Supplementary Information for:

Combined DFT protocol for calculation of ^{31}P NMR Shifts in Platinum complexes

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Table of contents **pages**

Calculational details

Non relativistic quantum chemical calculations were carried out within the frame-work of the generalized Kohn Sham density functional theory [1], with the Gaussian 16 [2] (Revision A.03) software packages by using a number of functionals (PBE0 [3], PBE [4-5], PBE50 [6], wB97XD [7]) and families of basis sets (Pople's [8-15], Dunning's [16-17], Jensen's [18-20]). To take into account dispersion interactions D3 version of Grimme's dispersion were used [21]. For the Pt center, the quasi-relativistic Stuttgart–Dresden ECP60MWB was used with corresponding (8s7p6d)/(6s5p3d) GTO valence basis set [22] (denoted as "SDD"), mDZP [23], def2-TZVPD [24], SARC-ZORA [25] and NMR-DKH (TZ2P) [26] basis sets. Wherever possible, geometry optimization was started from an X-ray structure. For most of the complexes, the calculations were carried out for all possible conformers/isomers, and results for the lowest energy forms were used in the analysis. To take into account the medium effects, calculations were carried out in the framework of the Polarizable Continuum Model [27] (denoted as "PCM") with the same solvent as that used in NMR experiments. ^{31}P NMR shifts were calculated by the GIAO method [28]. All ^{31}P data were referenced to H_3PO_4, which was calculated under the same conditions.

Fully relativistic DFT ^{31}P NMR shifts calculations have been carried out at the matrix Dirac-Kohn-Sham (mDKS) level [29] with the ReSpect-MAG code [30]. The four-component mDKS calculations have been done with PBE0 functional. The uncontracted Dyall valence double-ζ basis set [31] was used for the Pt center. For ligand atoms two locally dense basis sets (LDBS) schemes [32-35] were used: 1) the Dunning's triple-ζ quality basis sets (ucc-pVTZ) on spectator atoms and atoms vicinal to Pt center and double-ζ quality basis sets (ucc-pVDZ) [16-17, 36] on the remaining atoms were applied (de-noted as "TZ_DZ"); 2) the Dunning's triple-ζ quality basis sets (ucc-pVTZ) on spectator atoms and atoms vicinal to Pt center, double-ζ quality basis sets (ucc-pVDZ) on the next layer and unpolarized Jensen basis set (upc-0) [18-20, 37] on the remaining atoms were applied (denoted as "TZ_DZ_UPC").

The mDZP, def2-TZVPD, SARC-ZORA and NMR-DKH (TZ2P) basis sets were downloaded from the EMSL basis set library for the Gaussian package [38-40].

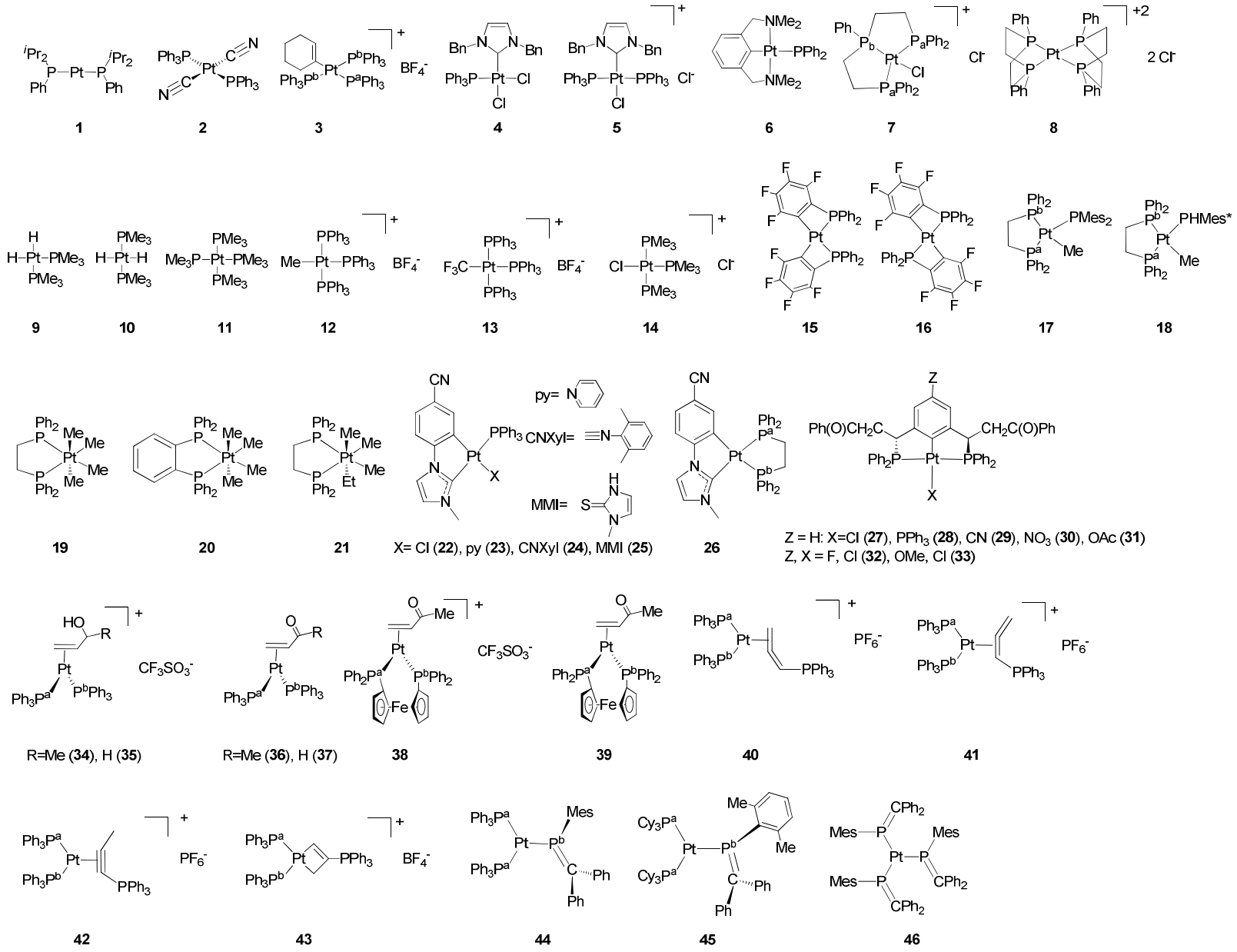

Figure S1a. Model Pt σ-complexes **1-46** (Mes = 1,3,5-trimethylbenzene, Mes* = 1,3,5-tri-*tert*-butylbenzene, Xyl = 2,6-dimethylphenyl, Bn = Benzyl, Cy = Cyclohexyl).

