The Role of Non-Covalent Interactions in the Reactions between Palladium Hydrido Complex with Amidoarylphosphine Pincer Ligand and Brønsted Acids

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Supplementary Materials

Table S1. Key spectral parameters of (PNP)PdH (**1**) in toluene-d_8

		ν_{PdH}, cm^{-1}		δ_{PdH}, ppm		δ_P, ppm	
	T, K	295	190	295	190	295	190
(PNP)PdH		1923	1928	-10.42	-10.18	59.1	58.3

Table S2. Key spectral parameters of palladium complexes formed by the interaction of **1** with acids. Toluene-d_8, 295 K.

Acids (AH)		**FA**	**TfOH**	**H[BF_4]**	**PFTB**	**HFIP**	**TFE**
	pK_a(MeCN)	20.9	0.7		20.5		
	pK_a(DMSO)				10.7	17.9	23.5
	pK_a(DMF)	18.9 [1]		3.4 [2]			
(PNP)PdH···HA	ν_{PdH}, cm^{-1}	1917				1926[#]	1924[#]
	δ_{PdH}, ppm	-10.43				-10.46[#]	-10.66
		-10.26[#]	–	–	–		
	δ_P, ppm	59.0				58.0[#]	58.9
		57.9[#]					
$[(PN(H)P)PdH]^+[A]^-$	ν_{PdH}, cm^{-1}	1994	1991[*]	1992[*]	1994[#]	1998[#]	
	ν_{NH}, cm^{-1}		2811[*]	[&]	2806[#]	[&]	
	δ_{PdH}, ppm	-11.95[#]	-12.04[*]	-12.12	[&]	-12.33[#]	–
	δ_{NH}, ppm	10.75[#]	10.41[*]	9.53	[&]	[&]	
	δ_P, ppm	55.9[#]	56.7[*]	56.9	[&]	54.3[#]	
$[(PN(H)P)PdH]^+$·AH	ν_{PdH}, cm^{-1}				2013[**]	2015[**]	2009[**]
	δ_{PdH}, ppm				[&]	-12.26[**]	[&]
	δ_{NH}, ppm	–	–	–	[&]	7.07[**]	[&]
	δ_P, ppm				[&]	55.8[**]	[&]
(PNP)Pd-A	δ_P, ppm		53.1[*]	–	–	–	–

[*] in benzene-d_6; [**] in neat alcohol; [#] at 190 K; [&] no data; – complex hasn't been detected.

1. Brian G. Cox. Acids and bases. Solvent effects on acid–base strength. OUP Oxford 2013
2. V. Fourmond, P. A. Jacques, M. Fontecave, V. Artero*, Inorg. Chem.* **2010**, *49*, 10338–10347

Table S3. DFT calculated frequencies of PdH stretching vibrations and formation energies [a] of **1** and its bimolecular complexes with TFE in toluene.

	1	**MH···HO**	**N···HO**
ν_{PdH}, cm^{-1}	2064	2030	2083
A_{PdH}, $km{\cdot}mol^{-1}$	401	382	377
$\Delta\nu_{PdH}$, cm^{-1}		-34	+18
ΔE, $kcal{\cdot}mol^{-1}$		-9.5	-9.0
ΔG, $kcal{\cdot}mol^{-1}$		+2.5	+5.7

[a] Relative to isolated reactants.

Table S4. DFT calculated frequencies of PdH stretching vibrations and formation energies [a] of **2** and its non-covalent adducts with pyridine and TFE.

	2	**NH···Py**	**MH···HO**	**NH···O**	**2**·2TFE
ν_{PdH}, cm^{-1}	2099	2108	2135	2108	2113
A_{PdH}, $km \cdot mol^{-1}$	210	221	185	221	186
$\Delta\nu_{PdH}$, cm^{-1}		9	36	9	14
ΔE, $kcal \cdot mol^{-1}$		-12.0	-7.2	-6.9	-18.5
ΔG, $kcal \cdot mol^{-1}$		+0.4	+5.0	+4.0	+7.8

[a] Relative to isolated reactants.

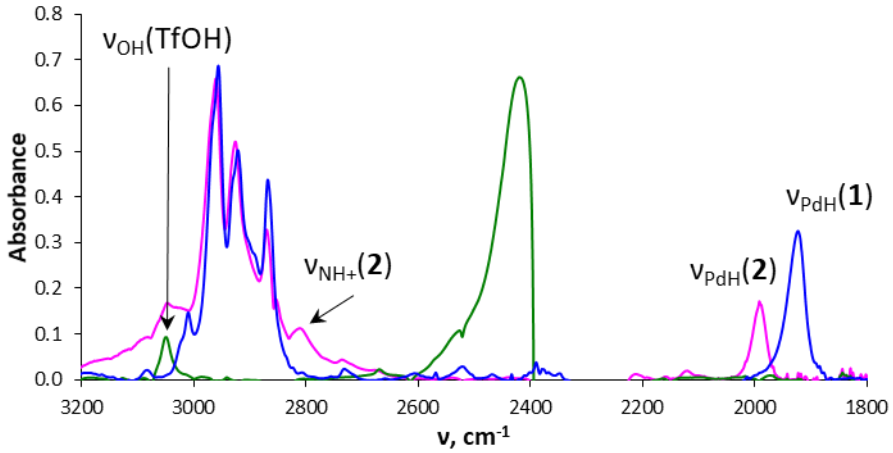


Figure S1. IR spectra of (PNP)PdH (c = 0.02 M) (blue), TfOH (c = 0.022 M) (green) and their 1:1.1 equiv. mixture (purple) in toluene-d_8 at 295 K, l = 0.1 cm.

