Supporting Information

Synthesis, characterization, and H/D exchange of μ-hydride-containing [FeFe]-hydrogenase subsite models formed by protonation reactions of (μ-TDT)$Fe_2(CO)_4(PMe_3)_2$ (TDT = SCH_2SCH_2S) with protic acids

Li-Cheng Song,*[1,2] An-Guo Zhu,[1,2] and Yuan-Qiang Guo[1,2]

[1]Department of Chemistry, State Key Laboratory of Elemento-Organic Chemistry,

[2]Collaborative Innovation Center of Chemical Science and Engineering (Tianjin)

Nankai University, Tianjin 300071, China

Contents:

Table S1 Selected bond lengths (Å) and angles (°) for **1**……page S3

Table S2 Selected bond lengths (Å) and angles (°) for **3–5**……page S3

Table S3 In situ ^{1}H NMR data of μ-H in complexes **2–7** taken after the 5 min protonation reactions of complex **1** with the corresponding acids…….. page S4

Table S4 In situ ^{31}P{^{1}H} NMR data of complexes **2–7** taken after the 5 min protonation reactions of complex **1** with the corresponding acids……page S5

Table S5 In situ ^{1}H NMR data of μ-H in complex **5** taken at time intervals during the protonation reactions of complex **1** with $HBF_4{\cdot}Et_2O$……page S6

Table S6 In situ ^{31}P{^{1}H} NMR data of complex **5** taken at time intervals during the protonation reactions of complex **1** with $HBF_4{\cdot}Et_2O$……page S7

Table S7 Selected bond lengths (Å) and angles (°) for **8**……page S7

Table S8 Crystal data and structure refinements details for **1**, **3**, and **4**……..page S8

Table S9 Crystal data and structure refinements details for **5** and **8**……...page S9

Fig. S1 In situ ^{1}H NMR spectra of μ-H in complexes **2–7** taken after the 5 min protonation reactions of complex **1** with the corresponding acids. ……..page S10

Fig. S2 In situ ^{31}P{^{1}H} NMR spectra of complexes **2–7** taken after the 5 min protonation reactions of complex **1** with the corresponding acids. ……page S10

Fig. S3 In situ ^{1}H NMR spectra of μ-H in complex **5** taken at time intervals during the protonation reactions of complex **1** with $HBF_4{\cdot}Et_2O$. ……page S11

Fig. S4 In situ ^{31}P{^{1}H} NMR spectra in complex **5** taken at time intervals during the protonation reactions of complex **1** with $HBF_4{\cdot}Et_2O$. ……....page S11

Discussion of the unsuccessful H/D exchange results ……..……page S12

Table S1 Selected bond lengths (Å) and angles (°) for **1**

Fe(1)–C(2)	1.750(4)	Fe(1)–S(1A)	2.2498(12)
Fe(1)–C(1)	1.758(4)	Fe(1)–Fe(1A)	2.5710(14)
Fe(1)–P(1)	2.2333(12)	S(1)–C(6)	1.831(4)
Fe(1)–S(1)	2.2481(12)	S(1A)–C(6)	1.709(4)
C(1)–Fe(1)–P(1)	96.15(13)	Fe(1)–S(1)–Fe(1A)	69.72(4)
C(1)–Fe(1)–S(1)	105.32(12)	S(1)–Fe(1)–S(1A)	85.65(4)
P(1)–Fe(1)–S(1)	89.50(5)	C(6)–S(1A)–C(6A)	99.4(2)
P(1)–Fe(1)–S(1A)	162.28(4)	C(3)–P(1)–Fe(1)	113.0(4)

