound which was synthesized from $[(i\text{-}Pr_3P)_2PdCl_2]$,[10] iodobenzene, and alkali (See Experi-

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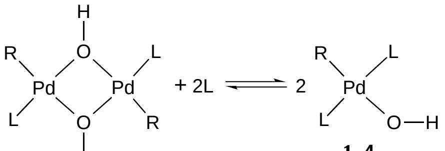
mental Section).[11] The above NMR experiments suggested that, in solution, the organopalladium hydroxo dimers were equilibrated with the corresponding monomers upon addition of free phosphine (eq 1).



1–4 (1)

1: L = Cy_3P, R = Ph
2: L = i-Pr_3P, R = Ph
3: L = Ph_3P, R = Ph
4: L = Ph_3P, R = Me

An attempt to isolate the new and novel mononuclear hydroxo complexes was a worthwhile goal. Treatment of $[(Cy_3P)_2Pd_2(Ph)_2(\mu\text{-}OH)_2]$[5d,8] in hexane with excess Cy_3P resulted in the formation and precipitation of $[(Cy_3P)_2Pd(Ph)(OH)]$ (**1**), which was isolated in 72% yield and found to be analytically and spectroscopically pure. As Tolman electronic parameters and cone angles for Cy_3P and i-Pr_3P are very close,[12] it seemed conceivable that $[(i\text{-}Pr_3P)_2Pd(Ph)(OH)]$ would be of comparable stability and perhaps isolable as well. When the triisopropylphosphine hydroxo dimer, $[(i\text{-}Pr_3P)_2Pd_2(Ph)_2(\mu\text{-}OH)_2]$, was treated with excess i-Pr_3P in hexane and the resulting solution was kept at −78 °C for a few hours, the desired complex, $[(i\text{-}Pr_3P)_2Pd(Ph)(OH)]$ (**2**) deposited as a crystalline solid which was successfully isolated. Both **1** and **2** are colorless compounds, which are quite air-stable in the solid state.[13] They were characterized by elemental analysis and ^{1}H and ^{31}P NMR spectral data. In the ^{1}H NMR spectra of freshly prepared samples of **1** and **2** in benzene-d_6, the OH resonances arose as sharp singlets at −3.2 and −3.3 ppm, respectively. Singlet resonances were also observed in the ^{31}P NMR spectra of the mononuclear organopalladium hydroxides, indicating that the complexes are of *trans* geometry.

In solution, equilibrium 1 established within minutes. In fact, the successful isolation of **1** and **2** was due to the presence of excess free phosphine which shifted equilibrium 1 toward the mononuclear species. When samples of **1** and **2** in benzene-d_6 or toluene-d_8 were prepared and immediately investigated by ambient-temperature ^{1}H and ^{31}P NMR, no traces of the dimers and free phosphines were detected. However, measuring the spectra of the same samples 10−15 min after they were prepared, revealed the presence of all three species, i.e., the monomer, the dimer, and the free ligand. All resonances appeared as sharp lines, suggesting that the direct and reverse processes were slow on the NMR time scale.

A similar approach was used in an effort to prepare $[(Ph_3P)_2Pd(R)(OH)]$ (R = Ph, Me) from the corresponding dimers and PPh_3. Although various temperatures and solvents were used, including pentane, hexane, benzene, toluene, dichloromethane, and chloroform, all attempts to isolate the monomeric hydroxides with triphenylphosphine ligands failed. No resonances that could be assigned to monomeric hydroxo species were observed in the ^{31}P NMR spectra when PPh_3 was added to solutions of $[(Ph_3P)_2Pd_2(R)_2(\mu\text{-}OH)_2]$ (R = Ph, Me) in benzene or toluene at room temperature. This observation was in line with the previously reported[8] reaction between $[(Ph_3P)_2Pd(Ph)(I)]$ in benzene with aqueous KOH in the presence of 18-crown-6, which gave $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}OH)_2]$, free triphenylphosphine, and no detectable mononuclear species. It is believed that the phase-transfer alkaline hydrolysis of $[(Ph_3P)_2Pd(Ph)(I)]$ led to $[(Ph_3P)_2Pd(Ph)(OH)]$ as the primary product, which quantitatively converted to the dimer upon facile elimination of PPh_3. Attempts to generate monomeric hydroxides from the triphenylphosphine hydroxo dimers and PPh_3 in hexane also failed, because of the very poor solubility of the binuclear complexes in saturated hydrocarbons. However, when dichloromethane was used as the solvent, both $[(Ph_3P)_2Pd(Ph)(OH)]$ (**3**; δ = 23.1 ppm) and $[(Ph_3P)_2Pd(Me)(OH)]$ (**4**; δ = 30.3 ppm) were detected by ^{31}P NMR spectroscopy. The ^{31}P NMR chemical shift of **3** is close to that (23.3 ppm in DMF) determined by Amatore et.al.[9] for the signal that arose upon addition of water to $[(Ph_3P)_2Pd(Ph)]^+ BF_4^-$ or when $[(Ph_3P)_2Pd(Ph)(I)]$ was treated with $[Bu_4N]^+ OH^-$.[14]