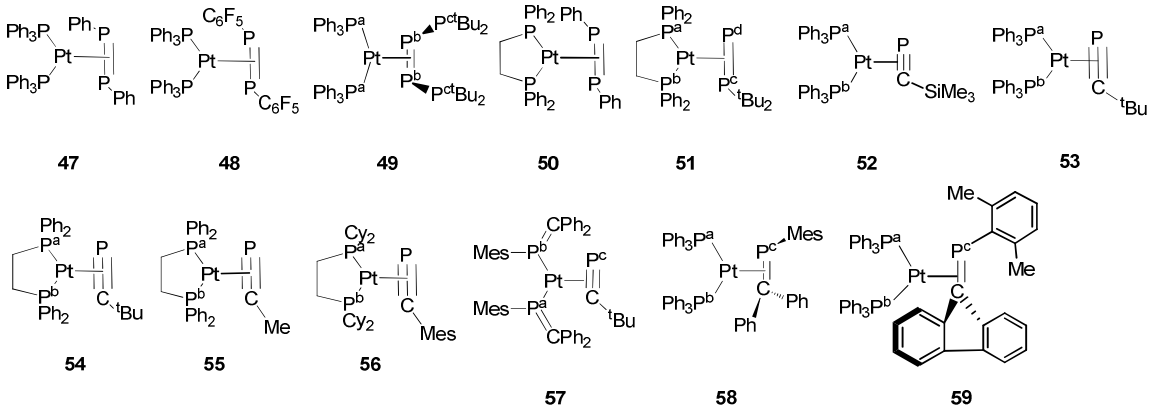

Figure S1b Model Pt π-complexes **47-59** (Mes = 1,3,5-trimethylbenzene, Mes* = 1,3,5-tri-*tert*-butylbenzene, Xyl = 2,6-dimethylphenyl, Bn = Benzyl, Cy = Cyclohexyl).

Table S1. Experimental and calculated ^{31}P NMR shifts (ppm) for all model Pt complexes **1-59.**

Complex	Atom	Experimental	Calculated						Reference
			PBE0/{6-311G(2d,2p); Pt(SDD)}// PBE0/{6-31+G(d); Pt(SDD)}	4c-mDKS/TZ_DZ// PBE0/{6-31+G(d); Pt(SDD)}	PBE0/{6-311G(2d,2p); Pt(SDD)} (PCM)// PBE0/{6-31+G(d); Pt(SDD)} (PCM)	4c-mDKS/TZ_DZ// PBE0/{6-31+G(d); Pt(SDD)} (PCM)	PBE0/{6-311G(2d,2p); Pt(mDZP)} (PCM)// wB97XD/{6-31+G(d); Pt(SDD)}	4c-mDKS/TZ_DZ// wB97XD/{6-31+G(d); Pt(SDD)}	
1		83.6	43.4	70.1	43.5	74.1	39.4	66.9	[41]
2		**14.4**	26.0	1.6	27.4	7.1	21.5	1.8	[42]
3	**P**[a]	19.4	26.7	6.6	14.0	11.1	15.1	7.5	[43]
	P[b]	21.5	13.4	6.5	27.4	11.3	23.5	7.9	
4		8.5	35.5	-8.3	41.5	-3.2	33.5	-10.3	[44]
5		17.5	27.7	7.7	28.1	12.2	23.1	8.0	[44]
6		0.1	-25.2	-9.6	-17.3	-2.4	-19.6	-9.1	[45]
7	**P**[a]	39.8	24.1	19.3	30.5	29.9	22.9	20.5	[46]
	P[b]	83.7	86.2	65.2	94.4	70.6	88.9	65.1	
8		44.3	34.1	32.6	35.8	37.9	32.1	35.9	[47]
9		-21.7	-26.5	-37.7	-23.6	-35.9	-26.5	-36.8	[48]
10		-21.1	-9.2	-39.4	-10.0	-37.6	-16.3	-38.7	[48]
11		-53.3	-35.5	-73.4	-35.4	-68.6	-30.8	-70.1	[48]
12 [a]	**P**[trans]	20.2	10.1	10.9	11.4	15.6	11.5	11.5	[49]
	P[cis]	28.4	36.0	16.8	37.0	21.5	32.0	15.7	
13 [a]	**P**[trans]	11.0	-26.8	0.4	19.7	3.4	19.7	0.7	[49]
	P[cis]	20.2	-13.8	9.1	31.2	12.4	28.7	10.3	
14	**P**[trans]	-26.8	5.2	-50.2	11.7	-45.7	-1.0	-49.2	[50]
	P[cis]	-12.0	-6.0	-27.8	-5.0	-22.4	-11.0	-26.9	

15		-55.6	-26.8	-79.1	-26.9	-75.9	-38.0	-78.2	[51]
16		-64.2	-35.4	-85.2	-34.6	-83.2	-44.3	-89.6	[51]
17 [a]	**$PMes_2$**	**-56.4**	-49.2	-76.4	-52.0	-72.1	-59.2	-70.5	[52]
	P^a	**45.1**	31.0	32.0	33.4	35.9	32.8	33.2	
	P^b	**34.0**	10.4	16.9	13.5	22.5	17.7	21.5	
18 [a]	**$PMes_2$**	**-71.1**	-66.5	-81.8	-69.3	-77.7	-85.1	-89.6	[52]
	P^a	**46.5**	28.5	34.6	31.6	39.6	32.7	35.5	
	P^b	**47.4**	30.0	41.7	31.5	46.1	31.7	41.1	
19		**6.8**	28.5	-13.5	44.1	9.9	31.8	-8.3	[53]
20		15.6	42.2	2.2	44.5	8.0	41.9	3.3	[53]
21		5.2	32.7	-7.6	33.6	-3.0	43.0	-19.1	[53]
22		28.6	37.1	18.9	37.5	24.5	29.1	17.5	[54]
23		28.2	33.4	17.3	33.7	21.9	31.1	17.2	[54]
24		19.3	29.7	6.8	29.5	11.0	26.8	7.7	[54]
25		26.1	38.1	17.6	36.7	21.2	37.9	19.3	[54]
26	**P^a**	50.2	50.9	36.6	51.8	41.5	48.9	36.0	[54]
	P^b	43.1	33.0	28.6	35.6	32.7	35.2	27.7	
27 [a]		**46.5**	33.5	28.3	36.2	35.2	35.5	36.3	[55]
28 [a]		54.1	44.3	35.9	43.9	40.0	41.5	37.4	[55]
	PPh_3	18.3	16.3	8.2	17.1	12.7	18.5	11.5	
29 [a]		49.3	43.8	34.0	45.4	38.8	39.6	34.3	[55]
30 [a]		**49.8**	35.4	33.2	38.1	40.0	35.2	37.0	[55]
31 [a]		48.8	36.5	34.9	37.7	39.9	36.0	38.5	[55]
32 [a]		46.5	36.7	31.2	39.2	38.1	36.8	37.3	[55]
33 [a]		46.4	35.0	29.4	37.5	36.1	35.9	36.7	[55]
34	**P^b**	23.1	11.9	7.0	12.9	13.2	14.0	6.5	[56]
	P^a	23.6	38.1	8.0	39.4	14.9	30.3	7.2	
35	**P^a**	20.7	27.3	4.9	27.6	9.1	22.1	4.3	[56]
	P^b	25.5	20.6	17.2	21.7	22.6	18.8	16.8	
36	**P^a**	29.3	22.3	16.3	24.0	20.3	22.7	18.2	[56]
	P^b	30.2	15.0	16.8	15.7	21.2	16.2	18.2	
37	**P^a**	30.2	22.8	15.9	24.4	20.7	23.6	16.6	[56]
	P^b	31.2	19.3	25.3	17.7	27.5	19.6	24.0	
38	**P^b**	21.0	24.6	6.8	11.9	12.9	14.1	7.3	[56]
39	**P^a**	25.7	18.3	12.5	19.9	14.7	19.9	11.7	[56]
	P^b	26.3	9.1	16.6	8.6	19.3	11.3	16.4	
40 [a]	**P^a**	**32.5**	20.5	16.3	22.7	23.6	21.8	19.6	[57]
	P^b	**27.7**	20.0	23.7	21.0	28.0	21.6	23.4	
41 [a]	**P^a**	**28.8**	27.4	17.9	29.6	14.1	23.6	15.5	[57]

