Supporting Information

Cooperative Activation of O-H and S-H Bonds Across the Co-P Bond of an N-heterocyclic Phosphido Complex

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Table of Contents

	Pages
Figure S1. ^{1}H NMR spectrum of **2**.	S1
Figure S2. ^{31}P{^{1}H} NMR spectrum of **2**.	S1
Figure S3. ^{13}C{^{1}H} NMR spectrum of **2**.	S1
Figure S4. ^{1}H NMR spectrum of **3**.	S2
Figure S5. ^{31}P{^{1}H} NMR spectrum of **3** with ^{31}P NMR spectrum showing central phosphorus splitting.	S2
Figure S6. ^{1}H NMR spectrum of **4**.	S3
Figure S7. ^{31}P{^{1}H} NMR spectrum of **4**.	S3
Figure S8. ^{13}C{^{1}H} NMR spectrum of **4**.	S3
Figure S9. ^{31}P{^{1}H} NMR spectra monitoring 3,5-dimethylbenzenethiol addition to **3**.	S4
Table S1. X-ray data collection, solution, and refinement details for **2**.	S5
Figure S10. Fully labeled ellipsoid representation of **2**.	S6
X-Ray data collection, solution, and refinement details for **2**.	S6-S7
Figure S11. ac projection showing cavity area.	S8
Table S2. DFT-optimized XYZ coordinates for **2**.	S8-S10
Table S3. DFT-optimized XYZ coordinates for **2***.	S11-S13
Table S4. DFT-optimized XYZ coordinates for **3**.	S14-S16
Table S5. DFT-optimized XYZ coordinates for **4**.	S17-S19
Table S6. Energy comparisons of **2** and **2***, **3** and **4**.	S20
References	S21

Figure S1. ^{1}H NMR spectrum of **2** with hydride resonance as inset (400 MHz, C_6D_6). Stars denote residual solvent, in this case C_6D_5H.

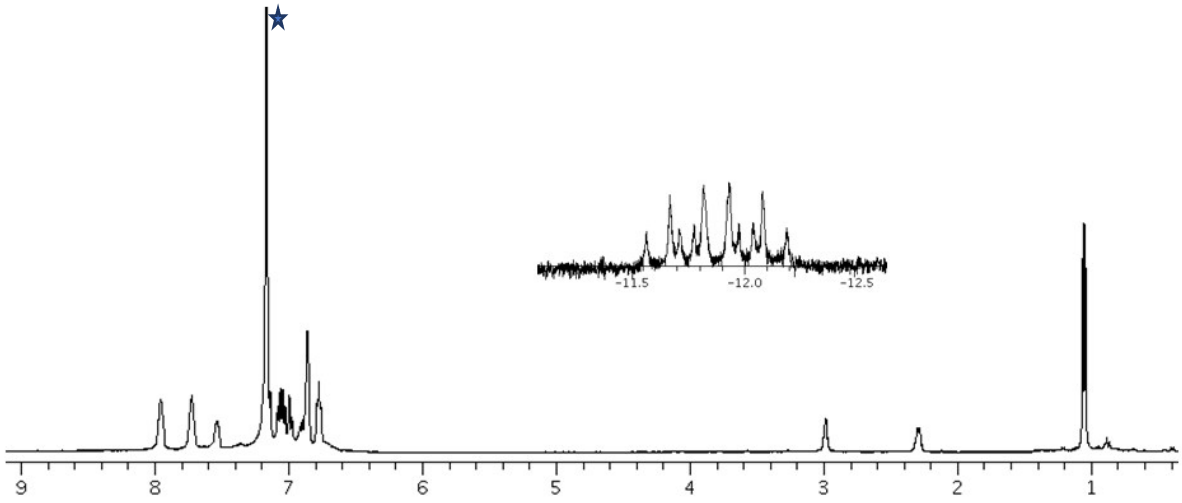


Figure S2. $^{31}P\{^{1}H\}$ NMR spectrum of **2** (161.8 MHz, C_6D_6).

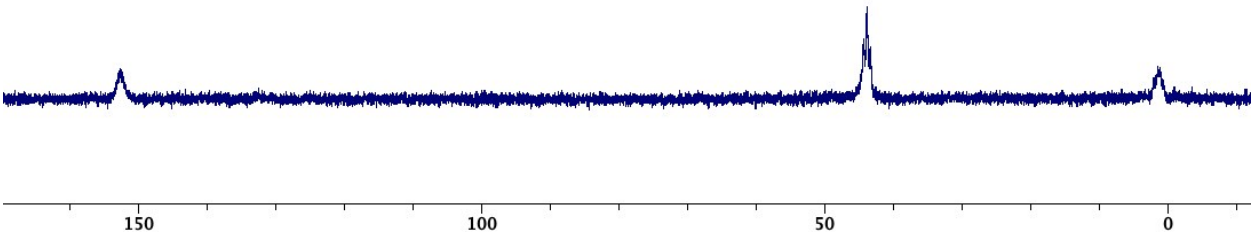


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of **2** (100.5 MHz, C_6D_6). Stars denote residual solvent, in this case C_6D_6 and toluene.