For **1** and **2**, equilibrium 1 was approached from both sides, whereas the significantly less stable triphenylphosphine derivatives **3** and **4**, which could not be isolated, were generated *in situ* by adding PPh_3 to dichloromethane solutions of the corresponding dimers. For all complexes **1**−**4**, the equilibrium was monitored by variable-temperature ^{31}P NMR spectroscopy. At each temperature, the systems were given enough time to establish equilibrium 1, so that the integral intensities measured could be used to compute equilibrium constants, K_{eq}. The ^{31}P NMR data, K_{eq}, and ΔG values obtained for eq 1 at various temperatures are presented in Table 1. As can be seen from Table 1, the ΔG values calculated for the formation of monomers vary in the range of ca. +20 to −15 kJ/mol, indicating that the monomeric organopalladium hydroxides are unstable species which are prone to dimerization via loss of phosphine. Negative ΔG values were observed for **1** and **2** at ambient and lower temperatures, whereas the triphenylphosphine complexes **3** and **4** exhibited positive free energies of formation over the whole range of temperatures from +18 to −38 °C. It is not surprising therefore that, unlike the Cy_3P and i-Pr_3P mononuclear hydroxides, their triphenylphosphine counterparts cannot be isolated as individual compounds.

From the above and literature[4−7] data it is clear that the equilibrium between $[L_2M(R)(OH)]$ and $[L_2M_2(R)_2(\mu\text{-}OH)_2]$, where M = Ni, Pd, Pt, is influenced by a number of factors, including the nature of M, R, L, and the solvent. For instance, $[(Ph_3P)_2Pd(C_6F_5)(OH)]$ is stable,[4b] whereas $[(Ph_3P)_2Pd(C_6H_5)(OH)]$ is not, readily losing triphenylphosphine and forming the dimer. This difference can be rationalized in terms of the strong electron-withdrawing effect of the pentafluorophenyl ligand, as compared to the phenyl. In the pentafluo-

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[11] In solution, the triisopropylphosphine binuclear hydroxo dimer, $[(i\text{-}Pr_3P)_2Pd_2(Ph)_2(\mu\text{-}OH)_2]$, exists as a 1:7 mixture of *cis* and *trans* isomers (see ^{1}H NMR data in the Experimental Section).

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[13] Even in the crystalline state, complex **2** loses i-Pr_3P, converting slowly to the corresponding dimer. This accounts for the unpleasant “phosphine odor” of **2** and the lower than anticipated values for both C and H obtained by combustion analysis of the complex (see Experimental Section).

[14] (a) It is worth noting that many square-planar σ-phenylpalladium(II) complexes, *trans*-$[(Ph_3P)_2Pd(Ph)(X)]$, exhibit very similar chemical shifts in solution ^{31}P NMR spectra.[14b] (b) Bartik, T.; Himmler, T. *J. Organomet. Chem.* **1985**, *293*, 343.

