Metal carbonyl complexes of phosphaamidines. Coordinative integrity detected in *C*-amino(λ^3,σ^2)-phosphaalkene isomers coordinated through *n*(P) HOMO-1 donor orbitals

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Supplementary Information

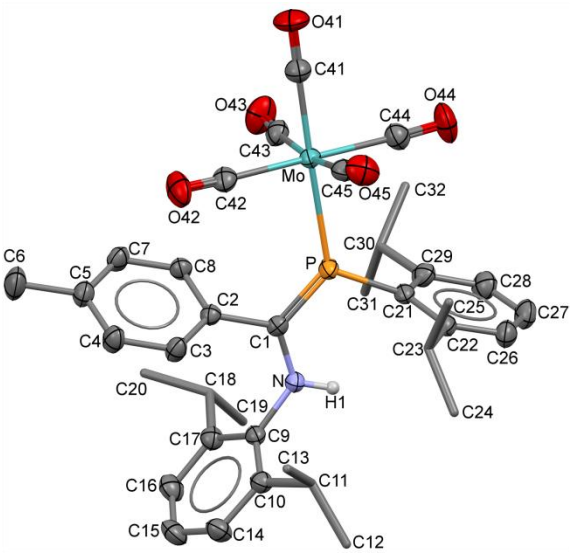

Figure S1. Displacement ellipsoids plot (30% probability) of the molecular structure of **11a** as found in the crystal structure (295 K). The atom numbering scheme is provided; H atoms on C are omitted and the ^{i}Pr are rendered as tubes for clarity.

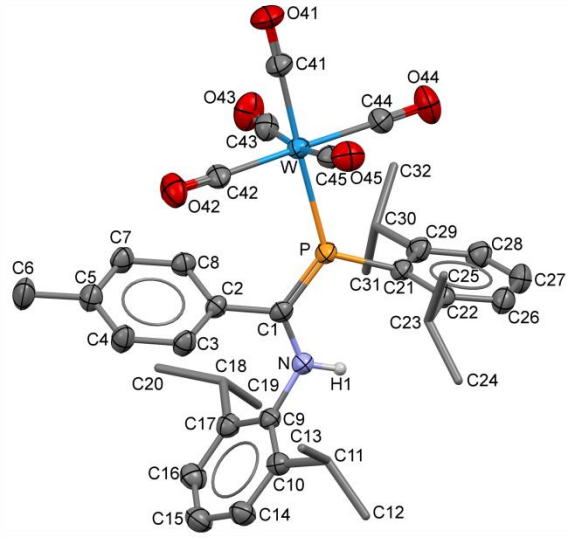

Figure S2. Displacement ellipsoids plot (30% probability) of **12** as found in the crystal (295 K). Atom numbering schemes are shown; H atoms on C are omitted and the ^{i}Pr are rendered as tubes for clarity.

Table S1. Compilation of P=C bond distances in crystal structures of acyclic phosphaalkenes [a]

CR[1]	CR[2]	PR	M	P=C (Å)	Class	Refcode	Lit. ref.
P=C	P=C	Ar	W	1.61(2)	P_2C cumulene	JENWAA	39
P=C	P=C	Ar	W	1.614(20)	P_2C cumulene	JENWAA	39
H	^{i}Pr	Vinyl	W	1.626(7)	Conventional P=C	JIKTOM	27
FeCpBr	FeCpBr	Mes	Cr	1.63(2)	P=C metal on C	WIJGEB	25
C=C	C=C	Ar	W	1.63(2)	PC_2 cumulene	VEXHAH	40
C=C	C=C	Ar	W	1.636(4)	PC_2 cumulene	UHUMUF	34
H	FeCO2Cp	$C(H)TMS_2$	Cr	1.64(2)	P=C metal on C	TACKOX	28
H	FeCO2Cp	$C(H)TMS_2$	Cr	1.66(2)	P=C metal on C	"	"
H	^{i}Pr	Ar	W	1.645(10)	Conventional P=C	SEPNIK	29
H	Ar	Cp*	W	1.647(8)	Conventional P=C	LEJSIE	20
H	^{t}Bu	C sp^3	W	1.649(6)	Conventional P=C	ROQGAF	22
TMS	TMS	vinyl	W	1.65(1)	P=C silanes on C	NEVQOU	23
H	^{i}Pr	Ar	W	1.652(9)	Conventional P=C	SEPNUW	29
C=C	C=C	Ar	W	1.656(6)	P_2C_2 cumulene	GOTTUE	36
H	CH_2 chain	Ar	W	1.660(7)	Conventional P=C	WUCGIK	21
C=C	C=C	Ar	W	1.665(7)	PC_3 cumulene	WEFPOM	37
TMS	TMS	VinylEtO	Cr	1.667(2)	P=C silanes on C	REGGEP	24
Me	Me	$C(H)TMS_2$	W	1.670(4)	Conventional P=C	GIRLAW	19
Ar	PhAcetyl	$C(H)TMS_2$	W	1.671(3)	Becker alkoxy P=C	OPABOX	41
Ar	PhAcetyl	$C(H)TMS_2$	W	1.676(4)	Alkoxy P=C	"	"
TMS	vinyl	$N(TMS)_2$	Mo	1.674(6)	P=C, 1 silane on C	GEDXOC	36
c.propene	c.propene	Ar	W	1.679(4)	Strained P=C?	SOTMET	26
Ph	Ph	Mes	Cr	1.679(2)	Conventional P=C	MESTCR [b]	31
Ar	EtO	$CH(amine)_2$	W	1.686(6)	Becker alkoxy P=C	IDOTAW	43
SMe	SMe	Ar	W	1.688(6)	Bis thiolato P=C	UHUXUQ	42
Me	EtO	$FeCO_2Cp$	W	1.69(1)	Alkoxy P=C, metal	NIYNUE	44
fluorene	fluorene	Ar	W	1.693(8)	Conjugated P=C	OHIBUC	35
Ar	EtO	TMS	W	1.694(3)	Becker alkoxy P=C	IDOSUP	43
Ar	EtO	^{t}Bu	W	1.695(2)	Becker alkoxy P=C	IDOSOJ	43
H	C-CH=P	Ar	W	1.696(5)	Vinylic P=C	PEWGIH	38
Ar	NHDipp	Dipp	Mo	1.697(2)	Amino P=C	**11b**	
Ar	NHDipp	Dipp	Cr	1.701(2)	Amino P=C	**10**	
Ar	NHDipp	Dipp	Mo	1.703(2)	Amino P=C	**11a**	
Ar	NHDipp	Dipp	W	1.707(5)	Amino P=C	**12**	
ring	ring	$C(H)TMS_2$	W	1.716(4)	Phenylene cumulene.	KAGTUJ	32
H	NMe_2	TMS	W	1.731(5)	Amino P=C	ENEBUU [c]	46
F	NMe_2	CF_3	Cr	1.798(3)	Side-on amino P=C	GEJYUP	47
F	NMe_2	CF_3	Cr	1.805(3)	Side-on amino P=C	"	"
OEt	NMe_2	CF_3	Cr	1.810(5)	Side-on amino P=C	VOJMUC	48
NMe_2	NMe_2	^{t}BuC(O)	Cr	1.832(2)	Side-on guanidine P=C	CODNUE	49