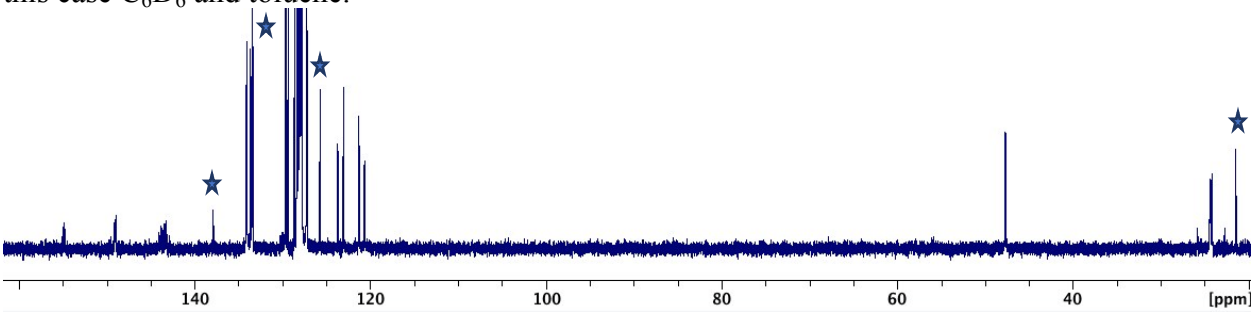


Figure S4. ^{1}H NMR spectrum of **3** (400 MHz, C_6D_6). Stars denote residual solvent, in this case C_6D_5H and THF. Diamonds denote resonances that correspond to **4**.

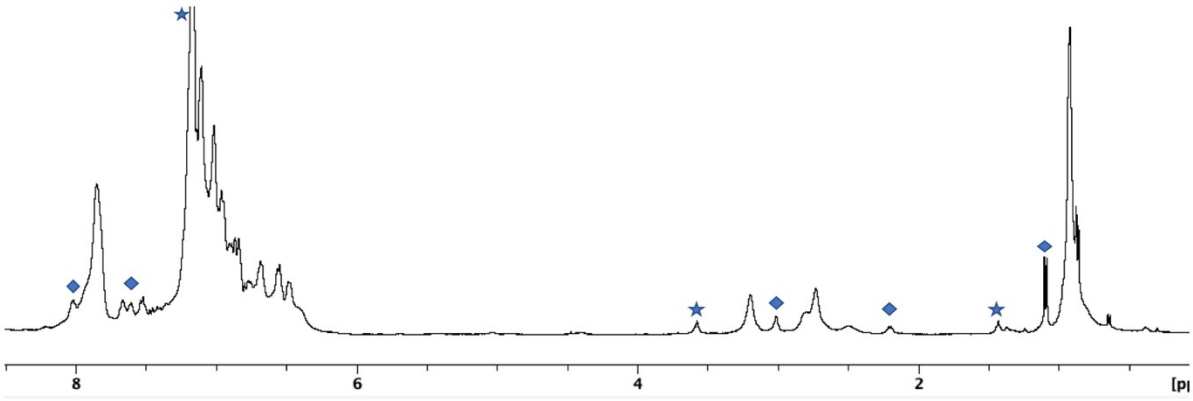


Figure S5. ^{31}P{^{1}H} NMR spectrum of **3** with ^{31}P NMR spectrum of the central phosphorus resonance (inset) showing $^{1}J_{P\text{-}H}$ coupling (161.8 MHz, C_6D_6).

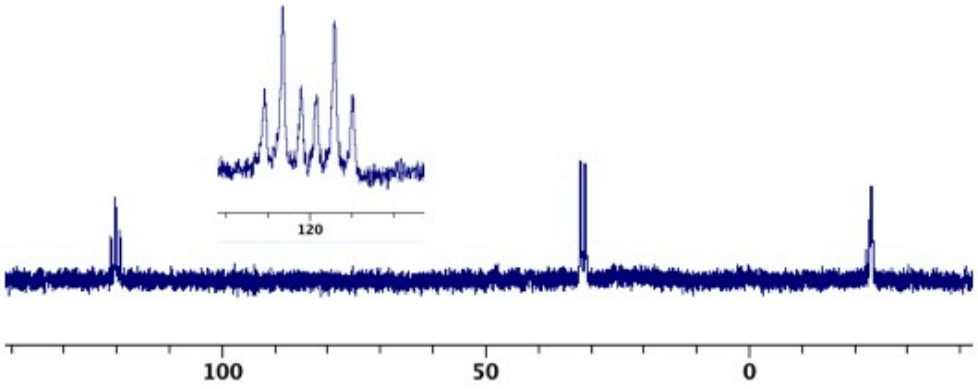


Figure S6. ^{1}H NMR spectrum of **4** with hydride resonance as inset (400 MHz, C_6D_6). Stars denote residual solvent, in this case C_6D_5H.

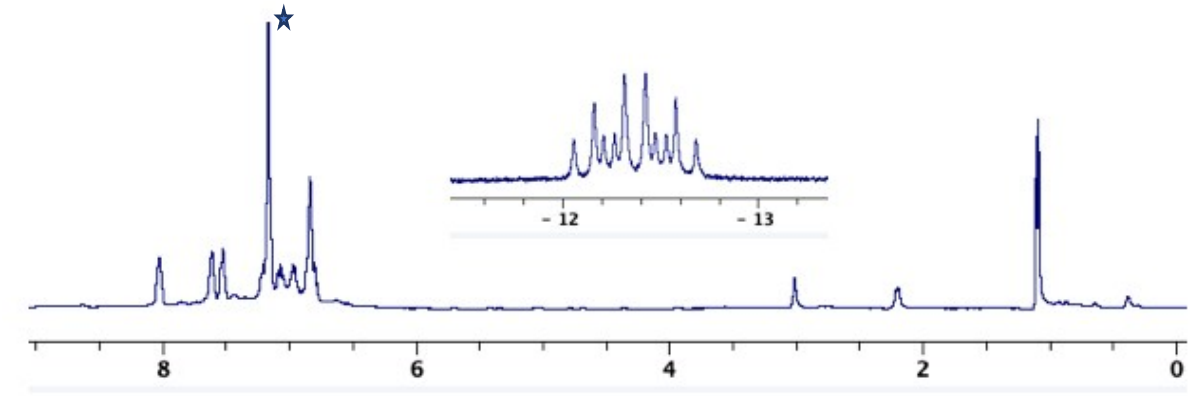


Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum of **4** (161.8 MHz, C_6D_6).