Table 1. ^{31}P NMR Data, K_{eq}, and ΔG Values for the System $[L_2Pd_2(R)_2(\mu\text{-}OH)_2] + 2L \rightleftharpoons 2[L_2Pd(R)(OH)]$

					^{31}P NMR chemical shifts, δ				
cmpd	L	R	solvent	T, K	dimer[a]	monomer	phosphine	K_{eq}	ΔG, kJ/mol
1	Cy_3P	Ph	benzene	291	38.0; 36.3	22.1	10.2	13	−6
			toluene	291	38.0; 36.3	22.2	10.2	8×10^{2}	−16
			toluene	333	37.8; 36.2	22.5	10.5	5×10^{-2}	+8
2	$i\text{-}Pr_3P$	Ph	hexane	245	49.2	32.1	19.0	4×10^{2}	−12
			hexane	275	48.9	32.2	19.4	10	−5
			hexane	291	48.7	32.2	19.8	5×10^{-1}	+2
			hexane	313	48.5	32.4	20.0	1×10^{-1}	+6
			hexane	333	48.2	32.6	20.3	8×10^{-3}	+13
3	Ph_3P	Ph	CH_2Cl_2	235	33.6; 33.0	23.1	−7.1	2×10^{-2}	+8
			CH_2Cl_2	255	33.6; 33.0	23.1	−6.7	1×10^{-2}	+10
			CH_2Cl_2	275	33.6; 33.0	23.2	−6.0	2×10^{-3}	+14
			CH_2Cl_2	291	33.6; 33.0	23.3	−5.5	4×10^{-4}	+19
4	Ph_3P	Me	CH_2Cl_2	235	39.6; 39.3	30.3	−6.8	7×10^{-2}	+5
			CH_2Cl_2	255	39.6; 39.3	30.1	−6.0	2×10^{-2}	+8
			CH_2Cl_2	275	39.5; 39.3	30.0	−5.5	2×10^{-3}	+14

[a] Two resonances are observed due to the *trans* and *cis* isomers. See refs 5d,f and 8.

rophenyl complex the metal center is more electron-deficient and hence should be more inclined to having two electron-donating phosphine ligands, rather than one, in the inner coordination sphere.

It is also clear that, in general, the tendency for complexes $[L_2M(R)(OH)]$ to dimerize with concomitant loss of phosphine increases in the order Pt < Pd < Ni. This is expected, as "softness" increases in going from Ni^{2+} to Pd^{2+} and further to Pt^{2+} ions and so does the affinity of the metal for soft ligands. In the dimers, each metal center has two hard hydroxo ligands and one soft phosphine, whereas in the monomers, the metal ion is bound to two soft phosphines and one hard hydroxide. Therefore, among the nickel triad metals, the hardest Ni^{2+} adopts the dimeric structure, whereas mononuclear hydroxides are preferably formed by the softest Pt^{2+}. The palladium ion is softer than Ni^{2+} and harder than Pt^{2+} and, therefore, capable of forming both binuclear and mononuclear hydroxides.

Our data suggest that equilibrium 1 is influenced by the nature of the tertiary phosphine. More studies are necessary before firm conclusions could be drawn concerning which of the two Tolman parameters (electronic and steric) governs the equilibrium. We believe that the relative stability of the mononuclear Cy_3P and $i\text{-}Pr_3P$ hydroxides may be more due to the large cone angles rather than enhanced basicity, as compared to those of triphenylphosphine. Very recently Driver and Hartwig[15] reported some reactions of $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}OH)_2]$, which were monitored by ^{31}P NMR spectroscopy, in the presence of $(o\text{-}CH_3C_6H_4)_3P$ as the *internal* standard. This certainly suggests that neither monomeric nor dimeric organopalladium hydroxo complexes with tri-*o*-tolylphosphine ligand ($\Theta > 190°$), if formed at all, were sufficiently stable to be observed by ^{31}P NMR techniques. Therefore, in order to stabilize mononuclear organopalladium hydroxides, $[L_2Pd(R)(OH)]$, where L = tertiary phosphine, optimal steric and electronic parameters for the L are required. The position of equilibrium 1 seems to be dependent on solvent. More experiments are needed to understand which solvents stabilize the mononuclear hydroxides. Unfortunately, a number of obstacles emerge making these studies difficult, if not impossible, in many cases. Some organopalladium hydroxo dimers are insufficiently soluble for NMR studies. For instance, the complexes $[(Ph_3P)_2Pd_2(R)_2(\mu\text{-}OH)_2]$ (R = Ph, Me) are insoluble in alkanes, acetone, alcohols, toluene, and ether and only slightly soluble in benzene at room temperature. On the other hand, polychlorinated solvents are not always inert toward basic and nucleophilic tertiary phosphines that participate in the equilibrium between mononuclear and binuclear organopalladium hydroxides.