[a] Data taken from the CSD Release 5.36 May 2015. [b] Line structure **15** in main article. [c] Line structure **13** in main article. Structure diagrams of all the complexes from the CSD are provided in Figure S3 for readers without direct access to the database.

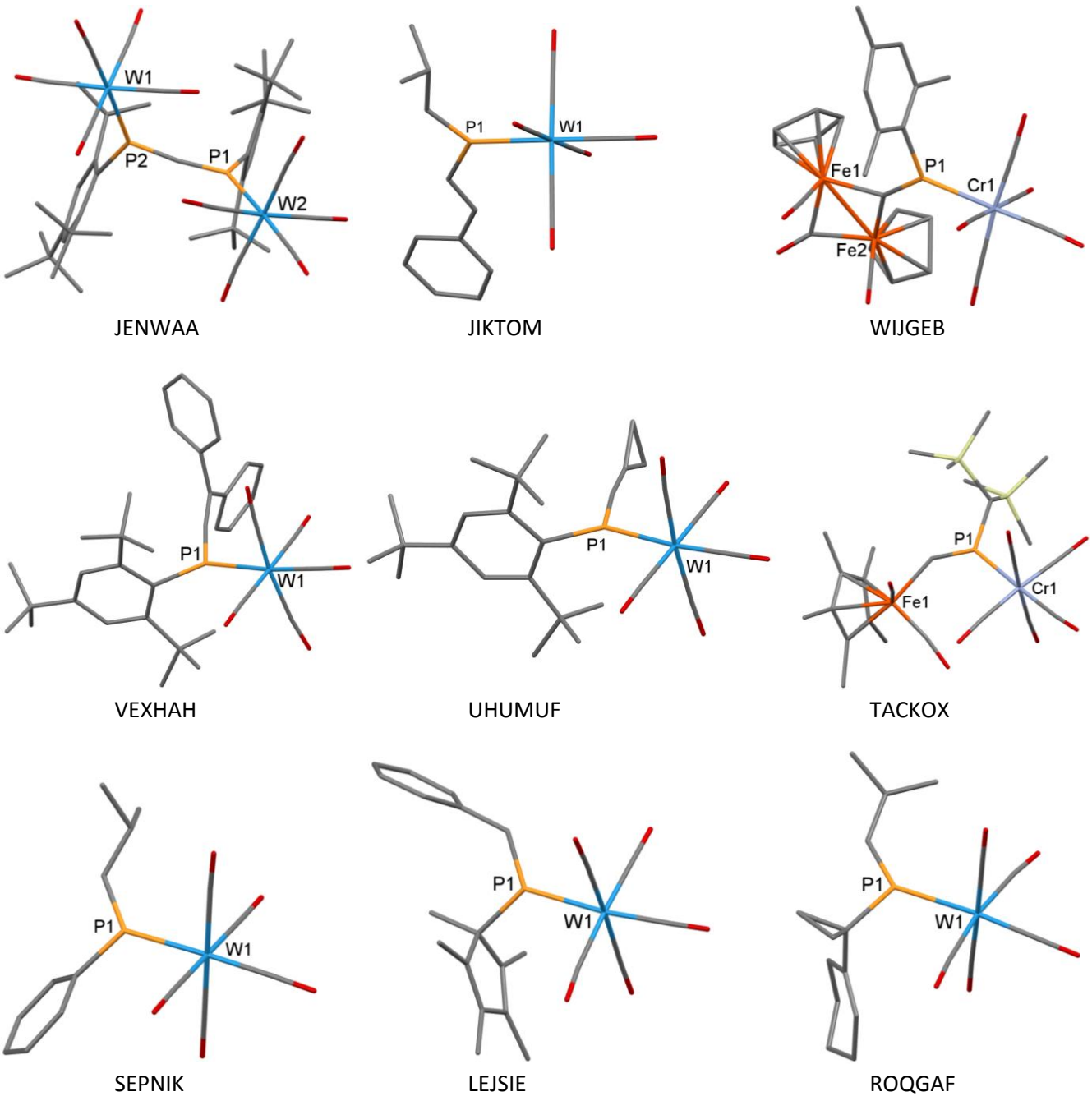

Figure S3 – part 1. Structure diagrams for the structures from the CSD reported in Table S1. Presented in the same order as the Table (i.e. by increasing C=P bond lengths), duplicates omitted. (Continued…)