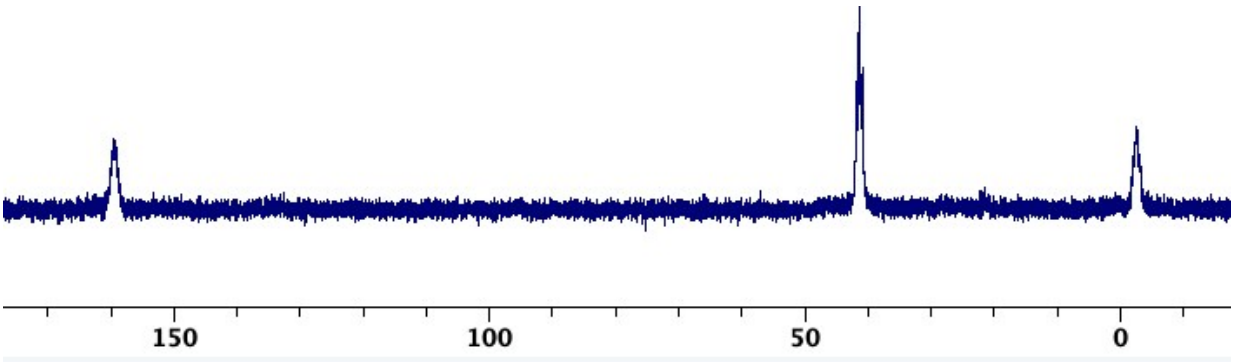


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of **4** (100.5 MHz, C_6D_6). Stars denote residual solvent, in this case C_6D_6.

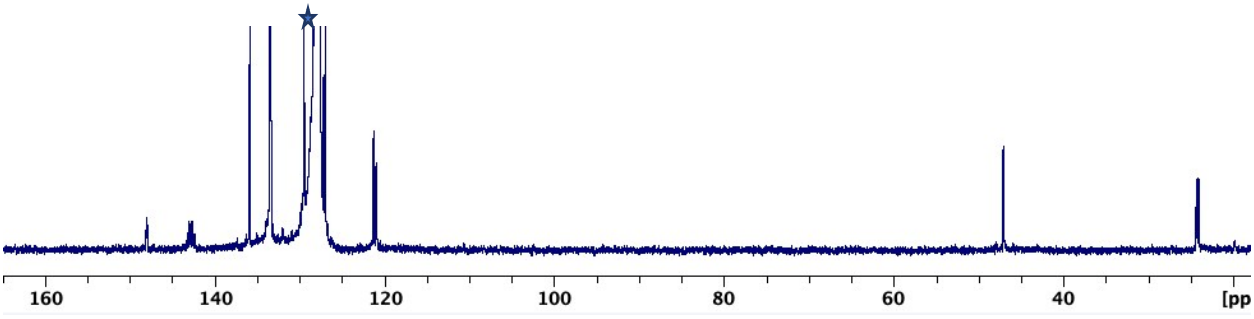
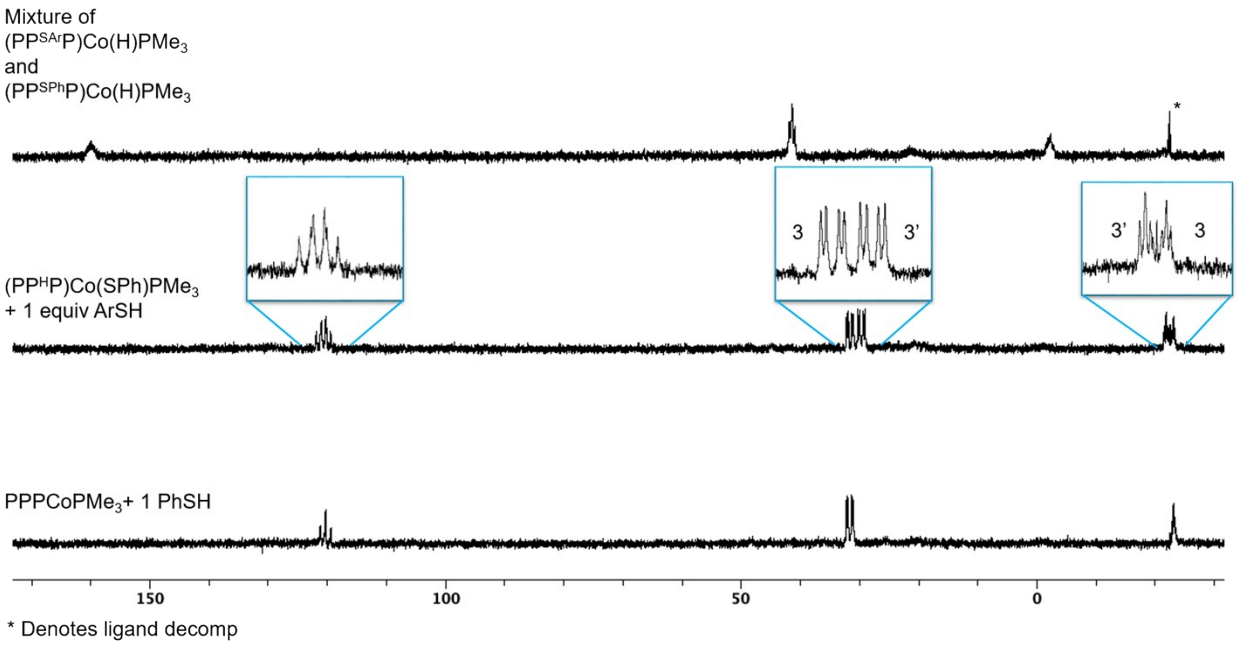