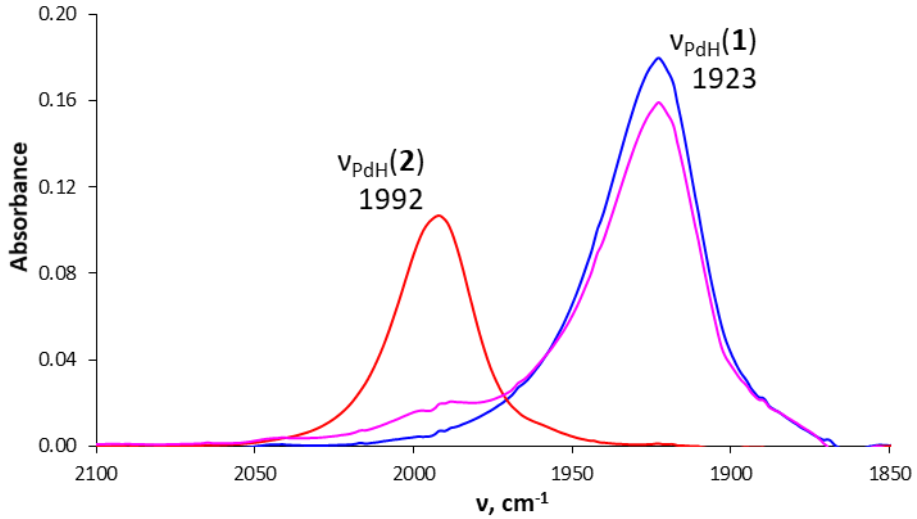


Figure S2. IR spectra of (PNP)PdH (c = 0.02 M) (blue), with 1 equivalent of $H[BF_4]\cdot Et_2O$ (c = 0.02 M) (red) and their 1:1:1 equiv. mixture with pyridine (purple, residual ν_{PdH}^{NH+} at 1992 cm^{-1} is because of inaccuracy of addition) in benzene-d_6 at 295 K, l = 0.1 cm.

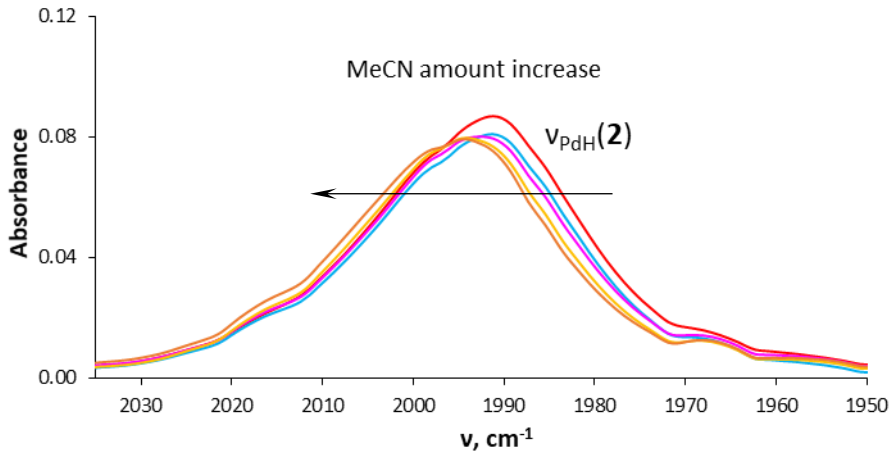


Figure S3. IR spectra of ν_{PdH} stretching vibrations region of $[(PN(H)P)PdH]^+[BF_4]^-$ (c = 0.02 M) (red), with 5 (sky blue), 20 (purple), 50 (yellow) and 100 (orange) equiv. MeCN in benzene-d_6, 295 K, l = 0.1 cm.