Table S2 Selected bond lengths (Å) and angles (°) for **3–5**

3			
P(1)–C(3)	1.813(3)	S(1)–Fe(2)	2.2783(6)
P(1)–Fe(1)	2.2588(7)	Fe(1)–Fe(2)	2.5774(4)
S(1)–Fe(1)	2.2645(7)	Fe(1)–H(1)	1.6297
S(1)–Fe(1)–Fe(2)	55.687(17)	C(1)–S(1)–Fe(1)	113.05(9)
P(1)–Fe(1)–Fe(2)	109.72(2)	C(4)–P(1)–Fe(1)	114.57(10)
S(3)–Fe(1)–Fe(2)	55.083(17)	C(9)–Fe(1)–Fe(2)	112.64(7)
Fe(1)–S(1)–Fe(2)	69.13(2)	Fe(1) –Fe(2) –H	37.9
4			
P(1)-C(4)	1.786(5)	Fe(1)-C(1)	1.775(4)
P(1)-Fe(1)	2.2580(11)	Fe(1)-Fe(1A)	2.5799(10)
S(1)-Fe(1)	2.2536(11)	Fe(1)-H(1)	1.67(3)
S(1)-Fe(1)-Fe(1A)	55.85(3)	C(3)-S(1)-Fe(1)	111.4(3)
P(1)-Fe(1)-S(1)	165.75(4)	C(4)-P(1)-Fe(1)	114.7(2)
P(1)-Fe(1)-Fe(1A)	111.40(3)	C(1)-Fe(1)-Fe(1A)	141.66(16)
Fe(1)-S(1)-Fe(1A)	69.33(3)	Fe(1)-Fe(1A)-H	39.5(14)
5			
P(1)– C(3)	1.814(8)	S(1)–Fe(2)	2.306(16)
P(1)–Fe(1)	2.238(2)	Fe(1)–Fe(2)	2.5721(15)
S(1)–Fe(1)	2.258(17)	Fe(1)–H(1)	1.5810
S(1)–Fe(1)–Fe(2)	56.6(5)	C(2)–S(3)–Fe(1)	117.0(5)
P(1)–Fe(1)–Fe(2)	111.93(6)	C(3)–P(1)–Fe(1)	114.8(3)
S(3)–Fe(1)–Fe(2)	59.79(14)	C(9)–Fe(1)–Fe(2)	139.3(3)
Fe(1)–S(1)–Fe(2)	68.6(4)	Fe(1) –Fe(2)–H	35.5

Table S3. In situ ^{1}H NMR data of μ-H in complexes **2–7** taken after the 5 min protonation reactions of complex **1** with the corresponding acids

complex	spectral data/isomer assignment	molar ratio trans-ba/ba : cis-ba/ba : ap/ba
2	−15.02 (t, $J_{P\text{-}H}$ = 21.2 Hz)/trans-ba/ba	only trans-ba/ba
3	−15.00 (t, $J_{P\text{-}H}$ = 21.6 Hz)/trans-ba/ba −14.67 (t, $J_{P\text{-}H}$ = 20.0Hz)/cis-ba/ba −14.20 (d, $J_{P\text{-}H}$ = 22.0 Hz)/ap/ba	6.2 : 1.0 : 2.2
4	−15.02 (t, $J_{P\text{-}H}$ = 21.6 Hz)/trans-ba/ba −14.66 (t, $J_{P\text{-}H}$ = 20.4Hz)/cis-ba/ba −14.20 (d, $J_{P\text{-}H}$ = 22.0 Hz)/ap/ba	19.3 : 1.0 : 3.5
5	−15.02 (t, $J_{P\text{-}H}$ = 21.6 Hz)/trans-ba/ba −14.66 (t, $J_{P\text{-}H}$ = 19.6Hz)/cis-ba/ba −14.20 (d, $J_{P\text{-}H}$ = 22.0 Hz)/ap/ba	2.0 : 1.0 : 1.4
6	−15.03 (t, $J_{P\text{-}H}$ = 21.6 Hz)/trans-ba/ba −14.20 (d, $J_{P\text{-}H}$ = 22.0 Hz)/ap/ba	3.3 : 0 : 1.0
7	−15.03 (t, $J_{P\text{-}H}$ = 21.6 Hz)/trans-ba/ba −14.66 (t, $J_{P\text{-}H}$ = 19.6Hz)/cis-ba/ba −14.20 (d, $J_{P\text{-}H}$ = 22.0 Hz)/ap/ba	1.6 : 1.0 : 1.4

Table S4. In situ $^{31}P\{^{1}H\}$ NMR data of complexes **2–7** taken after the 5 min protonation reactions of complex **1** with the corresponding acids