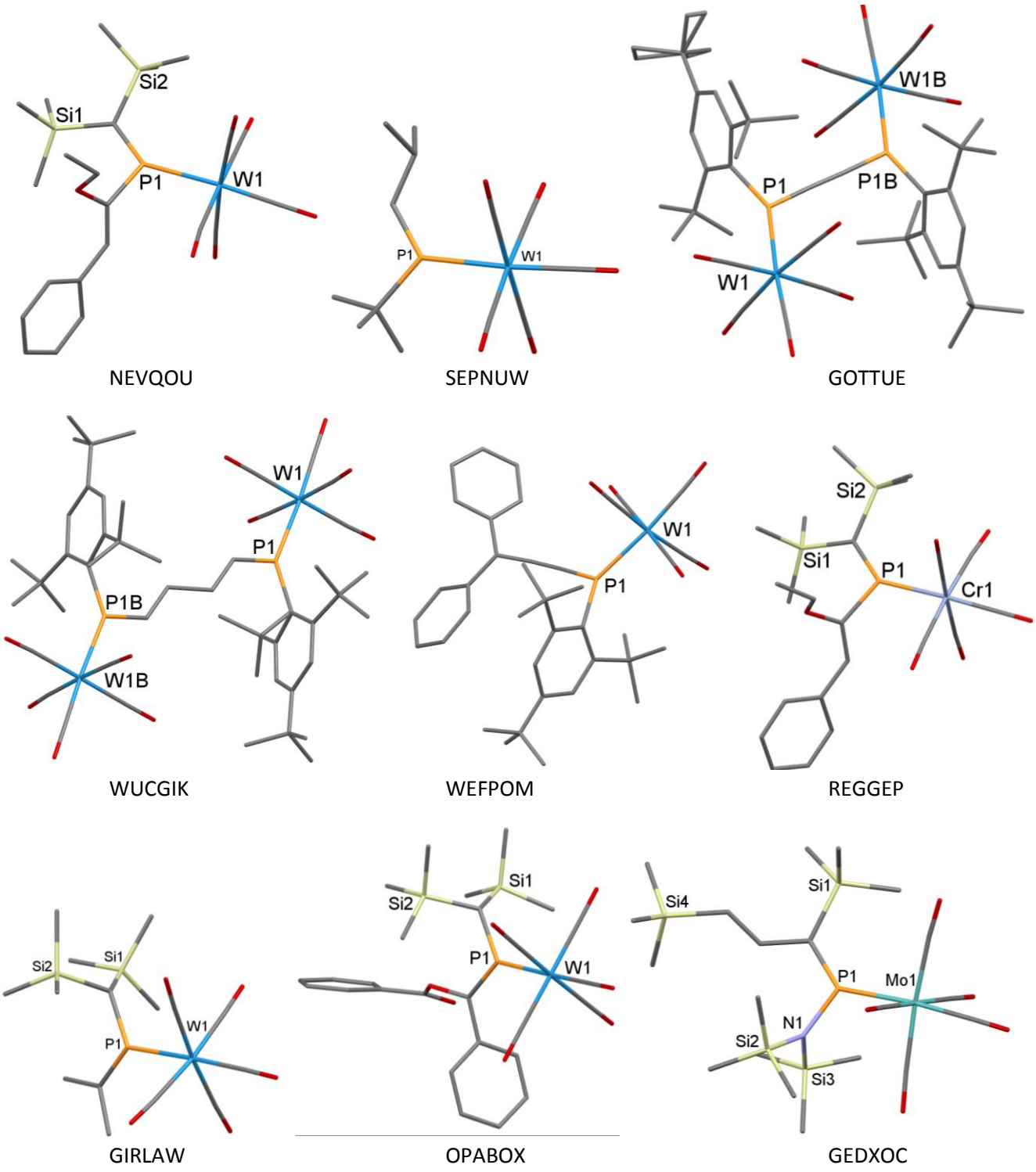

Figure S3 – part 2. Structure diagrams for the structures from the CSD reported in Table S1. Presented in the same order as the Table (i.e. by increasing C=P bond lengths), duplicates omitted. (Continued…)