	P[b]	**25.0**	14.3	16.2	17.2	12.1	16.5	16.1	
42 [a]	**P[a]**	**24.4**	34.7	13.0	35.7	17.0	33.8	13.3	[57]
	P[b]	**24.0**	24.9	11.4	25.5	17.9	27.3	14.4	
43 [a]	**P[a]**	**19.2**	10.4	11.7	23.2	7.8	24.1	11.9	[57]
	P[b]	**22.4**	13.6	13.7	31.1	10.8	30.7	15.2	
44 [a]	**P[a]**	48.0	14.8	38.1	14.1	41.8	18.1	42.6	[58]
	P[b]	247.5	223.3	265.0	223.7	267.6	229.9	264.4	
45 [a]	**P[a]**	61.1	23.5	46.4	23.8	50.8	27.2	48.1	[58]
	P[b]	245.2	214.7	251.8	215.8	256.3	217.4	256.9	
46 [a]		226.6	208.4	235.6	207.3	240.6	211.4	241.8	[59]
47 [a]		28.3	14.9	14.2	15.8		5.3		[60]
	P=P	18.1	30.9	27.5	25.5		16.2		
48 [a]		27.8	18.9	18.0	20.0		19.9		[60]
	P=P	-22.0	-16.0	-23.2	-21.9		-43.0		
49 [a]	**P[c]**	57.1	42.1	43.8	42.4		35.8		[61]
	P[a]	26.3	23.5	13.6	14.0		13.2		
	P[b]	0.6	13.4	14.6	20.3		-2.1		
50		**55.6**	29.3	35.6	31.4		29.6	34.3	[60]
	P=P	**-23.5**	-23.3	-28.6	-27.7		-40.0	-19.7	
51	**P[a]**	**58.3**	51.0	49.4	51.3		49.3	47.1	[62]
	P[b]	**42.6**	16.1	27.7	18.8		22.2	27.1	
	P[c]	**71.5**	67.2	63.6	66.9		66.9	63.3	
	P[d]	**-48.2**	-9.1	-21.7	-37.0		-49.8	-19.4	
52 [a]	**P[a]**	**32.6**	27.8	21.5	27.9		30.0	21.7	[63]
	P[b]	**29.5**	23.5	19.5	23.9		21.2	17.6	
	P≡C	**230.0**	264.2	272.5	266.2		245.0	253.3	
53	**P[b]**	**28.8**	28.4	23.5	29.8		31.3	24.1	[64]
	P[a]	**26.3**	29.0	16.6	29.0		30.9	18.2	
	P≡P	**84.1**	103.3	112.1	104.7		97.4	108.2	
54	**P[b]**	**47.4**	32.3	35.9	33.7		36.5	36.6	[65]
	P[a]	**53.1**	41.2	41.9	41.9		43.9	41.0	
	P≡P	**87.7**	103.5	111.2	103.7		100.0	110.8	
55	**P[a]**	54.9	40.8	44.0	41.2		44.0		[66]
	P[b]	51.0	31.3	35.0	32.8		34.1		
	P≡C	102.4	110.0	117.9	110.0		101.3		
56	**P[a]**	**82.9**	60.2	61.4	61.5		63.6	60.5	[67]
	P[b]	**60.5**	46.5	52.4	49.8		50.7	51.7	
	P≡C	**140.0**	164.1	169.7	168.1		150.2	161.4	
57	**P[a]**	**203.0**	219.1	217.9	218.1		214.7	217.6	[59]

	P[b]	**202.0**	215.9	224.6	225.6		223.6	228.6	
	P[c]	**39.0**	63.5	70.1	60.5		48.6	64.0	
58 [a]	**P[b]**	**22.4**	16.8	13.8	17.6		15.7	14.3	[58]
	P[a]	**25.0**	37.1	22.1	37.0		39.0	24.0	
	P[c]	**-30.3**	10.1	5.7	6.4		-19.6	-4.9	
59 [a]	**P[b]**	26.2	16.0	17.1	17.0		17.3		[58]
	P[a]	25.2	28.8	16.9	28.6		29.1		
	P[c]	-34.7	-20.3	-26.1	-19.1		-49.9		
R^2 (all)			**0.910**	**0.966**	**0.918**		**0.941**	**0.976**	
R^2 (σ-P in σ- compl.)			**0.908**	**0.995**	**0.914**	**0.995**	**0.930**	**0.994**	
R^2 (σ-P in π-compl.)			**0.961**	**0.988**	**0.965**		**0.961**	**0.985**	
R^2 (σ-P all)			**0.914**	**0.993**	**0.915**		**0.930**	**0.993**	
R^2 (π-P in π-compl.)			**0.971**	**0.975**	**0.980**		**0.991**	**0.982**	
Complex	Atom	Experimental	PBE0/{6-311G(2d,2p); Pt(SDD)}// PBE0/{6-31+G(d); Pt(SDD)}	4c-mDKS/TZ_DZ// PBE0/{6-311G(2d,2p); Pt(SDD)} (PCM)// PBE0/{6-31+G(d); Pt(SDD)} (PCM)	PBE0/{6-311G(2d,2p); Pt(SDD)} (PCM)// PBE0/{6-31+G(d); Pt(SDD)} (PCM)	4c-mDKS/TZ_DZ// PBE0/{6-31+G(d); Pt(SDD)} (PCM)	PBE0/{6-311G(2d,2p); Pt(mDZP)} (PCM)// wB97XD/{6-31+G(d); Pt(SDD)}	4c-mDKS/TZ_DZ// wB97XD/{6-31+G(d); Pt(SDD)}	Reference
			Calculated						

[a] with the "TZ_DZ_UPC" LDBS.

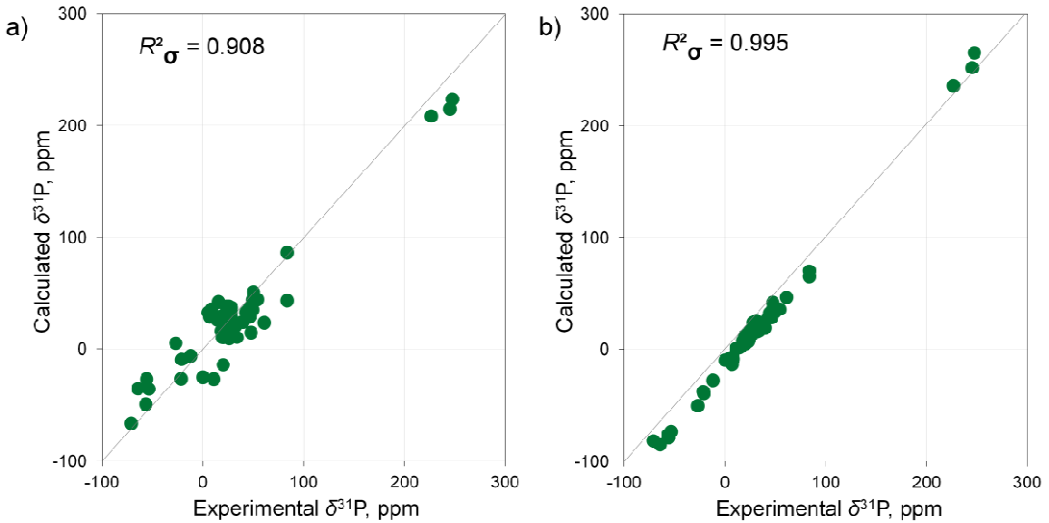

Figure S2. Correlation of calculated versus experimental ^{31}P NMR shifts for σ-complexes of Pt. Level of calculation: a) NR (PBE0/{6-311G(2d,2p); Pt(SDD)}//PBE0/{6-31+G(d); Pt(SDD)}); b) 4c-mDKS/TZ_DZ// PBE0/{6-31+G(d); Pt(SDD)}.