complex	spectral data/isomer assignment	molar ratio trans-ba/ba : cis-ba/ba : ap/ba
2	21.10 (s)/trans-ba/ba	only trans-ba/ba
3	18.83 (s)/cis-ba/ba 21.08 (s)/trans-ba/ba 22.78(d, *J* = 7.8 Hz), 21.66 (d, *J* = 7.8 Hz)/ap/ba	2.4 : 0.5 : 1.0
4	18.79 (s)/cis-ba/ba 21.10 (s)/trans-ba/ba 22.75(d, *J* = 7.8 Hz), 21.63 (d, *J* = 7.8 Hz)/ap/ba	4.6 : 0.2 : 1.0
5	18.80 (s)/cis-ba/ba 21.10 (s)/trans-ba/ba 22.77(d, *J* = 7.8 Hz), 21.65 (d, *J* = 7.8 Hz)/ap/ba	1.1 : 0.5 : 1.0
6	21.05 (s)/trans-ba/ba 22.76 (d, *J* = 7.8 Hz), 21.60 (d, *J* = 7.8 Hz) ap/ba	2.6 : 0 : 1.0
7	18.79 (s)/cis-ba/ba 21.10 (s)/trans-ba/ba 22.75(d, *J* = 7.8 Hz), 21.63 (d, *J* = 7.8 Hz)/ap/ba	1.1 : 0.6 : 1.0

Table S5. In situ ^{1}H NMR data of μ-H in complex **5** taken at time intervals during the protonation reactions of complex **1** with $HBF_4{\cdot}Et_2O$

reaction time (min)	spectral data/isomer assignment	molar ratio trans-ba/ba : cis-ba/ba : ap/ba
5	–14.99 (t, $J_{P\text{-}H}$ = 21.6 Hz)/trans-ba/ba –14.63 (t, $J_{P\text{-}H}$ = 22.0 Hz)/cis-ba/ba –14.17 (d, $J_{P\text{-}H}$ = 22.0 Hz)/ap/ba	1.3 : 1.0: 1.2
15	–14.99 (t, $J_{P\text{-}H}$ = 21.6 Hz)/trans-ba/ba –14.63 (t, $J_{P\text{-}H}$ = 22.0 Hz)/cis-ba/ba –14.17 (d, $J_{P\text{-}H}$ = 22.0 Hz)/ap/ba	3.0 : 1.0 : 1.9
25	–14.99 (t, $J_{P\text{-}H}$ = 21.6 Hz)/trans-ba/ba –14.63 (t, $J_{P\text{-}H}$ = 22.0 Hz)/cis-ba/ba –14.17 (d, $J_{P\text{-}H}$ = 22.0 Hz)/ap/ba	7.5 : 1.0: 2.4
35	–14.99 (t, $J_{P\text{-}H}$ = 21.6 Hz)/trans-ba/ba –14.63 (t, $J_{P\text{-}H}$ = 22.0 Hz)/cis-ba/ba –14.17 (d, $J_{P\text{-}H}$ = 22.0 Hz)/ap/ba	15.3 : 1.0 : 2.4
45	–14.99 (t, $J_{P\text{-}H}$ = 21.6 Hz)/trans-ba/ba –14.63 (t, $J_{P\text{-}H}$ = 22.0 Hz)/cis-ba/ba –14.17 (d, $J_{P\text{-}H}$ = 22.0 Hz)/ap/ba	28.2 : 1.0 : 3.1
85	–14.99 (t, $J_{P\text{-}H}$ = 21.6 Hz)/trans-ba/ba	only trans-ba/ba

Table S6. In situ $^{31}P\{^{1}H\}$ NMR data of complex **5** taken at time intervals during the protonation reactions of complex **1** with $HBF_4{\cdot}Et_2O$

reaction time (min)	spectral data/isomer assignment	molar ratio trans-ba/ba : cis-ba/ba : ap/ba
5	18.80 (s)/cis-ba/ba 21.10 (s)/trans-ba/ba 22.75(d, *J* = 7.8 Hz), 21.63 (d, *J* = 7.8 Hz)/ap/ba	2.1 : 1.0 : 2.0
15	18.80 (s)/cis-ba/ba 21.10 (s)/trans-ba/ba 22.75(d, *J* = 7.8 Hz), 21.63 (d, *J* = 7.8 Hz)/ap/ba	3.1 : 0.82 : 2.0
25	18.80 (s)/cis-ba/ba 21.10 (s)/trans-ba/ba 22.75(d, *J* = 7.8 Hz), 21.63 (d, *J* = 7.8 Hz)/ap/ba	6.1 : 0.75 : 2.0
35	18.80 (s)/cis-ba/ba 21.10 (s)/trans-ba/ba 22.75(d, *J* = 7.8 Hz), 21.63 (d, *J* = 7.8 Hz)/ap/ba	11.5 : 0.76 : 2.0
45	18.80 (s)/cis-ba/ba 21.10 (s)/trans-ba/ba 22.75(d, *J* = 7.8 Hz), 21.63 (d, *J* = 7.8 Hz)/ap/ba	17.8 : 0.80 : 2.0
85	21.10 (s)/trans ba/ba	only trans-ba/ba