Figure S9. $^{31}P\{^{1}H\}$ NMR spectra of $(PP^{H}P)Co(SPh)PMe_3$ (**3**) generated *in situ* via addition of 1 equiv PhSH to $(PPP)CoPMe_3$ (**1**) in C_6D_6 (bottom), the roughly 50:50 mixture of **3** and $(PP^{H}P)Co(SAr)PMe_3$ (**3'**, Ar = 3,5-dimethylphenyl) generated via addition of 3,5-dimethylbenzenethiol to the aforementioned sample of **3** (middle), and the spectroscopically indistinguishable mixture of $(PP^{SPh}P)Co(H)PMe_3$ (**4**) and $(PP^{SAr}P)Co(H)PMe_3$ (**4'**) generated upon allowing this mixture to react for 67 hours.



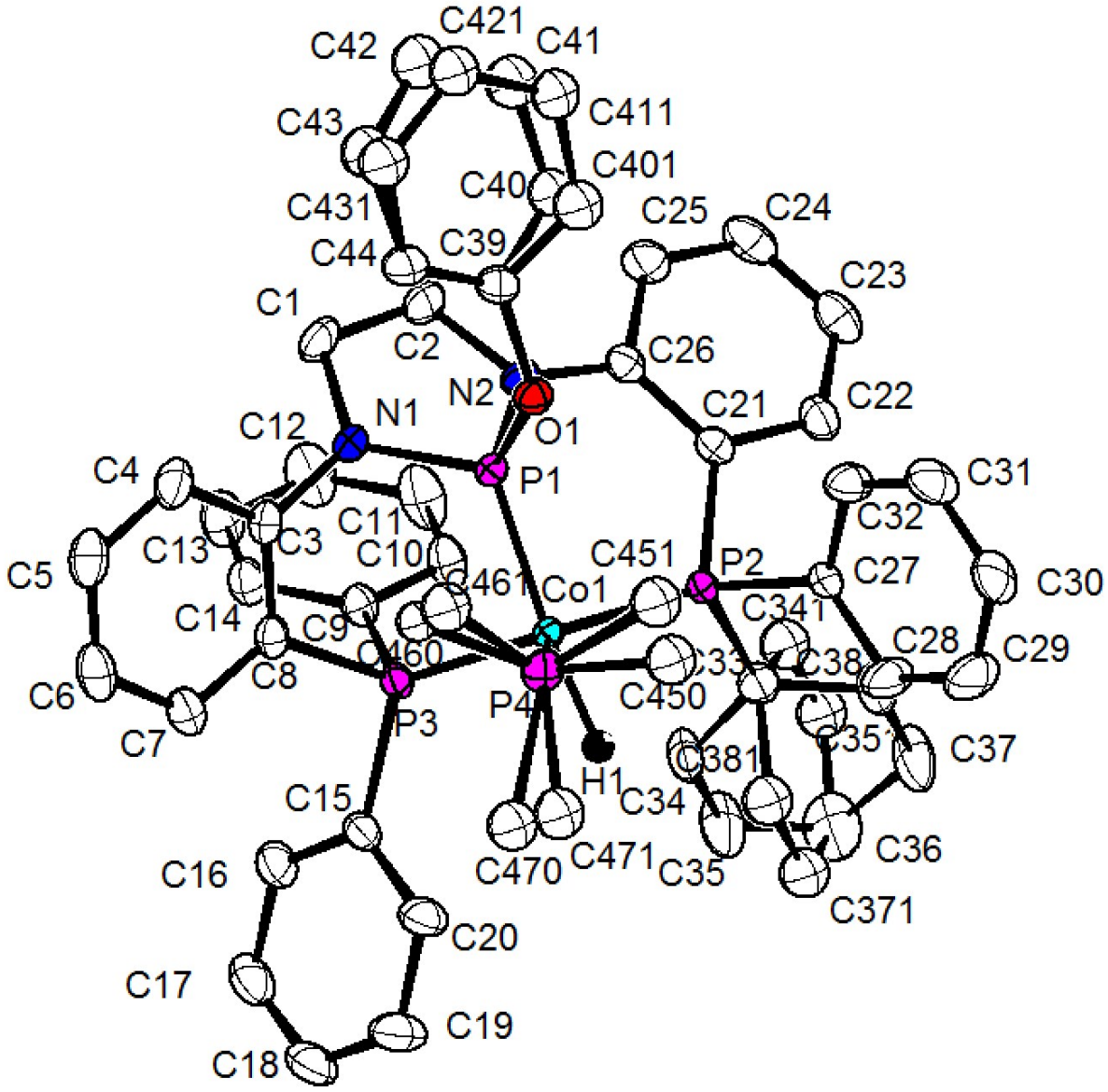
* Denotes ligand decomp

Table S1. X-Ray data collection, solution, and refinement details for complex **2**.

	2
Chemical formula	$C_{47}H_{47}CoN_2OP_4$
fw	838.73
T (K)	120
λ (Å)	0.71073
a (Å)	11.4224(7)
b (Å)	12.7223(7)
c (Å)	16.9771(10)
α (deg)	80.067(3)
β (deg)	75.461(3)
γ (deg)	77.245(3)
V (Å^3)	2311.2(2)
Space group	$P\bar{1}$
Z, Z'	2, 1
$Dcalcd$ (g/cm^3)	1.168
μ (cm^{-1})	5.44
R_1 (I > 2σ(I))[a]	0.0420
wR_2 (all data)[a]	0.1144

[a] $R_1 = \sum||F_o| - |F_o||/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)_2]/\sum[w(F_o^2)^2]\}^{1/2}$

Figure S10. Fully labeled ellipsoid representation of **2** (protons except for the hydride have been omitted for clarity).