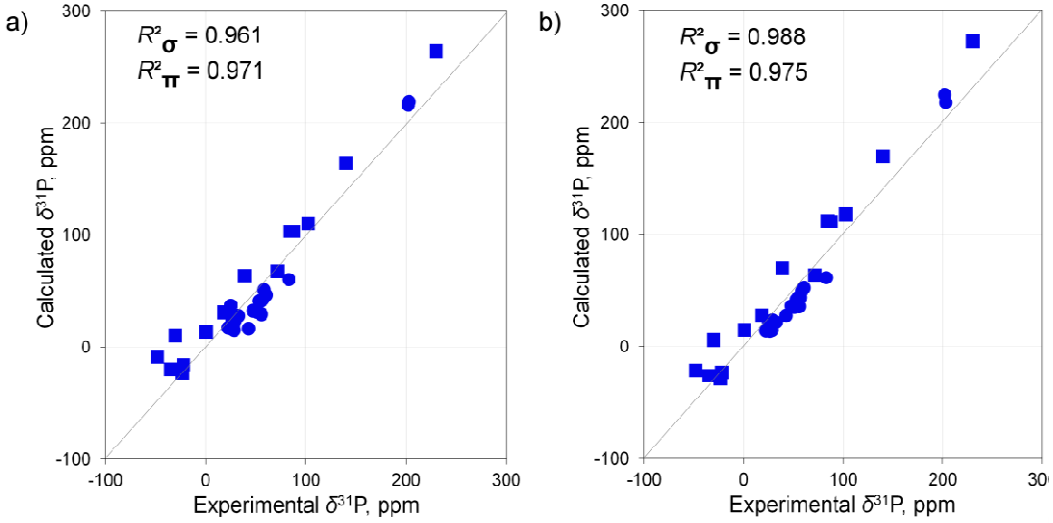

Figure S3. Correlation of calculated versus experimental ^{31}P NMR shifts for π-complexes of Pt: σ-donor P atoms (●), π-donor P atoms (■). Level of calculation: a) NR (PBE0/{6-311G(2d,2p); Pt(SDD)}//PBE0/{6-31+G(d); Pt(SDD)}); b) 4c-mDKS/TZ_DZ// PBE0/{6-31+G(d); Pt(SDD)}.

Table S2. Experimental and calculated (**at different levels of theory during shielding calculation**) ^{31}P NMR shifts (ppm) for **"training" set №1** of model σ-complexes of Pt.

Complex	Atom	Experimental	Calculated					
			PBE0/{6-311G(2d,2p); Pt(SDD)}// PBE0/{6-31+G(d); Pt(SDD)}	4c-mDKS/TZ_DZ// PBE0/{6-31+G(d); Pt(SDD)}	PBE0/{6-311G(2d,2p); Pt(SDD)}// PBE0/{**6-311+G(2d)**; Pt(SDD)}	4c-mDKS/TZ_DZ// PBE0/{**6-311+G(2d)**; Pt(SDD)}	PBE0/{6-311G(2d,2p); Pt(**NMR-DKH**)}// PBE0/{6-31+G(d); Pt(SDD)}	PBE0/{6-311G(2d,2p); Pt(**SARC-ZORA**)}// PBE0/{6-31+G(d); Pt(SDD)}
2		14.4	26.0	1.6	28.5	1.3	21.6	21.9
17 [a]	**$PMes_2$**	-56.4	-49.2	-76.4	-49.3	-78.9	-57.2	-58.4
	P^a	45.1	31.0	32.0	33.8	31.8	26.8	27.7
	P^b	34.0	10.4	16.9	13.7	17.2	3.7	5.2
18 [a]	**$PMes_2$**	-71.1	-66.5	-81.8	-64.5	-84.2	-71.3	-73.0
	P^a	46.5	28.5	34.6	31.6	34.4	25.2	26.0
	P^b	47.4	30.0	41.7	33.2	41.5	24.9	26.5
19		6.8	28.5	-13.5	35.8	-7.7	20.5	17.2
27 [a]		46.5	33.5	28.3	35.0	28.1	28.9	29.7
30 [a]		49.8	35.4	33.2	36.7	32.6	30.4	31.0
40 [a]	**P^a**	32.5	20.5	16.3	24.7	17.7	13.7	15.1
	P^b	27.7	20.0	23.7	23.6	23.4	14.9	16.2
41 [a]	**P^a**	28.8	27.4	17.9	30.3	5.6	21.8	22.7
	P^b	25.0	14.3	16.2	17.3	4.2	8.2	9.5
42 [a]	**P^a**	24.4	34.7	13.0	37.7	11.4	28.9	30.1
	P^b	24.0	24.9	11.4	27.6	13.2	18.8	20.2
43 [a]	**P^a**	19.2	10.4	11.7	25.5	0.1	16.8	18.1
	P^b	22.4	13.6	13.7	33.6	3.0	24.6	25.7
46 [a]		226.6	208.4	235.6	211.6	237.2	236.8	231.4
	R^2		**0.959**	**0.993**	**0.952**	**0.992**	**0.954**	**0.960**

[a] with the "TZ_DZ_UPC" LDBS.

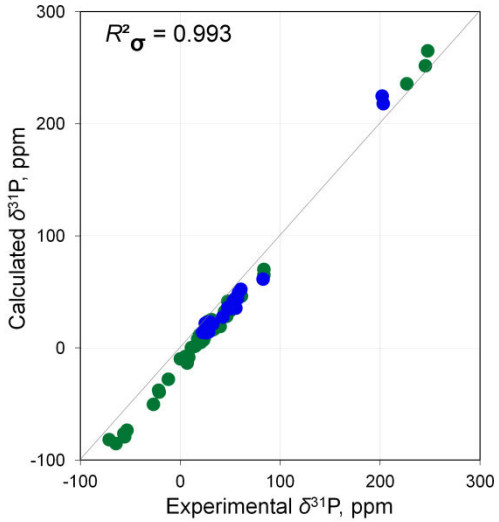

Figure S4. Correlation of calculated (4c-mDKS/TZ_DZ//PBE0/{6-31+G(d); Pt(SDD)}) *versus* experimental ^{31}P NMR shifts for σ-donor P atoms in σ- (green) and in π-complexes (blue).