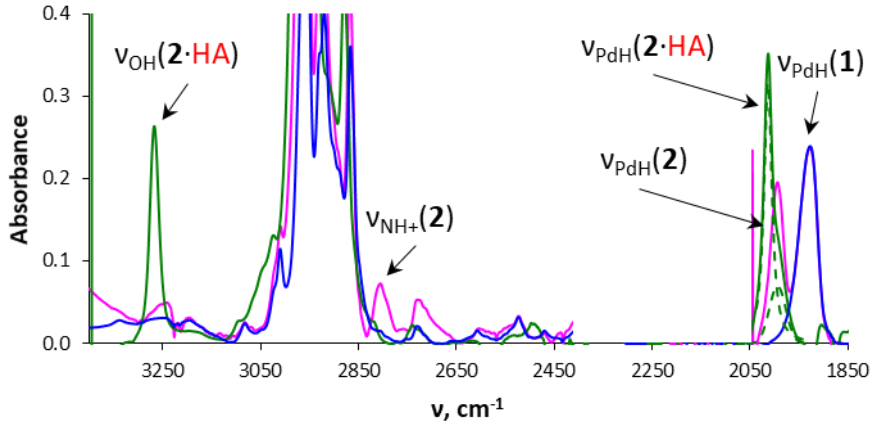


Figure S4. IR spectra in the PdH stretching vibrations region of (PNP)PdH at 190 K (c = 0.032 M in toluene-d_8; blue, normalized intensity*), with 5 equiv. PFTB in toluene-d_8 at 190 K (purple) and in neat PFTB at 295 K (c = 0.032 M; green). Green dashed lines show the result of the band deconvolution.
* - Intensity of initial ν_{PdH}(**1**) was normalized by multiplication to make it coincide with the intensity in the maximum point (1928 cm^{-1}) of ν_{PdH} observed in **1**/PFTB mixture.

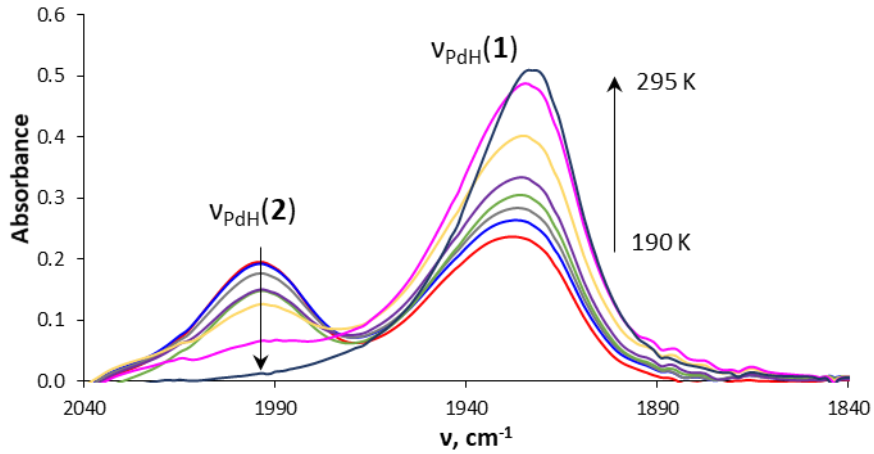


Figure S5. IR spectra of ν_{CO} stretching vibrations region of (PNP)PdH (c = 0.032 M) with 5 equiv. PFTB (c = 0.16 M) in toluene-d_8 at 190-295 K, l = 0.1 cm.

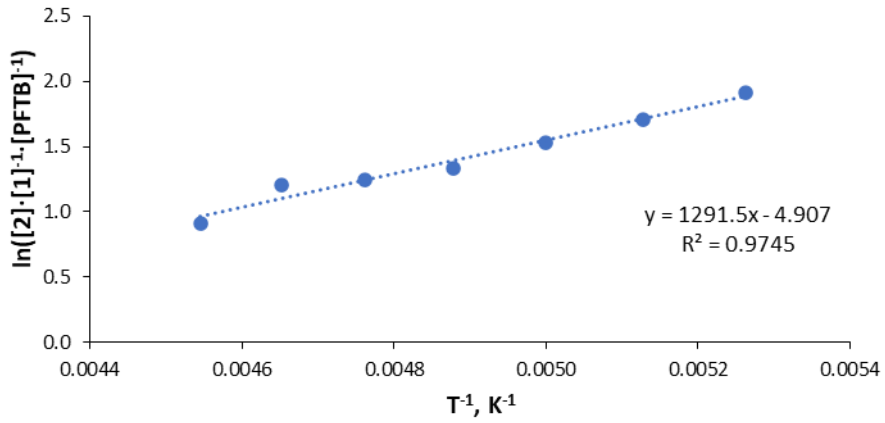


Figure S6. The temperature dependence of equilibrium constant for **1** + PFTB ↔ **2[OC(CF$_3$)$_3$]** in toluene-d_8.