Table S7 Selected bond lengths (Å) and angles (°) for **8**

Fe(1)–C(2)	1.789(5)	Fe(1)–Fe(2)	2.5866(13)
Fe(1)–P(1)	2.2597(13)	S(1)–C(5)	1.838(4)
Fe(1)–S(1)	2.2681(12)	S(2)–C(6)	1.757(5)
Fe(1)–D	1.70(4)	Fe(2)–D	1.61(4)
C(1)–Fe(1)–P(1)	91.58(16)	Fe(1)–S(1)–Fe(2)	69.40(4)
C(1)–Fe(1)–S(1)	169.21(14)	P(1)–Fe(1)–D	87.0(14)
P(1)–Fe(1)–S(1)	88.40(5)	C(2)–Fe(1)–D	178.1(13)
P(1)–Fe(1)–S(3)	163.30(5)	Fe(1)–Fe(2)–D	39.9(14)

Table S8 Crystal data and structure refinements details for **1**, **3** and **4**

	1	**3**	**4**
Formula	$C_{12}H_{22}Fe_2O_4P_2S_3$	$C_{12}H_{23}ClFe_2O_8P_2S_3$	$C_{12}H_{23}F_6Fe_2O_4P_3S_3$
M_w	500.12	600.57	646.09
Cryst syst	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	P2(1)/n	C2/c
a (Å)	17.214(9)	13.1779(5)	20.742(3)
b (Å)	10.277(5)	8.7547(3)	8.9084(11)
c (Å)	12.324(6)	20.2242(7)	13.7249(17)
α (°)	90	90	90
β (°)	100.177(6)	103.3770(10)	103.040(2)
γ (°)	90	90	90
V (Å^3)	2145.9(19)	2269.93(14)	2470.6(5)
Z	4	4	4
Crystal size (mm)	0.18 × 0.16 × 0.10	0.18 × 0.17 × 0.15	0.46 × 0.34 × 0.30
D_c (g·cm^{-3})	1.548	1.757	1.737
μ (mm^{-1})	1.804	1.848	1.683
F(000)	1024	1224	1304
Reflns collected	5618	12755	6507
Reflns unique	1893	4001	2190
$\theta_{min/max}$ (°)	2.32/25.00	2.07/25.00	2.50/25.02
Final R	0.0315	0.0244	0.0404
Final R_W	0.0867	0.0582	0.1141
GOF on F^2	1.094	1.072	1.052
$\Delta\rho_{max/min}$ (e Å^{-3})	0.350/–0.303	0.520/–0.266	0.386/–0.440

Table S9 Crystal data and structure refinements details for **5** and **8**

	5	**8**
Formula	$C_{12}H_{23}BF_4Fe_2O_4P_2S_3$	$C_{13}H_{22}DF_3Fe_2O_7P_2S_4$
M_w	587.93	651.20
Cryst syst	Monoclinic	Monoclinic
Space group	P21/c	P2(1)/c
a (Å)	13.2814(7)	11.214(2)
b (Å)	17.4609(9)	18.025(4)
c (Å)	21.0295(9)	13.720(3)
α (°)	90	90
β (°)	111.970(2)	112.30(3)
γ (°)	90	90
V (Å^3)	4522.7(4)	2565.8(9)
Z	8	4
Crystal size (mm)	0.18 × 0.17 × 0.16	0.20 × 0.18 × 0.12
D_c (g cm^{-3})	1.727	1.686
μ (mm^{-1})	1.750	1.633
F(000)	2384	1324
Reflns collected	25853	25386
Reflns unique	7967	6063
$\theta_{min/max}$ (°)	1.57/25.01	2.26/27.85
Final R	0.0669	0.0624
Final R_W	0.1865	0.1845
GOF on F^2	0.925	1.096
$\Delta\rho_{max/min}$ (e Å^{-3})	1.926/–1.698	1.621/–0.661