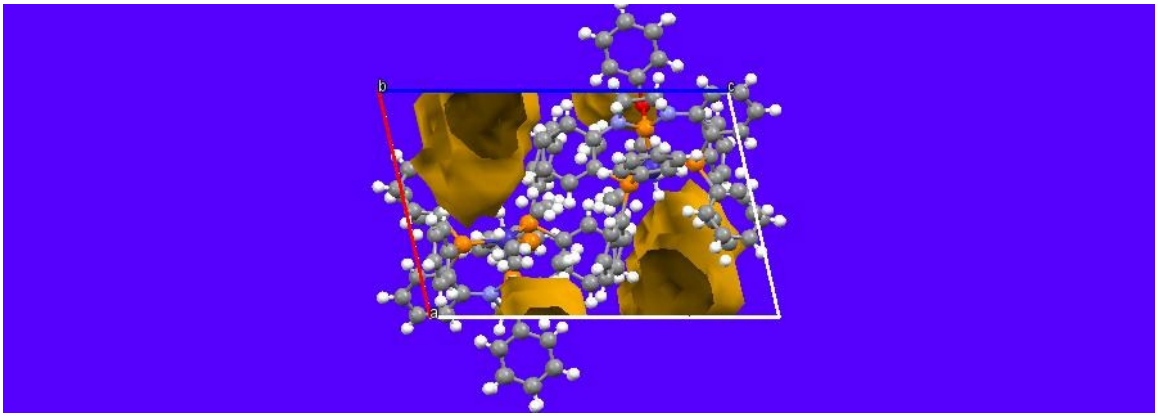


X-Ray data collection, solution, and refinement details for 2. All operations were performed on a Bruker-Nonius Kappa Apex2 diffractometer, using graphite-monochromated MoKα radiation. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections were carried out using the Bruker Apex2 software.[1] Preliminary cell constants were obtained from three sets of 12 frames. Data collection was carried out at 120 K, using a frame time of 20 seconds and a detector distance of 60 mm. The optimized strategy used for data collection consisted of four phi and seven omega scan sets, with 0.5° steps in phi or omega; completeness was 99.6%. A total of 3625 frames were collected. Final cell constants were obtained from the xyz centroids of 9870 reflections after integration.

From the systematic absences, the observed metric constants and intensity statistics, space group $P\bar{1}$ was chosen initially; subsequent solution and refinement confirmed the correctness of this choice. The structure was solved using *SIR-92*,[2] and refined (full-matrix-least

squares) using the Oxford University *Crystals for Windows* program.[3, 4] The asymmetric unit contains one molecule of the complex, and likely one molecule of highly disordered toluene, modeled using the SQUEEZE procedure (see below) ($Z = 2$; $Z' = 1$). All ordered non-hydrogen atoms were refined using anisotropic displacement parameters. After location of H atoms on electron-density difference maps, the H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C---H in the range 0.93--0.98 Å and U_{iso} (H) in the range 1.2-1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.[5] During the structure solution, electron density difference maps revealed that there were considerable disordered solvent molecules which could not be successfully modeled. From history, the remaining solvate was toluene in a volume of 412.7 Å^3 per unit cell (17.9%). It appeared that the cavity areas contained about two solvate molecules, located near ±(0.186, 0.226, 0.246), as shown in the *ac* projection below.[6]

Figure S11: ac projection showing cavity area.



Modeling with or without restraints was unsuccessful, as was step by step acquisition of peaks using successive electron density difference maps. Thus, the structure factors were modified using the PLATON SQUEEZE[7-9] technique, in order to produce a "solvate-free" structure factor set. PLATON reported a total electron density of 102 e- per unit cell, likely representing two toluene molecules, consistent with our earlier observations. Use of the SQUEEZE technique resulted in a decrease of ca. 4.4 % in R. Electron density difference maps as well as large ADPs suggested disorder on the PMe_3 group as well as one of the phenyl rings attached to P(2), and the phenyl ring attached to O(1). Test refinement showed that the phenyl ring disorder was correlated, and thus two pairs of the four ring orientations were placed into the same PARTs. The disorder was modeled in each case as a two-component disorder, and each component was refined such that the sum of the paired occupancies was constrained to be 1.0. The components and their occupancies are: phenyl ring disorder: [C(34,35,36,37,38,40,41,42,43) major / C(341,351,361,371,381,401,411,421,431) minor; occupancies 0.828/0.172(3)]; PMe_3 disorder: [C(451,460,471) major / C(450,461,470) minor; occupancies 0.600/0.400(9)] The disordered components were refined using isotropic displacement parameters. Distance, angle and vibration restraints were applied to a number of the atoms in the disordered phenyl groups; details appear in the CIF file. The final least-squares refinement converged to $R_1 = 0.0420$ ($I > 2\sigma(I)$, 10016 data) and $wR_2 = 0.1144$ (F^2, 13466 data, 511 parameters). The final CIF is available as supporting material.