It is worth mentioning that an attempt was made to synthesize a palladacarboxylic acid from the more stable $[(Cy_3P)_2Pd(Ph)(OH)]$ and CO in hexane and toluene, following the successful methodology reported for mononuclear platinum hydroxides.[16,17] Unfortunately, unlike the binuclear Pd hydroxides,[8] this mononuclear palladium hydroxo complex reacted with CO sluggishly at room temperature; the reaction led to a carbonyl phosphine Pd(0) cluster species, presumably $[(Cy_3P)_3Pd_3(CO)_3]$ (^{31}P NMR).[18] Carbonylation did occur, but the primary products of the reaction were unstable for isolation and detection, undergoing a series of fast β-elimination and/or reductive elimination processes. Similar experiments were conducted in the presence of excess Cy_3P, in hope that extra phosphine would stabilize primary carbonylation products, preventing them from decomposition. However, in the presence of an extra 2 equiv of Cy_3P, no reaction with CO was observed during 24 h at room temperature.

Experimental Section

A Varian XL 300 NMR spectrometer equipped with a temperature controller was used for measuring ^{1}H and ^{31}P NMR spectra. Combustion microanalysis was performed with a Perkin-Elmer 2400 Series II instrument. All chemicals were purchased from Aldrich Chemical Co. and Organometallics and were used as received. The organopalladium hydroxo dimers were synthesized as described in the literature.[5d,f,8]

$[(Cy_3P)_2Pd(Ph)(OH)]$ (1). Tricyclohexylphosphine (200 mg, 0.71 mmol) was added to a mixture of $[(Cy_3P)_2Pd_2(Ph)_2(\mu\text{-}OH)_2]$[8] (90 mg, 0.09 mmol) and oxygen-free hexane (6 mL), and the mixture was stirred under N_2 at 60 °C for 10 min. During that time, the dimer dissolved and the mononuclear hydroxo complex concomitantly precipitated. The mixture was stirred for 2 h at room temperature; the white solid was separated, washed with O_2-free hexane (3 × 2 mL), and dried

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under vacuum. The yield was 103 mg (72%). Anal. Calcd for $C_{42}H_{72}OP_2Pd$: C, 66.2; H, 9.5. Found: C, 65.9; H, 9.2. ^{1}H NMR (C_6D_6, 20 °C) δ: -3.2 (s, 1H, OH), 1.0−2.2 (m, 66H, C_6H_{11}), 6.9 (m, 1H, 4-C_6H_5), 7.1 (m, 2H, 3,5-C_6H_5), 7.7 (m, 2H, 2,6-C_6H_5). ^{31}P NMR (C_6D_6, 20 °C) δ: 22.2 (s).

[(*i*-Pr$_3$P)$_2$PdCl$_2$]. An O_2-free solution of triisopropylphosphine (2 mL, 1.64 g, 1 mmol) in EtOH (100 mL) was added dropwise to a vigorously stirred O_2-free solution of $Na_2[PdCl_4]$ obtained by dissolving $PdCl_2$ (0.6 g, 0.34 mmol) and NaCl (0.6 g, 1.03 mmol) in water (15 mL). The reaction mixture was worked up in air. Water (50 mL) was added, and the pale-yellow precipitate was filtered, washed with EtOH (50 mL), water (100 mL), and acetone (10 mL), and dried under vacuum. The yield was 1.62 g (96%). ^{1}H NMR ($CDCl_3$, 20 °C) δ: 1.4 (dd, 36H, $J_{H-H} = 7.1$ Hz; $J_{P-H} = 14.1$ Hz, CH_3), 2.8 (m, 6H, CH). ^{31}P NMR ($CDCl_3$, 20 °C) δ: 36.4 (s). This complex was originally prepared by the reaction between [(*i*-Pr$_3$P)$_3$Pd] and HCl.[10]