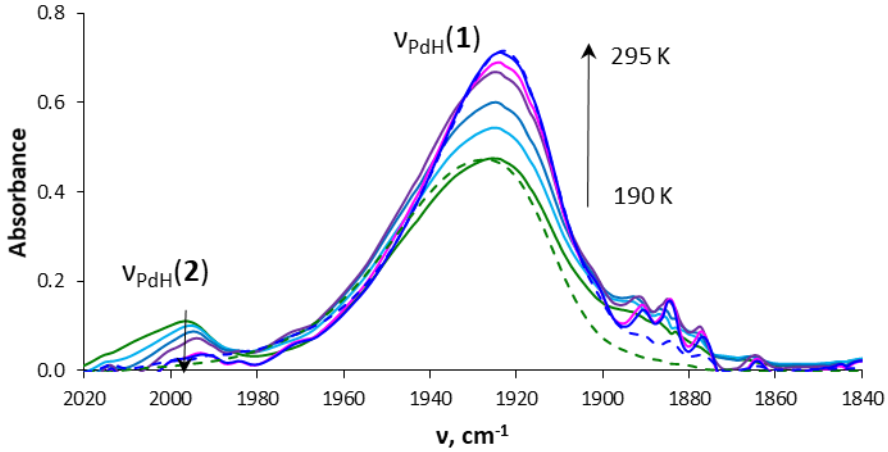


Figure S7. IR spectra of ν_{PdH} stretching vibrations region of (PNP)PdH (*c* = 0.0262 M) (dashed) and with 4 equiv. HFIP (c = 0.105 M) in toluene-d_8 at 190-295 K, l = 0.2 cm.

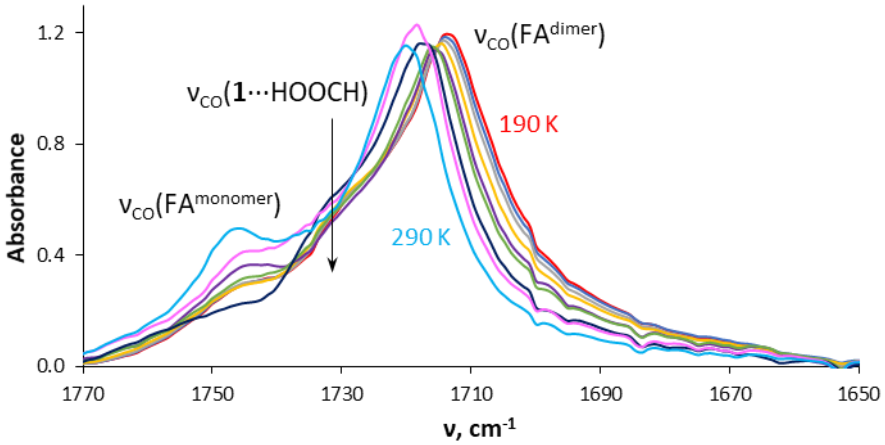


Figure S8. IR spectra of ν_{CO} stretching vibrations region of HCOOH (c = 0.12 M) with 0.5 equiv. (PNP)PdH (c = 0.06 M) in toluene at 190 - 290 K, l = 0.05 cm.

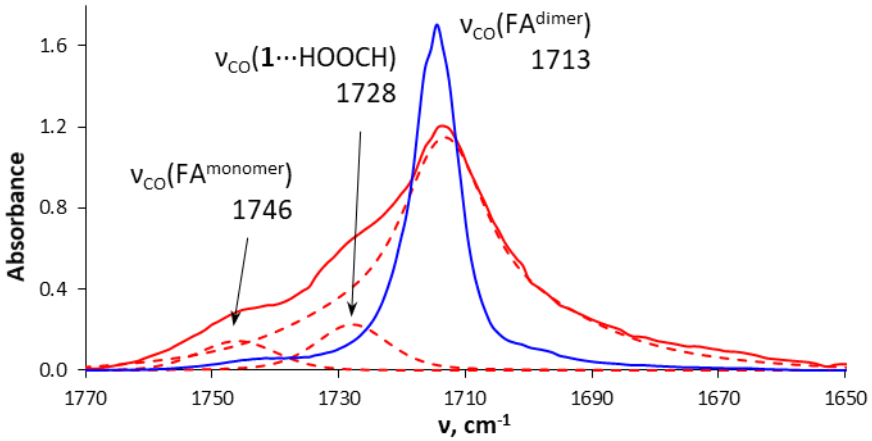


Figure S9. IR spectra of ν_{CO} stretching vibrations region of HCOOH (c = 0.12 M) (blue) and with 0.5 equiv. (PNP)PdH (c = 0.06 M) in toluene at 190 K (red, dashed lines are the result of band deconvolution), l = 0.05 cm.