Table S2. DFT-optimized XYZ coordinates of **2**.[10]

Tag	Symbol	X	Y	Z
1	Co	-0.285302	0.429646	-0.854871
2	P	-2.209137	-0.282759	-0.015203
3	P	0.66377	-1.204328	0.053106
4	P	1.056484	1.868389	0.076963
5	P	0.052055	-0.057994	-3.009927
6	O	1.986895	-1.886169	-0.820046
7	N	-0.273482	-2.575778	0.514947
8	N	1.320619	-1.08939	1.656853
9	C	-3.828265	0.521969	-0.506393
10	C	-5.038408	0.35054	0.208708
11	C	-6.224012	0.974819	-0.220516
12	C	-6.225119	1.780628	-1.375989
13	C	-5.027021	1.965216	-2.091144
14	C	-3.840452	1.345314	-1.655776
15	C	-2.441757	-0.472263	1.84838
16	C	-1.797896	0.445434	2.708301
17	C	-1.945209	0.359229	4.105438
18	C	-2.731618	-0.66119	4.673373
19	C	-3.36637	-1.594133	3.829698
20	C	-3.224615	-1.49774	2.432833
21	C	-2.474227	-2.069868	-0.506789
22	C	-3.601927	-2.536248	-1.21354
23	C	-3.746933	-3.895844	-1.55341
24	C	-2.753223	-4.818043	-1.179588
25	C	-1.605492	-4.370787	-0.500836
26	C	-1.447429	-3.007777	-0.174012
27	C	0.262722	-3.31744	1.675418
28	C	1.068055	-2.285703	2.510865
29	C	1.95222	0.047042	2.231323
30	C	2.621485	-0.148327	3.476402
31	C	3.293624	0.886149	4.135511
32	C	3.328224	2.171002	3.569147
33	C	2.663739	2.382135	2.354029
34	C	1.959815	1.368096	1.658117
35	C	2.497632	2.398662	-0.996811
36	C	3.78926	1.843025	-0.857864
37	C	4.814864	2.158877	-1.769286

38	C	4.569354	3.040417	-2.838357
39	C	3.28412	3.601063	-2.988798
40	C	2.25916	3.276406	-2.084031
41	C	0.342892	3.553568	0.524167
42	C	1.103506	4.747212	0.587618
43	C	0.504416	5.971227	0.934482
44	C	-0.871999	6.030348	1.227639
45	C	-1.644385	4.856722	1.148458
46	C	-1.042075	3.636024	0.79162
47	C	2.843238	-2.942578	-0.460236
48	C	2.654645	-4.204006	-1.058673
49	C	3.544212	-5.252596	-0.76106
50	C	4.617044	-5.045777	0.129503
51	C	4.800746	-3.77693	0.714968
52	C	3.919252	-2.720158	0.42211
53	C	1.811497	-0.12996	-3.631278
54	C	-0.694829	1.105132	-4.268791
55	C	-0.578205	-1.690604	-3.6771
56	H	-0.948574	1.65287	-1.404197
57	H	-5.061304	-0.256131	1.108411
58	H	-7.141221	0.834144	0.347221
59	H	-7.142029	2.263531	-1.70651
60	H	-5.010574	2.59664	-2.976835
61	H	-2.908597	1.516175	-2.185535
62	H	-1.164215	1.220515	2.289385
63	H	-1.439672	1.081133	4.742695
64	H	-2.844062	-0.7317	5.753025
65	H	-3.972215	-2.391674	4.255051
66	H	-3.715211	-2.234101	1.801508
67	H	-4.389539	-1.838345	-1.483418
68	H	-4.632217	-4.227474	-2.090402
69	H	-2.859392	-5.872095	-1.42522
70	H	-0.820962	-5.075668	-0.235238
71	H	0.90974	-4.150149	1.368234
72	H	-0.56673	-3.724235	2.264214
73	H	2.008615	-2.744411	2.840477
74	H	0.500388	-1.974501	3.397674
75	H	2.626414	-1.128907	3.935091
76	H	3.790544	0.682499	5.081519
77	H	3.851013	2.988134	4.058511

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79	H	4.002394	1.166047	-0.035508
80	H	5.800458	1.716396	-1.642058
81	H	5.361708	3.287068	-3.541247
82	H	3.080583	4.285507	-3.809691
83	H	1.271451	3.710565	-2.22116
84	H	2.160137	4.73781	0.334403
85	H	1.109792	6.874516	0.969636
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87	H	-1.654876	2.747847	0.678732
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92	H	4.060747	-1.735098	0.856747
93	H	2.279907	0.853186	-3.520616
94	H	1.848215	-0.432681	-4.68797
95	H	2.365026	-0.847946	-3.017989
96	H	-0.34988	2.125639	-4.064921
97	H	-0.410729	0.822828	-5.2925
98	H	-1.788653	1.087713	-4.186512
99	H	-0.054104	-2.511963	-3.173458
100	H	-1.649323	-1.791088	-3.468044
101	H	-0.409781	-1.772068	-4.760715
102	H	-1.335659	6.976816	1.496794

Table S3. DFT-optimized XYZ coordinates of **2***.[10]

Tag	Symbol	X	Y	Z
1	Co	0.031546	-0.02668	-0.7495
2	P	-2.06384	0.135577	0.238348
3	P	-0.22299	-2.13568	-0.73166
4	P	2.129679	-0.34742	0.089113
5	P	-0.18739	-0.02161	-3.14378
6	N	-1.77658	-2.85873	-0.43575
7	N	0.519442	-3.22583	0.410917
8	C	-2.96092	1.765509	0.287963
9	C	-3.87843	2.120217	1.303171
10	C	-4.54327	3.359713	1.264959
11	C	-4.30539	4.260117	0.209114
12	C	-3.38578	3.918513	-0.80077
13	C	-2.71532	2.683749	-0.75882
14	C	-2.29494	-0.52054	1.978123
15	C	-1.22171	-0.37719	2.884466
16	C	-1.3328	-0.82421	4.213662
17	C	-2.51983	-1.43973	4.655048
18	C	-3.59262	-1.60178	3.756121
19	C	-3.48275	-1.14205	2.430594
20	C	-3.30877	-0.93397	-0.66251
21	C	-4.53591	-0.43464	-1.14797
22	C	-5.47102	-1.26346	-1.79705
23	C	-5.18543	-2.62866	-1.9686
24	C	-3.95948	-3.1478	-1.51932
25	C	-3.01194	-2.31533	-0.88045
26	C	-1.61635	-4.29458	-0.15183
27	C	-0.32738	-4.41547	0.698098
28	C	1.803179	-3.1211	0.992521
29	C	2.287572	-4.23045	1.74903
30	C	3.561154	-4.23028	2.327707
31	C	4.406381	-3.1161	2.179112
32	C	3.929896	-2.00837	1.467522
33	C	2.643931	-1.96651	0.871143
34	C	3.402524	-0.11371	-1.26371
35	C	4.37606	-1.0804	-1.60744
36	C	5.26813	-0.85761	-2.67476
37	C	5.212357	0.33946	-3.41173