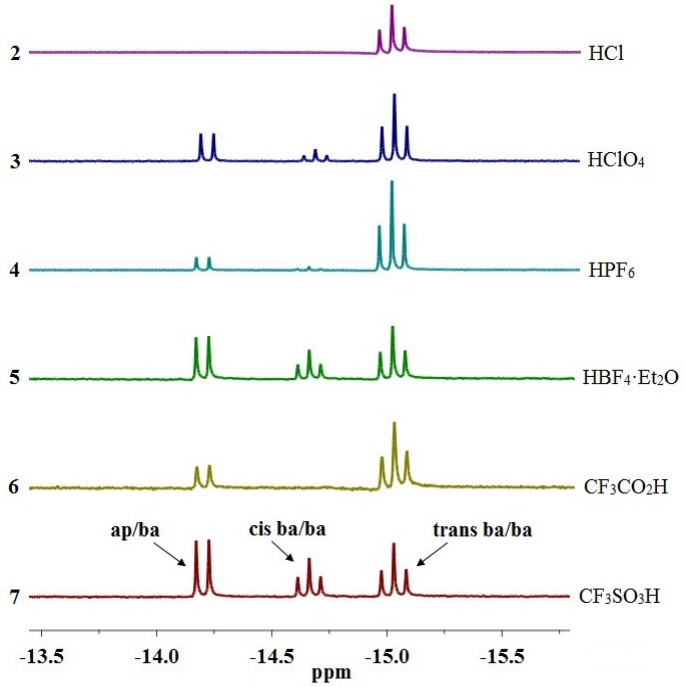

Fig. S1 In situ ^{1}H NMR spectra of μ-H in complexes **2–7** taken after the 5 min protonation reactions of complex **1** with the corresponding acids.

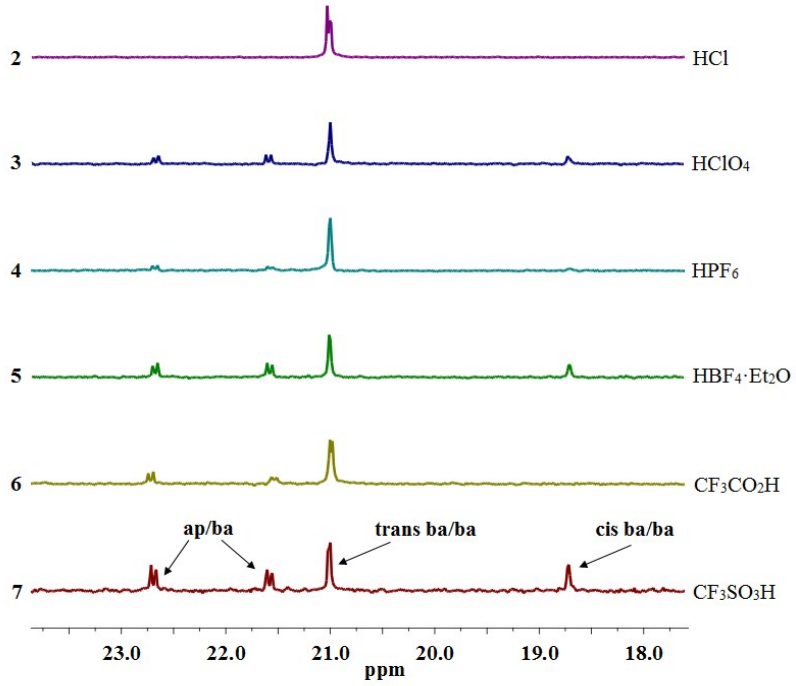

Fig. S2 In situ ^{31}P{^{1}H} NMR spectra of complexes **2–7** taken after the 5 min protonation reactions of complex **1** with the corresponding acids.