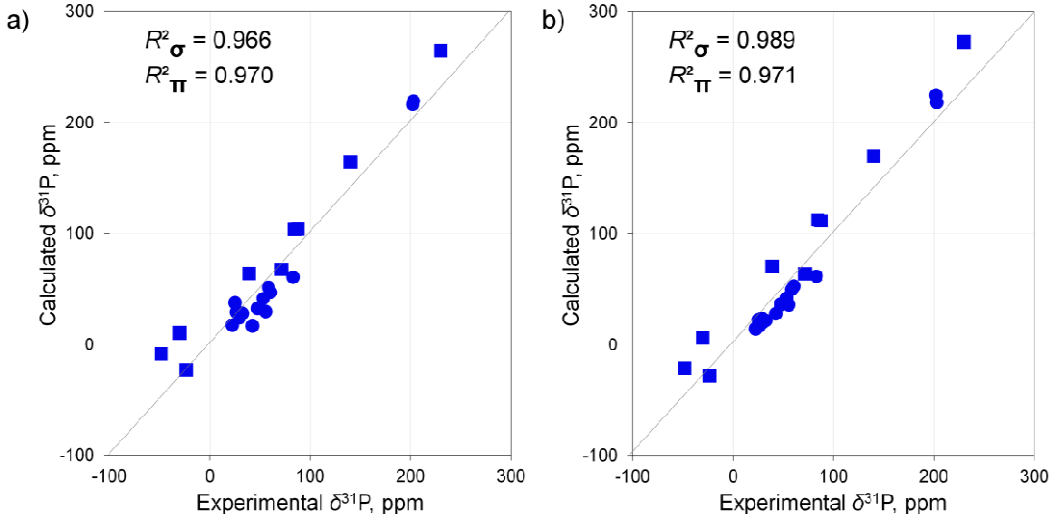

Figure S5. Correlation of calculated *versus* experimental ^{31}P NMR shifts for **the "training" set №2** of Pt π-complexes: σ-donor P atoms (●), π-donor P atoms (■). a) NR (PBE0/{6-311G(2d,2p); Pt(SDD)}//PBE0/{6-31+G(d); Pt(SDD)}); b) 4c-mDKS/TZ_DZ//PBE0/{6-31+G(d); Pt(SDD)}.

Optimization of computational protocol for π-complexes on the "training" set №2

Variation of parameters at the shielding calculation stage

At this stage, the parameters were varied at the shielding calculation, while maintaining the geometry optimized at the PBE0/{6-31+G(d); Pt(SDD)} level. It turned out that taking into account the **solvent effects** (PCM) at the shielding calculation stage leads to some improvement in the correlation (R^2 = 0.978 vs 0.970, Table S3, column 3).

Increasing the flexibility of the basis sets on the elements at the shielding calculation stage, namely adding d and f polarization and diffusion functions (6-311+G(3df,2p)), while maintaining the remaining parameters, does not provide a fundamental improvement (R^2 = 0.973, Table S3, column 4). Thus, it can be concluded that the relatively low correlation for π-donor phosphorus atoms in π-complexes is not due to the weakness of the basis sets on the elements and the 6-311G(2d,2p) basis set is already quite complete.

Next, the influence of basis sets on the platinum atom on ^{31}P NMR shifts was considered. The valence basis sets included in SDD is a bit small, a double-ζ quality. Therefore, first, while maintaining all other parameters, we replaced effective core potentials (ECP) SDD with def2-TZVPD, which also uses ECP for internal electrons, but a more flexible basis sets with diffusion functions for valence electrons. However, this did not lead to an improvement (R^2 = 0.970, Table S3, column 5).

The use of all-electron (AE) basis sets on platinum with diffusion d functions, mDZP leads to some improvement in the correlation (R^2 = 0.977, Table S3, column 6). At the same time, the use of the AE relativistically contracted basis set on platinum, SARC-ZORA, which was recommended for ^{195}Pt NMR CS calculations, leads to significantly worse results (R^2 = 0.896, Table S3, column 7). Similarly, the use of segmented relativistically contracted AE basis set of triple-ζ quality, Douglas–Kroll–Hess (NMR-DKH), which have been tested for $^{1}J_{\text{Pt-N}}$, $^{1}J_{\text{Pt-P}}$ and ^{195}Pt NMR shifts estimates, also leads to a significant deterioration in agreement (R^2 = 0.840, Table S3, column 8).

The next step was to try to increase the **flexibility of basis sets on phosphorus atoms**. The use of the pcS-2 basis set specially developed for calculating magnetic shielding, with the addition of a single tight p-type basis function, also only slightly improves the agreement (R^2 = 0.973, Table S3, column 9). The use of pcSseg basis set on phosphorus atoms also does not lead to a noticeable improvement (R^2 = 0.972, Table S3, column 10).

An attempt was also made to use another type of basis set on the ligand atoms, for example, Dunning's basis set. However, the use of both double- and triple-ζ quality basis sets of this type (cc-pVDZ and cc-pVTZ) only leads to a deterioration of the correlation (R^2 = 0.953 and 0.960, Table S3, column 11-12).

In principle, the type of **functional** used may also influence the results. For example, even the proportion of the exact exchange admixture in the functional may matter. To evaluate this effect, calculations were performed using the PBE functional with different exact exchange contribution: PBE (0%), PBE0 (25%) and PBE50 (50%). It turned out that when changing the proportion of the exact exchange admixture in the functional (from 0% to 25% and up to 50%) the main picture remains the same (R2 = 0.965, 0.970, 0.969, respectively, Table S3, column 13, 1, 14).

On the other hand, the use of functionals designed to take into account dispersion interactions also does not lead to an improvement in correlation. Namely, when using the PBE0-D3 (PBE0 functional with added D3 version of Grimme's dispersion) or wB97XD functionals, the correlation coefficients for π-P donor atoms are almost the same as for the original combination (R^2 = 0.970, Table S3, column 15-16).

As a result, at the shielding calculation stage only a small improvement is revealed when replacing on Pt ECP (SDD) on mDZP or taking into account the solvent effects (PCM). Therefore, it was interesting to see how combining these protocols (mDZP basis set on Pt and taking into account the solvent effects) would impact the quality of the shielding assessment. Calculations showed that this approach indeed yields the best correlation between calculation and experiment (R^2 = 0.982, Table S3, column 17).

Thus, varying a number of basis sets and functionals at the shielding calculation stage allowed us to identify a leading combination for evaluating the ^{31}P NMR of π-P-phosphors. Namely, the (PBE0/{6-311G(2d,2p); Pt(mDZP)}, PCM) protocol appears promising.

Variation of parameters at the geometry optimization stage

The next step was to systematically vary the calculation parameters at the geometry optimization stage, while maintaining the shielding calculation at a relatively high level (PBE0/{6-311G(2d,2p); Pt(SDD)}).

It turned out that taking into account the solvent effects (PCM) at the optimization stage has practically no effect (R^2 = 0.971, Table S4, column 1). Strengthening the basis set on ligand atoms (6-311+G(2d)) leads to only a slight improvement compared to initial level (R^2 = 0.973 vs 0.970, Table S4, column 2).

In the case of nickel complexes, it was important to include the diffusion function on the metal basis sets at the geometry optimization stage. Therefore, two basis sets, def-2TZVPD and mDZP, were tested on platinum, which include diffuse components. However, it turned out that this does not lead to significant changes compared to the initial approximation (R^2 = 0.971 and 0.969, Table S4, column 3-4).