38	C	4.236139	1.303013	-3.08734
39	C	3.330513	1.074369	-2.03705
40	C	2.72486	0.817298	1.432427
41	C	3.435545	2.006049	1.161746
42	C	3.812435	2.871747	2.205299
43	C	3.485384	2.567752	3.537854
44	C	2.779038	1.382238	3.820334
45	C	2.401562	0.519313	2.779003
46	H	-4.06955	1.44392	2.130631
47	H	-5.23991	3.620196	2.058764
48	H	-4.81474	5.220759	0.183358
49	H	-3.16902	4.62003	-1.60264
50	H	-1.96604	2.44993	-1.50789
51	H	-0.29585	0.073388	2.541402
52	H	-0.49642	-0.69729	4.897429
53	H	-2.60707	-1.79086	5.680848
54	H	-4.51279	-2.07974	4.085534
55	H	-4.31963	-1.27758	1.750661
56	H	-4.77908	0.612443	-0.99969
57	H	-6.41145	-0.84644	-2.14765
58	H	-5.90133	-3.28497	-2.45787
59	H	-3.73366	-4.19839	-1.67998
60	H	-1.51611	-4.88684	-1.07859
61	H	-2.48323	-4.67138	0.400869
62	H	0.195023	-5.34646	0.438638
63	H	-0.56907	-4.44041	1.769323
64	H	1.665236	-5.1054	1.887667
65	H	3.888985	-5.10011	2.892696
66	H	5.400086	-3.10243	2.617441
67	H	4.565549	-1.13121	1.386194
68	H	4.444609	-2.01158	-1.05473
69	H	6.005642	-1.61799	-2.92239
70	H	5.909237	0.51594	-4.22789
71	H	4.172228	2.227476	-3.65761
72	H	2.534713	1.785467	-1.83016
73	H	3.702781	2.270771	0.145657
74	H	4.349049	3.787201	1.968848
75	H	2.526924	1.127498	4.847629
76	H	1.88467	-0.40524	3.023321
77	C	1.102836	-0.90309	-4.17773

78	C	-0.15428	1.668283	-3.92631
79	C	-1.72853	-0.72518	-3.94545
80	H	2.084413	-0.45184	-4.00267
81	H	0.862175	-0.84115	-5.24871
82	H	1.157181	-1.96076	-3.89
83	H	0.724146	2.209872	-3.56697
84	H	-0.1351	1.590675	-5.02234
85	H	-1.04069	2.2349	-3.61934
86	H	-1.80756	-1.80084	-3.74155
87	H	-2.61849	-0.24051	-3.52878
88	H	-1.71138	-0.5759	-5.03436
89	H	0.135182	-2.85143	-1.93953
90	O	0.491739	1.867002	-0.96275
91	C	0.49247	2.99549	-0.2053
92	C	0.914113	4.211228	-0.82217
93	C	0.098493	3.05579	1.158798
94	C	0.942706	5.418792	-0.10609
95	H	1.208611	4.18236	-1.87001
96	C	0.128239	4.267996	1.865978
97	H	-0.22549	2.147607	1.655855
98	C	0.550203	5.463003	1.248258
99	H	1.269826	6.328645	-0.60827
100	H	-0.18033	4.277238	2.910489
101	H	0.569114	6.398404	1.802474
102	H	3.773617	3.240548	4.342104

Table S4. DFT-optimized XYZ coordinates of **3**.[10]

Tag	Symbol	X	Y	Z
1	Co	0.067209	-0.254113	-0.786789
2	P	-2.038339	-0.084757	0.111284
3	P	0.066987	-2.286766	-0.185977
4	P	2.184445	-0.077073	0.060922
5	P	-0.009336	-0.92248	-3.070796
6	N	-1.399055	-3.088045	0.289315
7	N	0.882872	-2.913066	1.223918
8	C	-3.115905	1.379235	-0.281389
9	C	-3.817577	2.123248	0.692003
10	C	-4.613658	3.222165	0.318496
11	C	-4.722631	3.593366	-1.033935
12	C	-4.018	2.864191	-2.011461
13	C	-3.216814	1.772533	-1.637085
14	C	-2.247525	-0.299467	1.964137
15	C	-1.122882	-0.145969	2.801223
16	C	-1.229907	-0.311212	4.194997
17	C	-2.469715	-0.641467	4.773086
18	C	-3.599321	-0.808211	3.946002
19	C	-3.488554	-0.63916	2.554447
20	C	-3.145639	-1.497993	-0.437706
21	C	-4.424889	-1.306359	-1.001181
22	C	-5.250772	-2.38944	-1.357977
23	C	-4.797645	-3.703518	-1.152677
24	C	-3.518168	-3.924351	-0.616166
25	C	-2.68333	-2.838697	-0.26452
26	C	-1.086483	-4.35109	0.9794
27	C	0.169201	-4.064238	1.838123
28	C	2.134189	-2.505561	1.735333
29	C	2.718008	-3.287462	2.777912
30	C	3.978863	-2.990598	3.304984
31	C	4.710661	-1.894924	2.812203
32	C	4.130818	-1.098592	1.81759
33	C	2.849612	-1.356892	1.265647
34	C	3.482631	-0.152208	-1.296271
35	C	4.423755	-1.206755	-1.38661
36	C	5.324709	-1.287449	-2.465704
37	C	5.312264	-0.312263	-3.479479