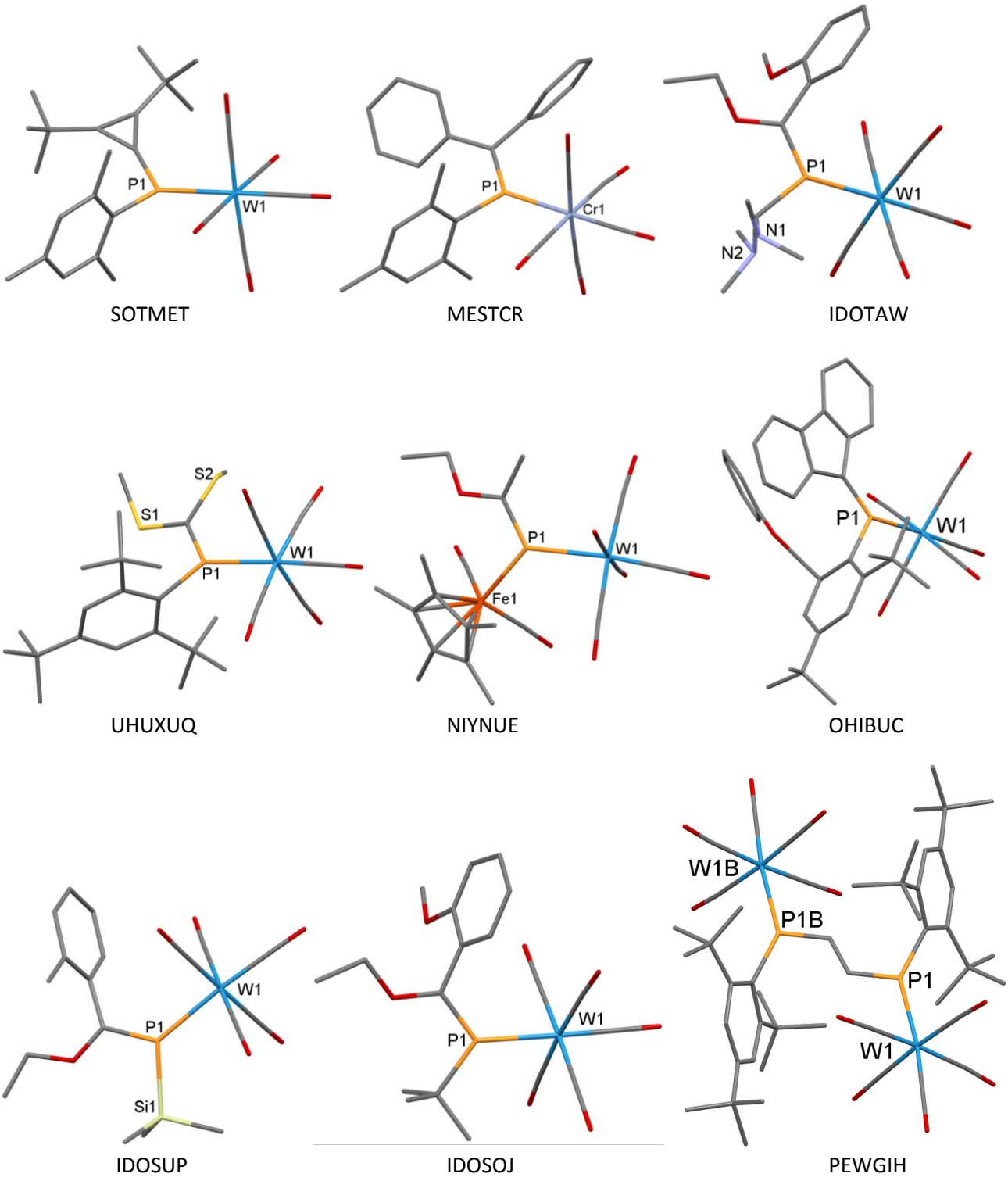

Figure S3 – part 3. Structure diagrams for the structures from the CSD reported in Table S1. Presented in the same order as the Table (i.e. by increasing C=P bond lengths), duplicates omitted. (Continued…)

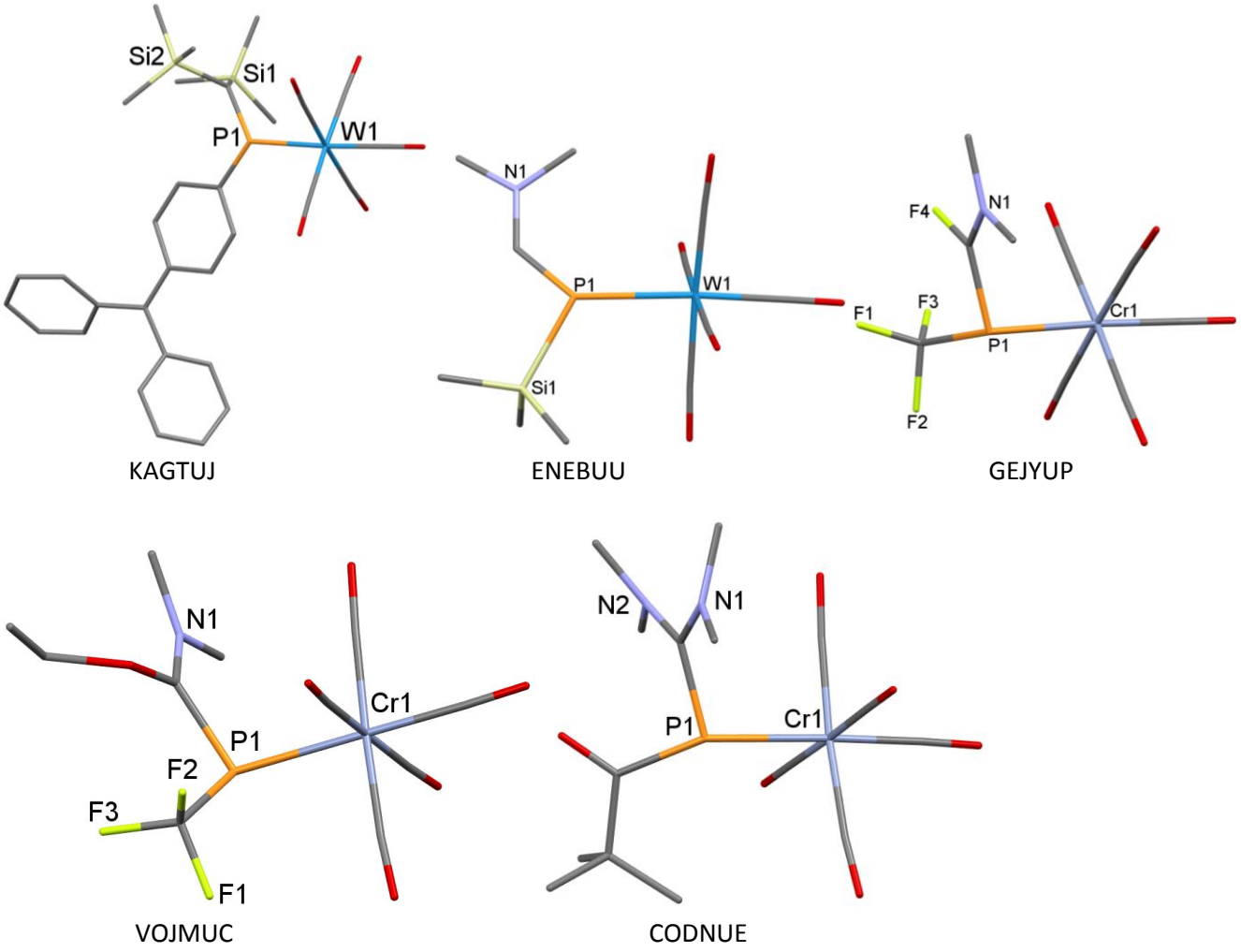

Figure S3 – part 4. Structure diagrams for the structures from the CSD reported in Table S1. Presented in the same order as the Table (i.e. by increasing C=P bond lengths), duplicates omitted.