Initially, the scalar relativistic (SR) effects of platinum on the geometry of the complex are taken into account by using pseudorelativistic ECP (SDD). This simplified description of the inner electrons may have limitations. Therefore, for verification, calculations were also carried out using relativistically contracted AE basis sets. However, it turned out that when using, for example, the SARC-ZORA basis set, the agreement deteriorates sharply (R^2 = 0.877, Table S4, column 5). A similar picture is also observed when using another popular AE basis set, NMR-DKH (R^2 = 0.789, Table S4, column 6) on platinum.

In the case of phosphorus atoms, there is a possibility of the influence of SR effects of the phosphorus itself on the geometry. Therefore, to test this assumption, calculations were carried out in which, at the optimization stage, pseudorelativistic ECP (SDD) was used to describe the core electrons of the phosphorus atom, and the valence electrons were described by the 6-31+G(d) basis set. It turned out that the use of such combination does not lead to noticeable changes (R^2 = 0.970, Table S4, column 7).

Thus, variation of basic sets on both elements and metal does not lead to positive changes. Therefore, we next tried to see how the type of functional at the geometry optimization stage could influence the results.

Longer-range interactions may be important for the coordination bond. Therefore, we assessed how taking into account dispersion interactions at the optimization stage can affect the geometry and then the ^{31}P NMR shifts using the example of two functionals: wB97XD and PBE0-D3. It turned out that in both cases there is a noticeable improvement in correlation (R^2 = 0.982, Table S4, column 8-9) when compared with the initial approach (R^2 = 0.970).

Table S3. Experimental and calculated (**at different levels of theory during shielding calculation**) ^{31}P NMR shifts (ppm) for **"training" set №2** of model π-complexes of Pt (**in all cases the geometry was fixed to the PBE0/{6-31+G(d); Pt(SDD)}**).

Complex	Atom	Experimental	Calculated															
			column 1	column 2	column 3	column 4	column 5	column 6	column 7	column 8	column 9	column 10	column 11	column 12	column 13	column 14	column 15	column 16	column 17
			PBE0/{6-311G(2d,2p); Pt(SDD)}	**4c-mDKS/TZ_DZ**	**PBE0/{6-311G(2d,2p); Pt(SDD)} (PCM)**	**PBE0/{6-311+G(3df,2p); Pt(SDD)}**	**PBE0/{6-311G(2d,2p); Pt(def2-TZVPD)}**	**PBE0/{6-311G(2d,2p); Pt(mDZP)}**	**PBE0/{6-311G(2d,2p); Pt(SARC-ZORA)}**	**PBE0/{6-311G(2d,2p); Pt(NMR-DKH)}**	**PBE0/{6-311G(2d,2p); P(pcS-2); Pt(SDD)}**	**PBE0/{6-311G(2d,2p); P(pcSseg); Pt(SDD)}**	**PBE0/{cc-pVDZ; Pt(SDD)}**	**PBE0/{cc-pVTZ; Pt(SDD)}**	**PBE/{6-311G(2d,2p); Pt(SDD)}**	**PBE50/{6-311G(2d,2p); Pt(SDD)}**	**wB97XD/{6-311G(2d,2p); Pt(SDD)}**	**PBE0(ED)/{6-311G(2d,2p); Pt(SDD)}**	**PBE0/{6-311G(2d,2p); Pt(mDZP)} (PCM)**
50		55.6	29.3	35.6	31.4	27.5	28.6	29.6	25.2	24.2	36.1	35.9	33.3	16.2	34.2	26.0	32.5	29.4	45.7
	P=P	-23.5	-23.3	-28.6	-32.8	-22.2	-26.4	-35.3	26.4	39.9	-17.5	-16.4	-2.5	-26.1	0.8	-45.6	-33.5	-23.5	-44.2
51	**P^{a}**	58.3	51.0	49.4	51.6	52.1	50.3	52.0	49.2	48.4	57.1	57.1	50.1	38.6	57.0	45.8	53.2	50.9	52.3
	P^{b}	42.6	16.1	27.7	18.8	16.0	15.3	19.0	14.0	12.8	22.2	22.3	22.4	6.2	19.0	14.1	19.7	15.9	21.2
	P^{c}	71.5	67.2	63.6	66.6	69.8	65.9	64.7	87.3	91.6	72.5	71.8	66.9	58.3	82.0	53.1	64.3	67.2	63.9
	P^{d}	-48.2	-9.1	-21.7	-38.5	-12.2	-13.3	-22.0	33.3	48.5	-9.6	-7.2	19.0	-7.2	17.5	-33.7	-17.8	-9.1	-50.2
52 [a]	**P^{a}**	32.6	27.8	21.5	28.4	26.5	27.5	29.3	21.6	19.6	35.3	34.5	29.1	16.6	31.8	25.4	32.5	27.9	29.6
	P^{b}	29.5	23.5	19.5	24.6	23.7	22.6	25.1	18.3	16.6	30.5	29.9	27.8	15.0	27.6	21.4	27.3	23.7	25.6
	P≡C	230.0	264.2	272.5	265.2	272.0	269.6	265.1	258.2	257.0	269.2	270.0	263.0	261.5	266.8	267.5	271.5	265.9	263.3
53	**P^{b}**	28.8	28.4	23.5	30.0	28.1	28.2	30.8	24.1	22.6	36.4	35.7	33.7	17.3	33.9	26.3	32.6	29.3	31.1
	P^{a}	26.3	29.0	16.6	28.9	32.5	28.2	30.5	22.7	20.8	35.6	34.6	28.9	20.8	32.9	26.2	32.6	28.8	30.3
	P≡P	84.1	103.3	112.1	102.9	107.7	108.5	105.8	86.5	83.5	107.3	108.1	116.4	103.1	111.5	102.5	109.3	105.1	102.9
54	**P^{b}**	47.4	32.3	35.9	34.1	32.0	31.4	35.3	28.8	27.4	38.6	38.5	36.4	20.1	37.6	28.8	35.7	32.4	36.3
	P^{a}	53.1	41.2	41.9	42.0	43.7	40.8	45.0	37.4	35.7	48.1	47.4	40.1	32.7	45.7	38.3	45.3	41.3	45.2
	P≡P	87.7	103.5	111.2	100.2	108.4	109.2	108.9	82.0	77.7	106.8	108.3	119.3	102.8	114.2	101.0	107.2	105.6	102.1
56	**P^{a}**	82.9	60.2	61.4	62.6	62.9	59.6	63.5	57.1	55.6	68.3	68.6	56.9	40.4	64.7	56.0	65.2	59.9	65.5
	P^{b}	60.5	46.5	52.4	50.3	49.1	45.5	48.5	41.4	39.9	53.5	53.9	46.2	28.5	52.1	41.5	50.0	46.1	51.5