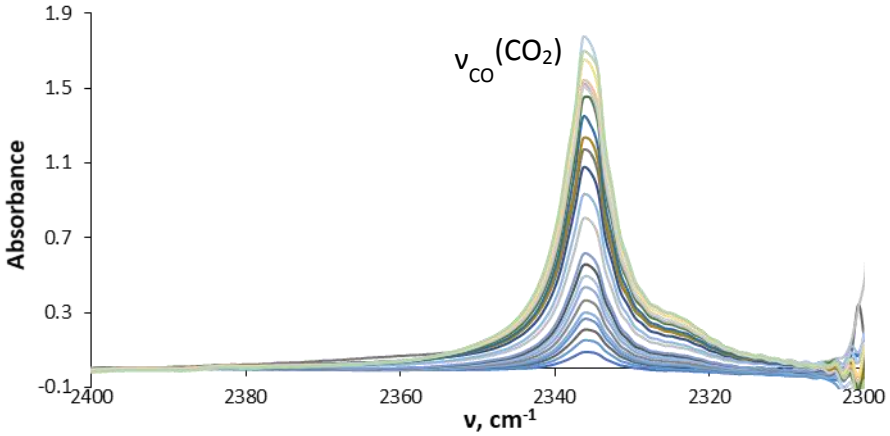


Figure S10. IR spectra of ν_{CO} stretching vibrations region of CO_2 evolved from HCOOH (c = 0.04 M) with 0.5 equiv. (PNP)PdH (c = 0.02 M) in toluene-d_8 at 295 K, t = 80-10000 s, l = 0.1 cm.

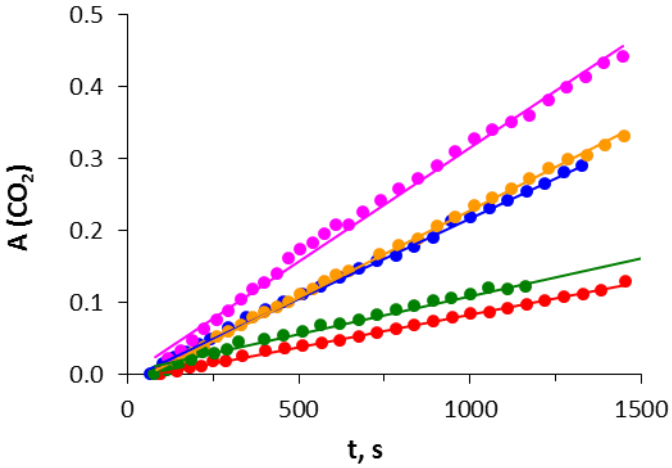


Figure S11. Kinetics of CO_2 evolution from formic acid, monitored by change of ν_{CO2} band intensity for the mixture of (PNP)PdH (*c* = 0.02 M) with 0.5 (blue), 1 (orange), 2 (purple), 5 (red) and 10 (green) equiv. HCOOH. 295 K, toluene-d_8.

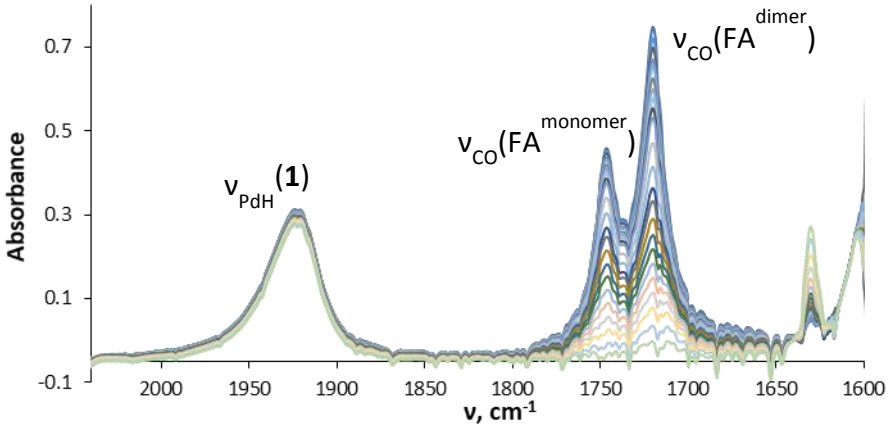


Figure S12. IR spectra of ν_{PdH} of (PNP)PdH (c = 0.02 M) and ν_{CO} of HCOOH (c = 0.04 M) stretching vibrations regions in toluene-d_8 at 295 K, t = 80-10000 s, l = 0.1 cm.

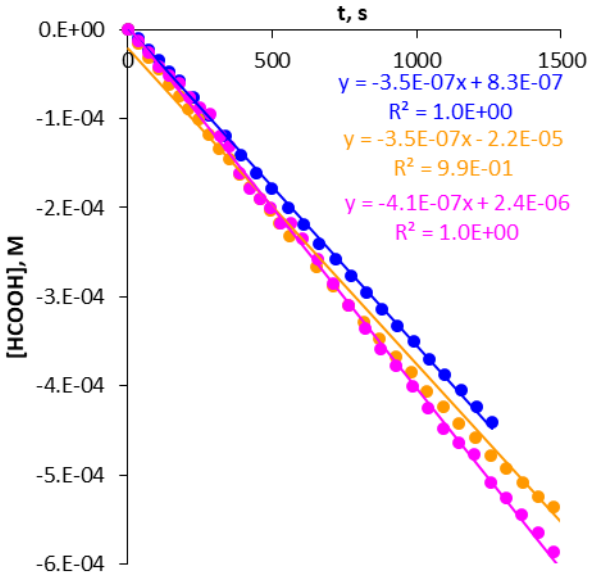


Figure S13. Kinetics of formic acid decomposition monitored by change of $\nu_{CO}(FA^{monomer})$ band intensity for the mixture of (PNP)PdH (*c* = 0.02 M) with 0.5 (blue), 1 (orange) and 2 (purple) equiv. HCOOH. 295 K, toluene-d_8.