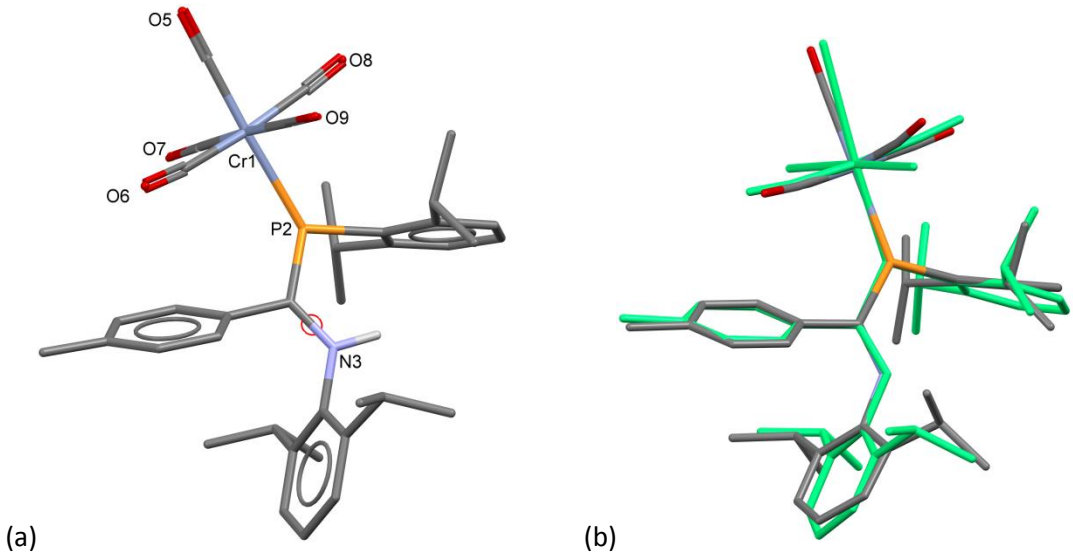

Figure S4. (a) B3PW91/LANL2DZ optimized geometry of **10**. (b) Overlay of DFT (green) with X-ray geometry.

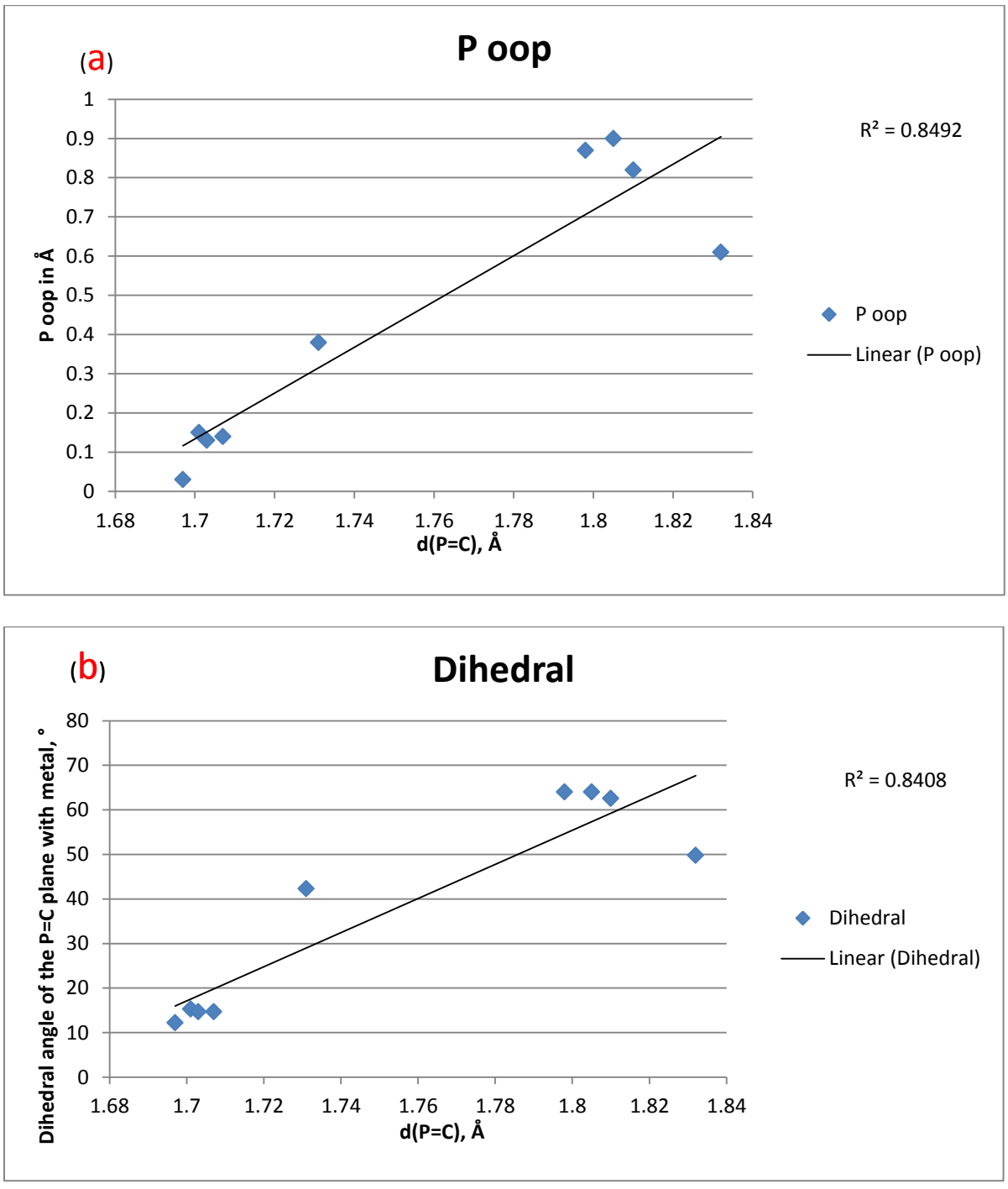

Figure S5. Correlations of *d*(P=C) in Å with (a) the phosphorus atom out-of-plane distance in Å and (b) with the dihedral angle between the plane of the P=C double bond and the perpendicular plane of the metal, phosphorus and three CO carbon atoms.°

Table S2. Additional IR data for phosphaamidines and metal complexes [a]

$CHCl_3$	NH	CO $A_1(1)$	CO B_2	CO $A_1(2)$	CO E_a	CO E_b
9a	3350 *w*					
9b	3350 *w*					
11a	3349 *w*	2071 *m*	1992 *w*	1949 *vs*	-	1915 *sh*
11b	3351 *w*	2071 *m*	1990 *w*	1949 *vs*	1940 *sh*	1915 *sh*
12	3349 *w*	2069 *m*	1983 *w*	1945 *sh*	1938 *vs*	1915 *sh*

KBr	NH	CO $A_1(1)$	CO B_2	CO $A_1(2)$	CO E_a	CO E_b
9a	3351 *m*					
9b	3357 *m*					
10	3357 *w*	2060 *m*	1983 *w*	1949 *vs*	1927 *vs*	1906 *s*
11a	3358 *w*	2069 *m*	1988 *w*	1955 *vs*	1929 *vs*	1906 *s*
11b	3362 *w*	2071 *m*	1991 *w*	1953 *sh*	1934 *vs*	1908 *s*
12	3357 *w*	2067 *m*	1979 *w*	1946 *vs*	1923 *vs*	1901 *s*

[a] FTIR data; conditions as listed. For data in *n*-heptane, see the main article.