	P≡C	140.0	164.1	169.7	161.5	167.7	169.2	170.1	153.2	151.4	166.7	167.7	173.0	158.2	169.5	163.4	169.3	165.1	164.1
57	**P[a]**	203.0	219.1	217.9	218.7	219.1	217.9	214.9	235.2	239.8	221.5	221.1	213.0	209.0	204.1	233.1	235.2	218.9	214.8
	P[b]	202.0	215.9	224.6	226.1	230.7	228.6	223.2	244.1	248.3	231.3	231.2	221.4	217.9	215.1	242.2	244.2	228.8	220.6
	P[c]	39.0	63.5	70.1	59.3	63.5	64.2	59.0	43.2	40.9	62.7	64.0	77.2	61.0	70.8	57.7	60.2	61.8	55.8
58 [a]	**P[b]**	22.4	16.8	13.8	17.9	12.5	15.9	16.4	10.0	8.4	25.2	23.8	23.6	4.5	20.8	13.8	20.5	16.6	17.3
	P[a]	25.0	37.1	22.1	37.5	30.5	36.2	37.1	32.0	30.5	46.4	44.4	39.7	23.3	41.6	33.4	40.6	36.9	37.3
	P[c]	-30.3	10.1	5.7	5.7	10.5	8.9	-5.0	34.3	42.6	14.9	14.6	19.7	10.0	28.8	-5.2	4.4	9.9	-8.6
	R^2 (σ-P)		**0.966**	**0.989**	**0.969**	**0.969**	**0.9641**	**0.968**	**0.967**	**0.967**	**0.962**	**0.965**	**0.961**	**0.955**	**0.965**	**0.962**	**0.964**	**0.964**	**0.978**
	R^2 (π-P)		**0.970**	**0.971**	**0.978**	**0.973**	**0.970**	**0.977**	**0.896**	**0.840**	**0.973**	**0.972**	**0.953**	**0.960**	**0.965**	**0.969**	**0.970**	**0.970**	**0.982**

Table S4. Experimental and calculated (**at different approximations during geometry optimization**) ^{31}P NMR shifts (ppm) for **"training" set №2** of model π-complexes of Pt (**the PBE0/{6-311G(2d,2p); Pt(SDD)} shielding in all cases**).

Complex	Atom	Experimental	Calculated								
			column 1	column 2	column 3	column 4	column 5	column 6	column 7	column 8	column 9
			PBE0/{6-31+G(d); Pt(SDD)} (PCM)	**PBE0/{6-311+G(2d); Pt(SDD)}**	**PBE0/{6-31+G(d); Pt(def2-TZVPD)}**	**PBE0/{6-31+G(d); Pt(mDZP)}**	**PBE0/{6-31+G(d); Pt(SARC-ZORA)}**	**PBE0/{6-31+G(d); Pt(NMR-DKH)}**	**PBE0/{6-31+G(d); P, Pt(SDD)}**	**wB97XD/{6-31+G(d); Pt(SDD)}**	**PBE0(ED)/{6-31+G(d); Pt(SDD)}**
50		55.6	29.5	30.8	28.5	27.7	20.4	18.3	38.5	28.1	27.6
	P=P	-23.5	-17.3	-15.1	-15.7	-7.4	3.3	6.7	-2.0	-17.5	-19.3
51	**P^a**	58.3	50.8	53.6	51.1	51.7	41.1	37.3	61.3	48.0	50.5
	P^b	42.6	15.9	18.6	15.9	14.8	12.7	11.2	25.4	16.9	15.2
	P^c	71.5	67.7	70.7	66.0	71.7	80.8	84.1	81.9	70.7	68.9
	P^d	-48.2	-5.9	-12.2	-8.2	5.5	21.8	33.2	14.3	-6.7	-16.8
52 [a]	**P^a**	32.6	27.6	30.7	27.8	26.5	24.6	23.2	37.5	28.1	26.1
	P^b	29.5	23.2	26.1	23.4	24.1	20.9	21.4	33.6	20.2	22.7
	P≡C	230.0	267.0	269.2	270.9	271.7	214.4	203.9	274.2	246.8	272.0
53	**P^b**	28.8	29.3	31.8	29.1	29.0	26.6	25.6	39.4	29.6	28.7
	P^a	26.3	29.0	32.5	29.0	28.4	22.9	21.1	38.5	29.3	27.8
	P≡P	84.1	107.4	104.7	108.9	108.1	63.5	51.4	112.7	100.5	106.6
54	**P^b**	47.4	32.2	34.5	32.9	31.4	23.1	19.4	41.8	32.6	32.1
	P^a	53.1	41.4	43.3	42.2	40.8	27.2	22.9	50.8	40.1	40.3
	P≡P	87.7	109.5	106.6	109.3	108.3	65.2	54.5	113.6	104.2	106.7
56	**P^a**	82.9	58.8	61.5	60.1	59.2	46.2	42.0	69.5	57.9	59.6
	P^b	60.5	45.5	47.7	46.3	45.2	34.8	31.2	55.7	45.4	45.1
	P≡C	140.0	174.0	166.2	168.5	169.2	121.8	110.7	172.7	155.9	162.2
57	**P^a**	203.0	218.6	221.3	218.4	219.4	218.0	217.8	228.3	218.6	220.6
	P^b	202.0	228.7	230.6	228.9	229.0	224.2	223.0	238.7	231.8	231.6

	P[c]	39.0	63.2	60.4	63.9	66.1	17.1	6.7	70.1	55.0	60.4
58 [a]	**P[b]**	22.4	16.4	18.7	16.5	16.8	13.1	10.9	26.4	15.3	14.6
	P[a]	25.0	36.6	39.3	36.6	38.0	35.9	34.6	46.8	38.9	38.3
	P[c]	-30.3	10.8	15.8	9.9	10.4	25.0	28.9	18.4	4.3	-3.3
	R^2 (σ-P)		**0.963**	**0.962**	**0.964**	**0.961**	**0.946**	**0.940**	**0.963**	**0.960**	**0.962**
	R^2 (π-P)		**0.971**	**0.973**	**0.971**	**0.969**	**0.877**	**0.789**	**0.970**	**0.982**	**0.982**

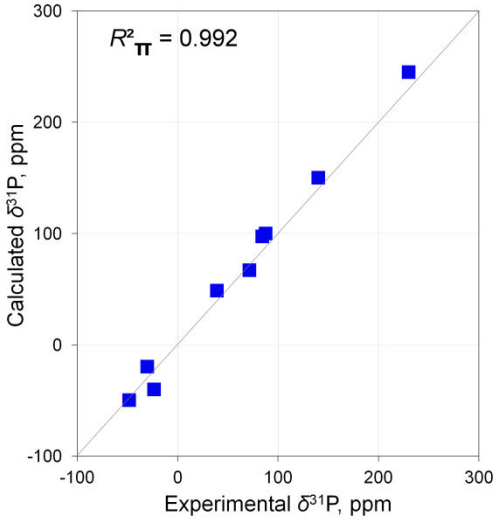

Figure S6. Correlation of calculated (PBE0/{6-311G(2d,2p); Pt(mDZP)} (PCM)//wB97XD/{6-31+G(d); Pt(SDD)}) *versus* experimental ^{31}P NMR shifts **for the "training" set №2** of Pt π-complexes: π-donor P atoms (■).

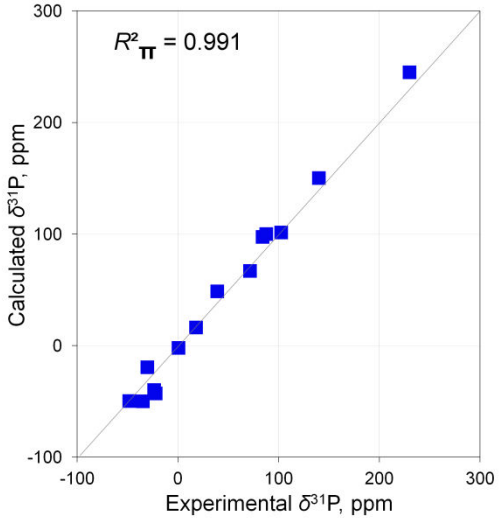

Figure S7. Correlation of calculated (PBE0/{6-311G(2d,2p); Pt(mDZP)} (PCM)//wB97XD/{6-31+G(d); Pt(SDD)}) *versus* experimental ^{31}P NMR shifts **for all π-complexes**: π-donor P atoms (■).