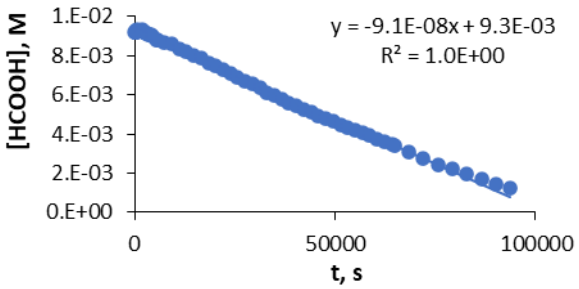


Figure S14. Kinetics of formic acid decomposition, monitored by change of $\nu_{CO}(FA^{monomer})$ band intensity for the mixture of (PNP)PdH (*c* = 0.02 M) with 5 equiv. HCOOH. 295 K, toluene-d_8.

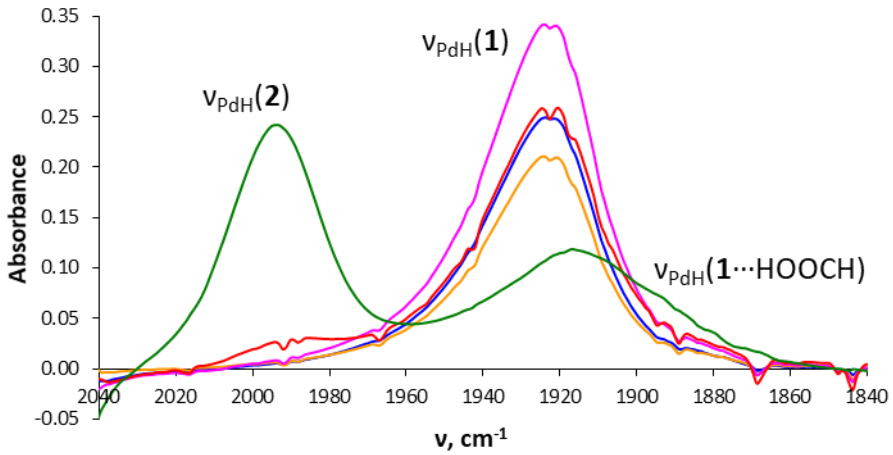


Figure S15. IR spectra in the ν_{PdH} stretching vibrations region of (PNP)PdH (c(**1**) = 0.02 M) in the presence of 0.5 (blue), 1 (orange), 2 (purple), 5 (red) and 10 (green) equiv. HCOOH measured in 150 s after mixing. 295 K, toluene-d_8, l = 0.1 cm.