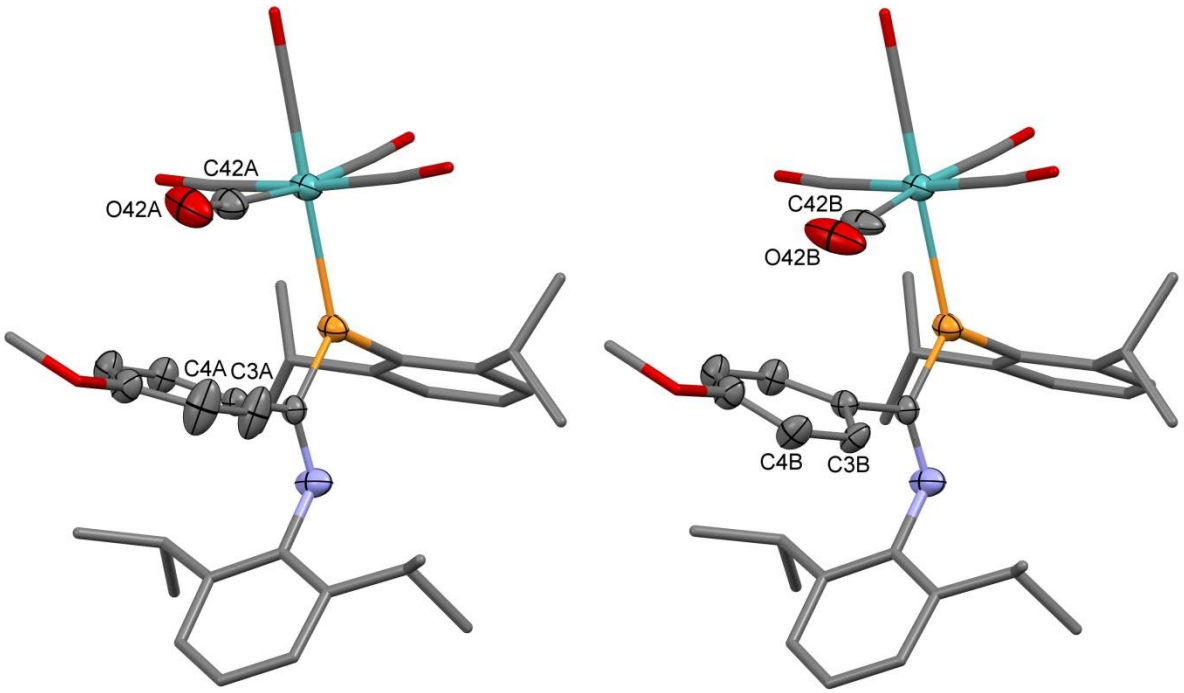

Figure S6. Depiction of the disorder model adopted to describe the crystal structure of **11b**. At left, the major (refined occupancy 65%) component; at right, the minor (35%) component. The minor rotomer with its CO group closer to the edge of the backbone phenyl ring induces a less-perpendicular orientation of the phenyl ring, indicative of significant steric interaction between this ring and the $Mo(CO)_5$ unit.

Table S3. Crystal, structure determination and refinement parameters

Param. \ Comp.	**10**	**11a**	**11b**	**12**	**9b**
Formula	$C_{37}H_{42}CrNO_5P$	$C_{37}H_{42}MoNO_5P$	$C_{37}H_{42}MoNO_6P$	$C_{37}H_{42}WNO_5P$	$C_{32}H_{42}NOP$
FW (amu)	663.68	707.62	723.62	795.53	487.63
Temperature (K)	293(2) K	293(2)	293(2)	293(2)	293(2)
Radiation, λ (Å)	Mo, 0.71073	Mo, 0.71073	Mo, 0.71073	Mo, 0.71073	Mo, 0.71073
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a (Å)	10.4722(8)	10.5913(8)	10.7566(8)	10.5413(9)	18.1914(16)
b (Å)	12.1314(11)	12.2632(10)	13.4617(11)	12.2130(11)	10.1898(5)
c (Å)	14.7650(13)	14.8639(13)	14.2564(12)	14.8135(14)	18.1080(12)
α (°)	84.600(11)	84.783(10)	104.733(10)	84.662(11)	
β (°)	79.559(10)	79.008(10)	108.862(9)	79.167(11)	117.319(9)
γ (°)	71.687(10)	71.596(9)	92.700(9)	71.661(10)	
Volume (Å^3)	1749.9(3)	1797.2(3)	1870.3(3)	1776.8(3)	2982.2(4)
Z	2	2	2	2	4
D_{calc} (g/cm^3)	1.260	1.308	1.285	1.487	1.086
μ (mm^{-1})	0.414	0.450	0.436	3.337	0.115
F(000)	700	736	752	800	1056
Crystal size (mm^3)	0.660 x 0.320 x 0.120	0.560 x 0.210 x 0.080	0.400 x 0.160 x 0.140	0.360 x 0.270 x 0.240	0.430 x 0.300 x 0.160
θ range (°)	2.808 to 25.68°	2.793 to 25.681	2.992 to 25.677	2.802 to 25.681	2.941 to 25.35
Index ranges:	$-12 \le h \le 12$ $-14 \le k \le 14$ $-17 \le l \le 17$	$-12 \le h \le 12$ $-14 \le k \le 14$ $-18 \le l \le 18$	$-12 \le h \le 12$ $-16 \le k \le 16$ $-17 \le l \le 17$	$-12 \le h \le 12$ $-14 \le k \le 14$ $-18 \le l \le 18$	$-21 \le h \le 21$ $-12 \le k \le 12$ $-20 \le l \le 20$
Total rfl.	24627	25323	26266	25048	30504
Indep. rfl.	6221	6402	6658	6327	5133
R(int)	0.1285	0.0699	0.0548	0.1372	0.1008
Compl. θ 25.5°	93.8 %	93.8 %	93.8 %	93.9	94.2
Abs. corr.	Analytical	Numerical	Numerical	Numerical	Analytical
Max. and min. transmission	0.95354 0.87344	0.943 0.775	0.987 0.845	0.955 0.718	0.9879 0.9008
Data / restraints / parameters [a]	6221 / 360 / 418	6402 / 360 / 418	6658 / 418 / 464	6327 / 361 / 418	5133 / 267 / 328
GOF, F^2	0.879	0.912	0.930	1.025	0.843
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0397, wR_2 = 0.0900	R_1 = 0.0283, wR_2 = 0.0649	R_1 = 0.0376, wR_2 = 0.0849	R_1 = 0.0532, wR_2 = 0.1279	R_1 = 0.0471, wR_2 = 0.1005
R indices (all data)	R_1 = 0.0635, wR_2 = 0.0978	R_1 = 0.0402, wR_2 = 0.0675	R_1 = 0.0581, wR_2 = 0.0911	R_1 = 0.0568, wR_2 = 0.1302	R_1 = 0.1097, wR_2 = 0.1190
Larg. pk (e/Å^{-3})	0.234	0.238	0.403	2.494	0.181
Larg. hole (e/Å^{-3})	-0.202	-0.415	-0.297	-2.814	-0.130