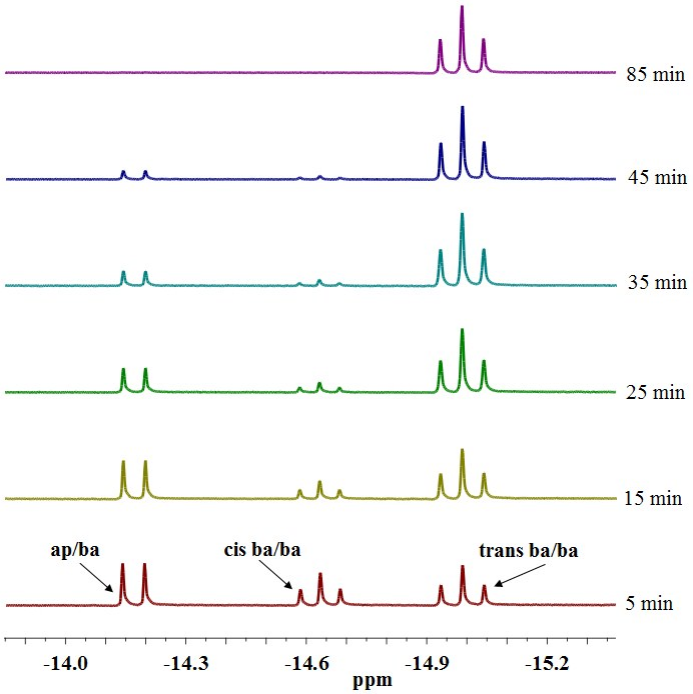

Fig. S3 In situ ^{1}H NMR spectra of μ-H in complex **5** taken at time intervals during the protonation reactions of complex **1** with $HBF_4 \cdot Et_2O$.

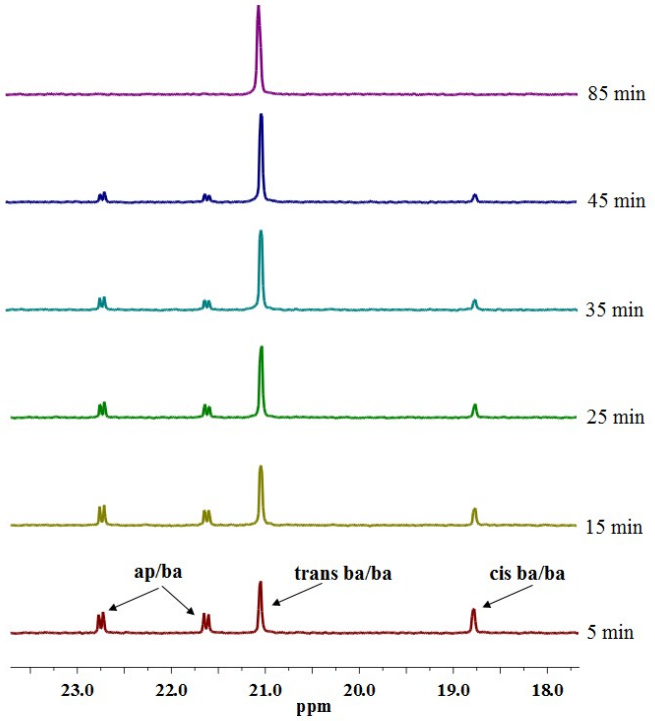

Fig. S4 In situ $^{31}P\{^{1}H\}$ NMR spectra in complex **5** taken at time intervals during the protonation reactions of complex **1** with $HBF_4 \cdot Et_2O$.

Discussion of the unsuccessful H/D exchange results

(i) Attempted H/D exchange between **7** and D_2

As described in Experimental Section, the H/D exchange reaction of complex **7** with D_2 was carried out at room temperature in a J-Young NMR tube containing a CD_2Cl_2 (for ^1H NMR determination) or CH_2Cl_2 (for ^2H NMR determination) solution of complex **7** and filled with D_2 pressured to 2 bar. Unfortunately, after the reaction system was exposured to ambient laboratory light for 3 days or left in the dark for 3 days, the in situ ^1H and ^2H NMR spectra proved that the H/D exchange reaction between **7** and D_2 did not occur under such conditions. This is because the ^1H NMR signal for the expected H/D exchange product HD (δ_H: a triplet at 4.57 ppm with $J_{D\text{-}H}$ = 42.51 Hz, see: D. Sellmann and A. Fürsattel, *Angew. Chem. Int. Ed.*, 1999, **38**, 2023-2026) or the ^2H NMR signal for the expected H/D exchange product **8** ($\delta_{\mu\text{-}D}$: a triplet at −14.33 ppm with $J_{P\text{-}D}$ = 3.23 Hz) was not observed.

(ii) Attempted H/D exchange between **7** and D_2O

Similarly, the study on the H/D exchange reaction between **7** and D_2O was carried out at room temperature in an NMR tube containing an acetone-d_6 (for ^1H NMR determination) or acetone (for ^2H NMR determination) solution of complex **7** and excess D_2O under irradiation of ambient laboratory light for 3 days or in the dark for 3 days. The in situ ^2H NMR spectra demonstrated that the H/D exchange reaction of **7** with D_2O could not occur also under such conditions, since no ^2H NMR signal for the expected μ-deuterium complex **8** ($\delta_{\mu\text{-}D}$: a triplet at −14.33 ppm with $J_{P\text{-}D}$ = 3.23 Hz) was observed.