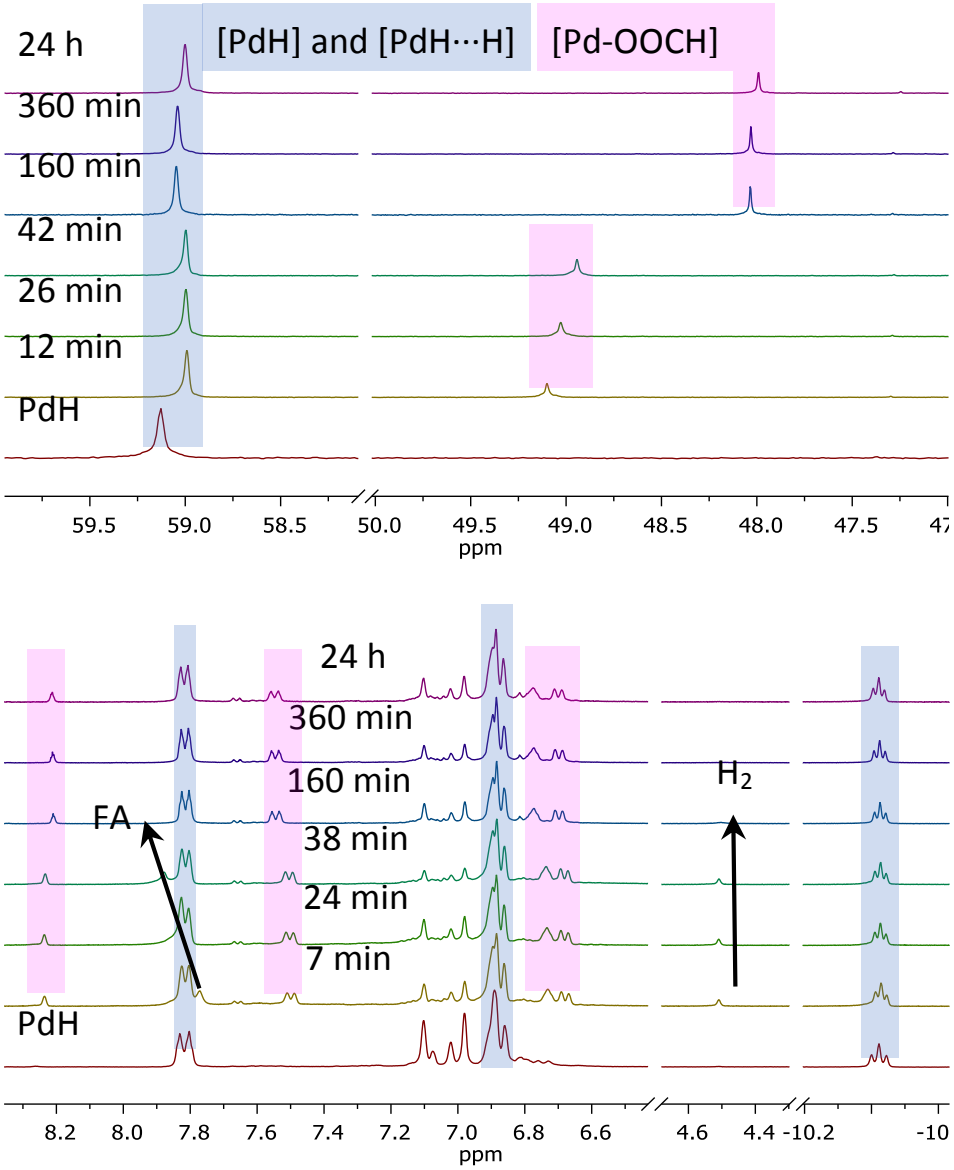
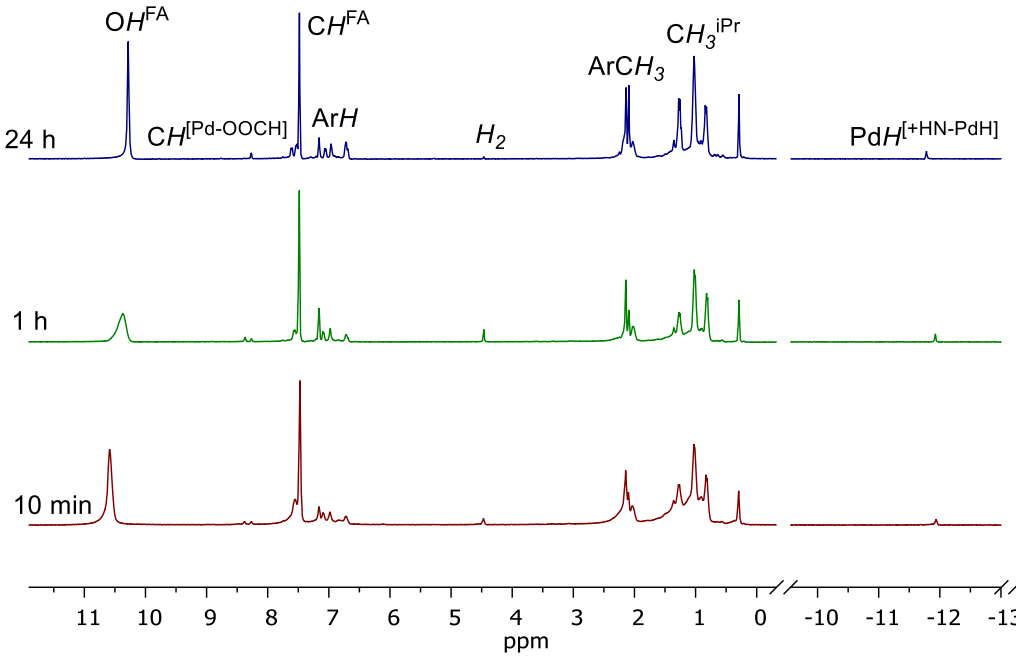
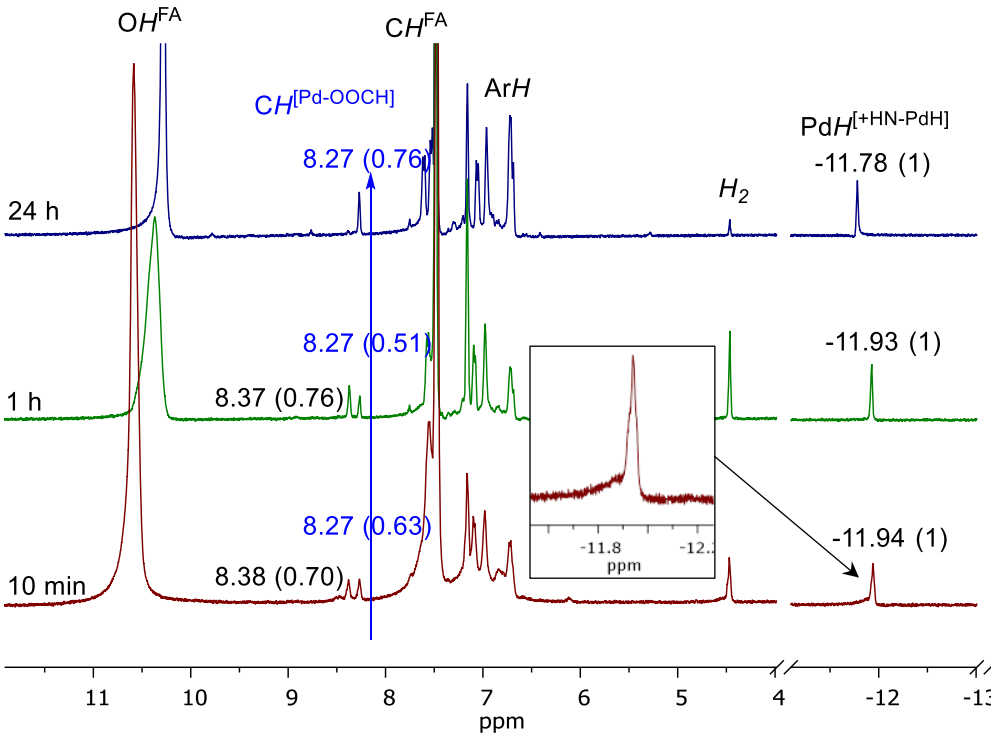