[(*i*-Pr$_3$P)$_2$Pd$_2$(Ph)$_2$(μ-OH)$_2$]. A mixture of [(*i*-Pr$_3$P)$_2$PdCl$_2$] (0.4 g, 0.8 mmol), iodobenzene (0.35 g, 1.3 mmol), benzene (6 mL), and a solution of KOH (2 g) in water (4 mL) was vigorously stirred under reflux (N_2) for 4 h. Benzene (5 mL) was added, the organic layer was separated and evaporated, and the residual oil was stirred with CH_2Cl_2 (4 mL) and 50% KOH (4 g) under N_2 for 3 h. The mixture was worked up in air. The organic layer was separated, filtered through cotton, and evaporated. The oily residue was dissolved in hexane (2 mL), and the solution was kept at −17 °C overnight. The colorless crystals were separated, washed with cold hexane, and dried under vacuum. The yield was 0.12 g (41%). Anal. Calcd for $C_{30}H_{54}O_2P_2Pd_2$: C, 49.9; H, 7.55. Found: C, 49.8; H, 7.45. ^{1}H NMR (C_6D_6, 20 °C) δ: -3.4 (br s, 0.12H, OH-*cis*), -1.8 (d, 1.76H, $J_{P-H} = 2.7$ Hz, OH-*trans*), -0.6 (br t, 0.12H, OH-*cis*), 1.0 (dd, 31.5H, $J_{H-H} = 7.2$ Hz, $J_{P-H} = 13.9$ Hz, CH_3-*trans*), 1.1 (dd, 4.5H, $J_{H-H} = 7.2$ Hz, $J_{P-H} = 13.8$ Hz, CH_3-*cis*), 2.2 (m, 6 H, CH), 6.9−7.2 (m, 6H, 3,4,5-C_6H_5), 7.6−7.9 (m, 4H, 2,6-C_6H_5). ^{31}P NMR (C_6D_6, 20 °C) δ: 48.7 (s).

[(*i*-Pr$_3$P)$_2$Pd(Ph)(OH)] (2). Triisopropylphosphine (50 μL, 0.26 mmol) was added under N_2 to an O_2-free solution of [(*i*-Pr$_3$P)$_2$Pd$_2$(Ph)$_2$(μ-OH)$_2$] (72 mg, 0.1 mmol) in hexane (3 mL). The resulting solution was kept first at −17 °C for 3 h and then at −78 °C for 5 h. The cold mother liquor was quickly removed by pipet from the precipitated well-shaped crystals which were washed with cold (−78 °C) pentane (2 × 1 mL), and dried under vacuum, first at −78 °C, and then at room temperature. The yield was 60 mg (58%). Anal. Calcd for $C_{24}H_{48}OP_2Pd$: C, 55.3; H, 9.3. Found: C, 54.4; H, 9.1.[13] ^{1}H NMR (C_6D_6, 20 °C) δ: -3.3 (s, 1H, OH), 1.2 (dd, 36H, $J_{H-H} = 7.1$ Hz, $J_{H-P} = 13.4$ Hz, CH_3), 2.2 (m, 6H, CH), 6.9 (m, 1H, 4-C_6H_5), 7.1 (m, 2H, 3,5-C_6H_5), 7.6 (m, 2H, 2,6-C_6H_5). ^{31}P NMR (C_6D_6, 20 °C) δ: 32.1 (s).

Variable-Temperature ^{31}P NMR Studies. The samples were prepared and run under nitrogen; 85% H_3PO_4 was used as an external standard (20 °C). A standard 5-mm NMR tube was charged with an oxygen-free solvent (See Table 1 for specifics; 0.7 mL), a hydroxo complex (**1**, **2,** or one of the dimers; 10−15 mg), and tertiary phosphine (if a dimer was used; ca. 2 mol equiv/equiv of the dimer). At each temperature, the samples were run several times with $D_1 = 1$ s, at intervals of 10−45 min, until identical integration ratios (within experimental reproducibility) were obtained for three measurements in a row. Once equilibrium 1 established, two more spectra were obtained with $D_1 = 3$ and 5 s. No changes in the integration ratio were noticed.

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