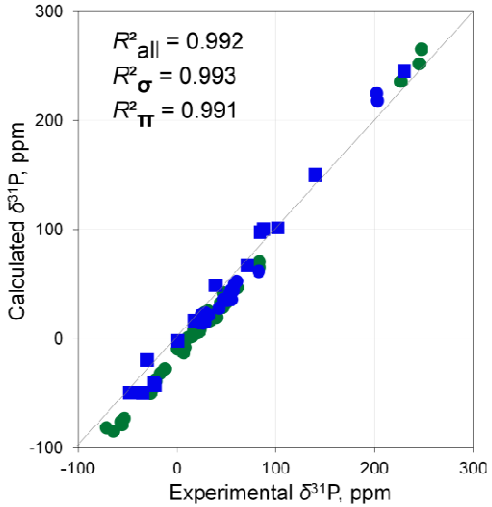

Figure S8. Correlation of calculated (non-scaled) *versus* experimental ^{31}P NMR shifts for all Pt complexes: σ-donor P atoms (●, 4c-mDKS//PBE0/{6-31+G(d); Pt(SDD)}), π-donor P atoms (■, PBE0/{6-311G(2d,2p); Pt(mDZP)} (PCM)//wB97XD/{6-31+G(d); Pt(SDD)}).

Table S5. Experimental and calculated (**with various all-electron basis sets at Pt during shielding calculation**) ^{31}P NMR shifts (ppm) for **"training" set №2** of model π complexes of Pt.

Complex	Atom	**Experimental**	**Calculated**							
			the geometry fixed to the **PBE0**/{6-31+G(d); Pt(SDD)}				the geometry fixed to the **wB97XD**/{6-31+G(d); Pt(SDD)}			
			PBE0/{6-311G(2d,2p); Pt(**SDD**)}	4c-mDKS/TZ_DZ	PBE0/{6-311G(2d,2p); Pt(**NMR-DKH**)}	PBE0/{6-311G(2d,2p); Pt(**SARC-ZORA**)}	PBE0/{6-311G(2d,2p); Pt(**mDZP**)} (PCM)	4c-mDKS/TZ_DZ	PBE0/{6-311G(2d,2p); Pt(**NMR-DKH**)} (PCM)	PBE0/{6-311G(2d,2p); Pt(**SARC-ZORA**)} (PCM)
50		55.6	29.3	35.6	24.2	25.2	29.6	34.3	24.4	25.5
	P=P	-23.5	-23.3	-28.6	39.9	26.4	-40.0	-19.7	33.6	20.7
51	**P^{a}**	58.3	51.0	49.4	48.4	49.2	49.3	47.1	45.1	46.0
	P^{b}	42.6	16.1	27.7	12.8	14.0	22.2	27.1	15.8	17.2
	P^{c}	71.5	67.2	63.6	91.6	87.3	66.9	63.3	94.4	89.9
	P^{d}	-48.2	-9.1	-21.7	48.5	33.3	-49.8	-19.4	9.5	-3.6
52 [a]	**P^{a}**	32.6	27.8	21.5	19.6	21.6	30.0	21.7	20.5	22.4
	P^{b}	29.5	23.5	19.5	16.6	18.3	21.2	17.6	13.1	14.7
	P≡C	230.0	264.2	272.5	257.0	258.2	245.0	253.3	235.9	237.2
53	**P^{b}**	28.8	28.4	23.5	22.6	24.1	31.3	24.1	22.8	24.3

	P[a]	26.3	29.0	16.6	20.8	22.7	30.9	18.2	21.1	23.0
	P≡P	84.1	103.3	112.1	83.5	86.5	97.4	108.2	75.0	78.3
54	**P[b]**	47.4	32.3	35.9	27.4	28.8	36.5	36.6	28.6	30.1
	P[a]	53.1	41.2	41.9	35.7	37.4	43.9	41.0	34.7	36.4
	P≡P	87.7	87.7	103.5	111.2	77.7	114.0	110.8	100.0	69.4
56	**P[a]**	82.9	60.2	61.4	55.6	57.1	63.6	60.5	56.8	58.0
	P[b]	60.5	46.5	52.4	39.9	41.4	50.7	51.7	42.8	44.1
	P≡C	140.0	164.1	169.7	151.4	153.2	150.2	161.4	135.9	137.2
57	**P[a]**	203.0	219.1	217.9	239.8	235.2	214.7	217.6	237.7	233.5
	P[b]	202.0	215.9	224.6	248.3	244.1	223.6	228.6	248.6	244.4
	P[c]	39.0	63.5	70.1	40.9	43.2	48.6	64.0	28.6	31.3
58[a]	**P[b]**	22.4	16.8	13.8	8.4	10.0	15.7	14.3	7.7	9.3
	P[a]	25.0	37.1	22.1	30.5	32.0	39.0	24.0	33.2	34.5
	P[c]	-30.3	10.1	5.7	42.6	34.3	-19.6	-4.9	26.0	17.7
	R^2 (σ-P)		**0.966**	**0.989**	**0.967**	**0.967**	**0.968**	**0.985**	**0.967**	**0.967**
	R^2 (π-P)		**0.970**	**0.971**	**0.840**	**0.896**	**0.992**	**0.982**	**0.897**	**0.940**

[a] with the "TZ_DZ_UPC" LDBS.

Table S6. Calculated energies (E, kcal/mol), ^{31}P NMR chemical shifts (ppm) for conformers of complexes **60**.

δ, exp	conformer	E[a]	δ, NR[b]	δ, 4c-mDKS[c]	δ, 4c-mDKS scal.[d]
4.4	1	0.0	54.7	-8.8	**6.0**
	2	0.2	54.2	-9.0	**5.9**

[a] PBE0/6-31+G(d);
[b] PBE0/{6-311G(2d,2p); Pt(SDD)}//PBE0/{6-31+G(d); Pt(SDD)};
[c] 4c-mDKS/TZ_DZ//PBE0/{6-31+G(d); Pt(SDD)};
[d] corrected according to eq. (1).

Table S7. Experimental, calculated ^{31}P NMR chemical shifts (ppm) and energies (E, kcal/mol) for the *cis* and *trans* isomers of $Pt(SiHPh_2)_2(PMe)_2$ (**61** and **62**).

Complex	δ, exp	E[a]	δ, NR[b]	δ, 4c-mDKS[c]	$\Delta\delta^{SO}$	δ, 4c-mDKS scal.[d]
cis-$Pt(SiHPh_2)_2(PMe_3)_2$ (**61**)	-17.0	0.9	-36.0	-32.3	+3.7	**-15.2**
trans-$Pt(SiHPh_2)_2(PMe_3)_2$ (**62**)	-24.0	0.0	-14.4	-45.6	-31.2	**-27.2**

[a] PBE0/6-31+G(d);
[b] PBE0/{6-311G(2d,2p); Pt(SDD)}//PBE0/{6-31+G(d); Pt(SDD)};
[c] 4c-mDKS/TZ_DZ//PBE0/{6-31+G(d); Pt(SDD)};
[d] corrected according to eq. (1).

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