[a] Full-matrix least-squares on F^2.

Table S4. Cartesian Coordinates of the DFT-minimized Geometry of **10**

Tag	Symbol	X	Y	Z
1	Cr	-2.9753000	1.3073000	-0.3098000
2	P	-1.0239000	-0.1854000	0.1874000
3	N	1.6703000	-0.7592000	-0.1712000
4	H	1.3470000	-1.7172000	-0.2872000
5	O	-5.4456000	2.9524000	-0.7912000
6	O	-1.4395000	3.8663000	-0.9122000
7	O	-3.0118000	1.9903000	2.6615000
8	O	-4.8517000	-1.0571000	0.0820000
9	O	-2.7089000	0.7762000	-3.2958000
10	C	0.6953000	0.1924000	-0.0086000
11	C	1.1036000	1.6194000	0.0537000
12	C	1.8282000	2.2180000	-0.9989000
13	H	2.0881000	1.6310000	-1.8735000
14	C	2.1854000	3.5683000	-0.9381000
15	H	2.7304000	4.0137000	-1.7675000
16	C	1.8411000	4.3675000	0.1727000
17	C	2.1932000	5.8362000	0.2101000
18	H	2.2352000	6.2147000	1.2369000
19	H	1.4372000	6.4249000	-0.3275000
20	H	3.1608000	6.0320000	-0.2659000
21	C	1.1285000	3.7624000	1.2246000
22	H	0.8498000	4.3531000	2.0941000
23	C	0.7577000	2.4122000	1.1663000
24	H	0.2144000	1.9624000	1.9926000
25	C	3.1045000	-0.5505000	-0.0788000
26	C	3.8833000	-0.6441000	-1.2631000
27	C	3.2769000	-1.0144000	-2.6141000
28	H	2.1864000	-0.9226000	-2.5351000
29	C	3.6123000	-2.4872000	-2.9539000
30	H	3.1533000	-2.7797000	-3.9064000
31	H	3.2571000	-3.1741000	-2.1756000
32	H	4.6973000	-2.6233000	-3.0440000
33	C	3.7386000	-0.0894000	-3.7611000
34	H	3.5692000	0.9678000	-3.5261000
35	H	3.1876000	-0.3269000	-4.6794000
36	H	4.8063000	-0.2153000	-3.9779000
37	C	5.2720000	-0.4417000	-1.1685000
38	H	5.8829000	-0.5079000	-2.0647000
39	C	5.8779000	-0.1489000	0.0582000
40	H	6.9506000	0.0178000	0.1115000
41	C	5.1000000	-0.0900000	1.2186000
42	H	5.5801000	0.1120000	2.1723000
43	C	3.7087000	-0.3036000	1.1811000
44	C	2.9417000	-0.3502000	2.5003000
45	H	1.8684000	-0.3962000	2.2832000

46	C	3.3230000	-1.6373000	3.2719000
47	H	3.0909000	-2.5382000	2.6911000
48	H	2.7802000	-1.6888000	4.2235000
49	H	4.3968000	-1.6518000	3.4970000
50	C	3.1921000	0.8931000	3.3806000
51	H	2.5485000	0.8606000	4.2689000
52	H	2.9789000	1.8179000	2.8352000
53	H	4.2308000	0.9359000	3.7315000
54	C	-1.1055000	-2.0796000	0.2855000
55	C	-1.1497000	-2.8904000	-0.8878000
56	C	-1.2247000	-2.3198000	-2.3031000
57	H	-1.0406000	-1.2396000	-2.2491000
58	C	-0.1766000	-2.9255000	-3.2594000
59	H	-0.3722000	-3.9874000	-3.4535000
60	H	0.8380000	-2.8416000	-2.8571000
61	H	-0.2080000	-2.4051000	-4.2247000
62	C	-1.2047000	-4.2924000	-0.7459000
63	H	-1.2339000	-4.9158000	-1.6354000
64	C	-1.2427000	-4.8927000	0.5151000
65	H	-1.2853000	-5.9754000	0.6040000
66	C	-1.2531000	-4.0928000	1.6623000
67	H	-1.3168000	-4.5643000	2.6389000
68	C	-1.1926000	-2.6882000	1.5768000
69	C	-1.3094000	-1.8864000	2.8744000
70	H	-0.9924000	-0.8558000	2.6671000
71	C	-2.7868000	-1.8351000	3.3316000
72	H	-3.1553000	-2.8423000	3.5649000
73	H	-3.4343000	-1.4163000	2.5550000
74	H	-2.8868000	-1.2160000	4.2317000
75	C	-0.4210000	-2.4278000	4.0128000
76	H	-0.7754000	-3.3993000	4.3796000
77	H	-0.4428000	-1.7346000	4.8631000
78	H	0.6186000	-2.5470000	3.6913000
79	C	-2.6445000	-2.5321000	-2.8803000
80	H	-2.8599000	-3.6022000	-2.9946000
81	H	-2.7315000	-2.0567000	-3.8641000
82	H	-3.4125000	-2.1077000	-2.2262000
83	C	-4.4713000	2.3087000	-0.6034000
84	C	-1.9656000	2.8479000	-0.6439000
85	C	-3.0059000	1.7148000	1.5158000
86	C	-4.0955000	-0.1638000	-0.0587000
87	C	-2.8150000	0.9435000	-2.1336000