Figure S16. $^{31}P\{^1H\}$ (161.94 MHz; at the top) and ^1H (400.01 MHz; in the bottom) NMR monitoring of (PNP)PdH (c = 0.04 M) with 2 equiv. HCOOH (c = 0.08 M) in toluene-d_8, 295 K.


OH^FA
CH^FA
CH3^iPr
ArCH3
24 h
CH^[Pd-OOCH]
ArH
H2
PdH^[+HN-PdH]
1 h
10 min
11 10 9 8 7 6 5 4 3 2 1 0 -10 -11 -12 -13
ppm


OH^FA
CH^FA
CH^[Pd-OOCH]
ArH
PdH^[+HN-PdH]
8.27 (0.76)
-11.78 (1)
H2
24 h
8.27 (0.51)
-11.93 (1)
1 h
8.37 (0.76)
8.27 (0.63)
-11.94 (1)
10 min
8.38 (0.70)
-11.8
ppm
11 10 9 8 7 6 5 4 -12 -13
ppm

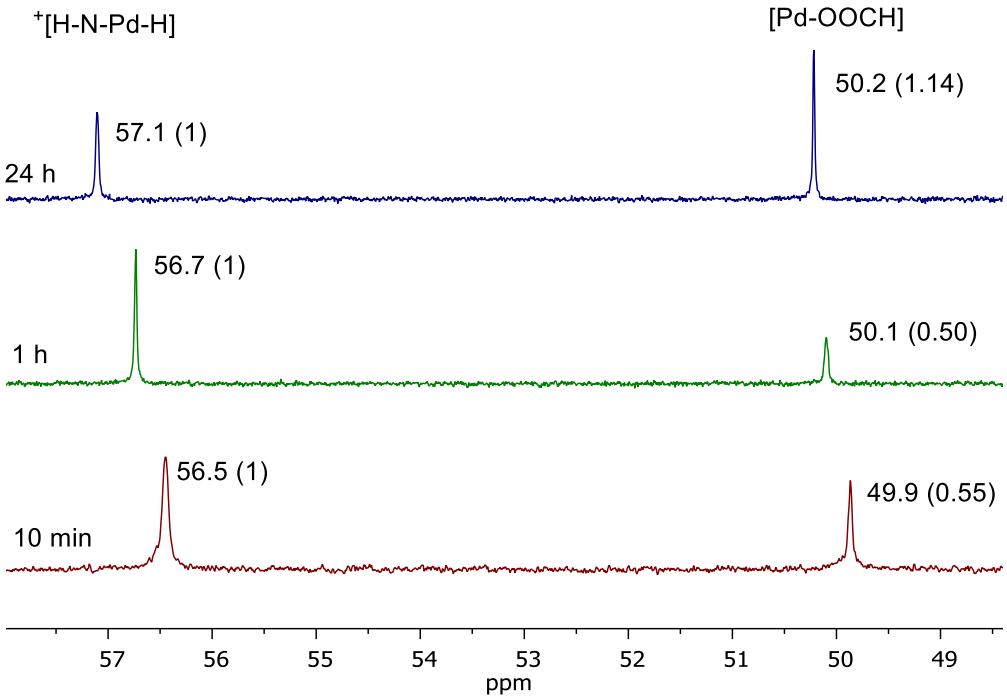


Figure S17. $^{31}P\{^{1}H\}$ (161.94 MHz; at the top) and ^{1}H (400.01 MHz; in the bottom) NMR monitoring of (PNP)PdH (c = 0.03 M) with 10 equiv. HCOOH (c = 0.3 M) in benzene-d_6, 295 K.