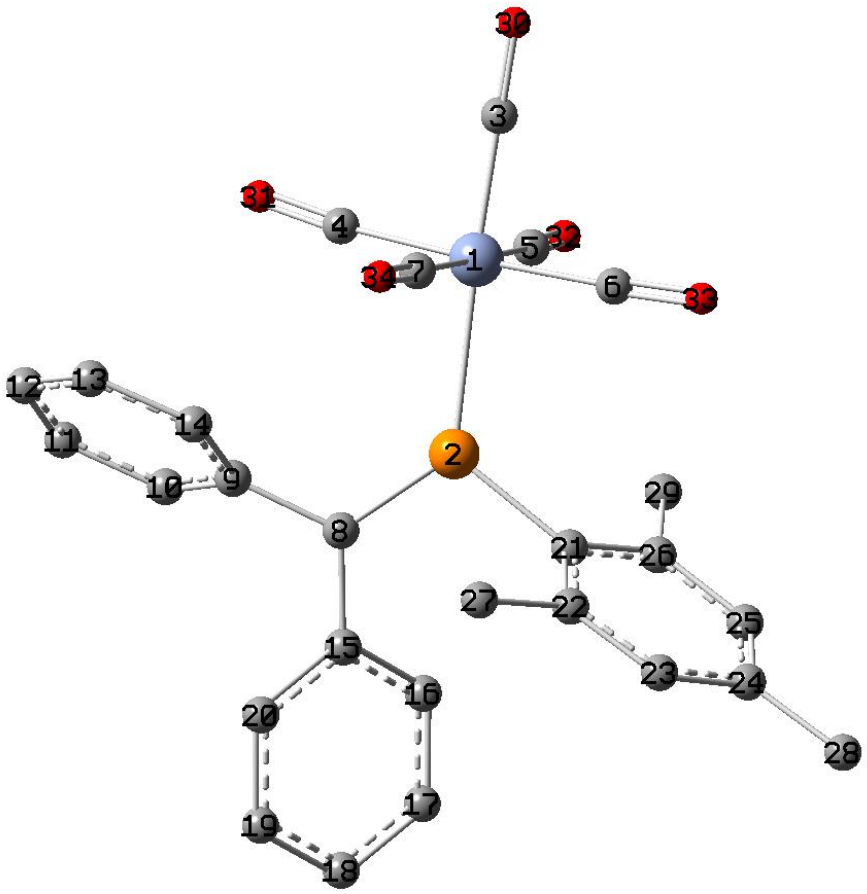

Figure S7. B3PW91/LANL2DZ optimized geometry of **18** with atom labels. The local geometry at the P atom is almost planar, with a deviation of P from the plane of the three connected atoms (P oop) only 0.050 Å.

Table S5. Cartesian Coordinates of the DFT-minimized Geometry of **18**

Tag	Symbol	X	Y	Z
1	Cr	2.0263740	-1.5052590	-0.0719520
2	P	0.0000000	-0.1338930	-0.0894120
3	C	3.4890850	-2.6053720	-0.0257620
4	C	3.1620530	-0.0830410	-0.5240070
5	C	1.8466060	-1.8250030	-1.9057080
6	C	0.9553120	-2.9859970	0.3218180
7	C	2.2379700	-1.1448480	1.7485780
8	C	-0.2078360	1.5936410	-0.1307300
9	C	0.9770300	2.4733270	0.0491160
10	C	1.2640500	3.4754480	-0.9078860
11	C	2.3623280	4.3272930	-0.7393060
12	C	3.1792140	4.2123440	0.4004320
13	C	2.8890510	3.2387150	1.3687260
14	C	1.7999270	2.3716570	1.1925120
15	C	-1.5088110	2.2772630	-0.3196330

16	C	-2.4766460	1.8295550	-1.2483640
17	C	-3.6913450	2.5094730	-1.4040040
18	C	-3.9699800	3.6498060	-0.6317740
19	C	-3.0142500	4.1139030	0.2888210
20	C	-1.7940830	3.4422760	0.4371410
21	C	-1.6870960	-0.9329090	0.1032710
22	C	-2.3387910	-0.8617410	1.3648670
23	C	-3.5723920	-1.5144590	1.5274960
24	C	-4.1760040	-2.2421420	0.4864650
25	C	-3.5078840	-2.3050130	-0.7459680
26	C	-2.2677240	-1.6728650	-0.9556160
27	C	-1.7530810	-0.1079260	2.5400230
28	C	-5.4922650	-2.9541460	0.7014910
29	C	-1.6060490	-1.8224330	-2.3085290
30	O	4.4305920	-3.3169830	0.0091510
31	O	3.9457270	0.7305500	-0.8499240
32	O	1.7822070	-2.0314580	-3.0635690
33	O	0.3253330	-3.9497760	0.5652080
34	O	2.3862280	-0.9229470	2.8967190
35	H	0.6306570	3.5699770	-1.7857740
36	H	2.5831080	5.0784850	-1.4928680
37	H	4.0290400	4.8766530	0.5318450
38	H	3.5075390	3.1509080	2.2577530
39	H	1.5624700	1.6376050	1.9566440
40	H	-2.2619620	0.9678570	-1.8703350
41	H	-4.4164240	2.1539660	-2.1310480
42	H	-4.9134600	4.1755110	-0.7525720
43	H	-3.2178470	4.9988180	0.8859210
44	H	-1.0567530	3.8119050	1.1441750
45	H	-4.0721330	-1.4534070	2.4925340
46	H	-3.9554940	-2.8622920	-1.5669610
47	H	-0.7342230	-0.4425630	2.7718460
48	H	-1.7071140	0.9701060	2.3435730
49	H	-2.3624110	-0.2573130	3.4369770
50	H	-5.3397330	-3.9002670	1.2384800
51	H	-6.1826760	-2.3477840	1.2992910
52	H	-5.9822870	-3.1901730	-0.2490710
53	H	-1.0061320	-0.9480960	-2.5863130
54	H	-0.9356820	-2.6910670	-2.3230210
55	H	-2.3525380	-1.9801540	-3.0945330