38	C	4.372986	0.735217	-3.409755
39	C	3.462432	0.808682	-2.340994
40	C	2.645622	1.456006	1.041667
41	C	3.182684	2.618083	0.447051
42	C	3.452429	3.763457	1.219614
43	C	3.191896	3.771711	2.600469
44	C	2.657725	2.61825	3.205497
45	C	2.384991	1.477531	2.434179
46	H	-3.737351	1.86637	1.743054
47	H	-5.136196	3.789785	1.084944
48	H	-5.333276	4.446363	-1.321131
49	H	-4.07617	3.154353	-3.057947
50	H	-2.647307	1.243091	-2.394137
51	H	-0.162531	0.090074	2.352782
52	H	-0.350512	-0.185222	4.822732
53	H	-2.556176	-0.770154	5.849751
54	H	-4.561363	-1.068078	4.382231
55	H	-4.3668	-0.782608	1.930358
56	H	-4.796885	-0.29738	-1.145222
57	H	-6.236089	-2.202523	-1.776912
58	H	-5.425696	-4.551679	-1.415047
59	H	-3.163449	-4.942769	-0.483661
60	H	-0.879608	-5.167256	0.265022
61	H	-1.927732	-4.655859	1.610218
62	H	0.806769	-4.958591	1.862539
63	H	-0.113571	-3.811558	2.869054
64	H	2.183751	-4.138592	3.180703
65	H	4.386614	-3.616187	4.095956
66	H	5.696131	-1.656674	3.20193
67	H	4.680554	-0.231709	1.462604
68	H	4.462352	-1.972848	-0.619771
69	H	6.035229	-2.110172	-2.507101
70	H	6.014184	-0.36953	-4.308209
71	H	4.340839	1.492795	-4.189946
72	H	2.70939	1.592243	-2.335166
73	H	3.392069	2.650115	-0.614482
74	H	3.856124	4.648784	0.734206
75	H	2.451935	2.605525	4.273684
76	H	1.994309	0.593609	2.930845
77	C	1.394476	-1.965906	-3.743266

78	C	-0.09727	0.368288	-4.417429
79	C	-1.45105	-2.001797	-3.592345
80	H	2.322222	-1.385115	-3.733866
81	H	1.180933	-2.28531	-4.773218
82	H	1.543044	-2.85805	-3.122698
83	H	0.783139	1.017078	-4.370241
84	H	-0.144636	-0.1178	-5.401787
85	H	-0.978609	1.002177	-4.274803
86	H	-1.452432	-2.942415	-3.02751
87	H	-2.39713	-1.489277	-3.385871
88	H	-1.39483	-2.236562	-4.664683
89	H	0.561869	-3.261883	-1.136732
90	S	0.201822	1.960081	-1.576905
91	C	-0.129948	3.29607	-0.436848
92	C	-0.138898	4.613706	-0.97238
93	C	-0.389358	3.143588	0.944198
94	C	-0.398717	5.726165	-0.156403
95	H	0.054972	4.752725	-2.034521
96	C	-0.649768	4.259401	1.759511
97	H	-0.374938	2.152133	1.380495
98	C	-0.658957	5.55932	1.220469
99	H	-0.401691	6.722157	-0.596241
100	H	-0.841496	4.107564	2.820633
101	H	-0.861376	6.420451	1.853525
102	H	3.395123	4.660278	3.193323

Table S5. DFT-optimized XYZ coordinates of **4**.[10]

Tag	Symbol	X	Y	Z
1	Co	-0.596288	0.351829	-0.843444
2	P	-1.903648	-1.215371	0.049961
3	P	1.069626	-0.721154	-0.118755
4	P	0.057798	2.192946	0.125245
5	P	-0.456388	0.132697	-3.076259
6	N	0.875912	-2.389479	0.26953
7	N	1.702707	-0.407306	1.466595
8	C	-3.759781	-1.211512	-0.214852
9	C	-4.634035	-2.140095	0.402432
10	C	-6.020868	-2.083306	0.178705
11	C	-6.564767	-1.092646	-0.66359
12	C	-5.708604	-0.158019	-1.27345
13	C	-4.319308	-0.217542	-1.048594
14	C	-1.825262	-1.623008	1.892961
15	C	-1.610651	-0.571141	2.81181
16	C	-1.565419	-0.814488	4.197375
17	C	-1.720378	-2.123045	4.693199
18	C	-1.917576	-3.184786	3.788314
19	C	-1.971738	-2.935493	2.40433
20	C	-1.377032	-2.880341	-0.623581
21	C	-2.214935	-3.750172	-1.35157
22	C	-1.74443	-4.985456	-1.839375
23	6	-0.413397	-5.371717	-1.598808
24	C	0.449474	-4.505167	-0.904387
25	C	-0.012328	-3.260869	-0.428748
26	C	1.753172	-2.87035	1.356666
27	C	2.057704	-1.631332	2.241021
28	C	1.869072	0.871282	2.057726
29	C	2.66843	0.944528	3.237406
30	C	2.934233	2.155447	3.884354
31	C	2.413996	3.354554	3.368527
32	C	1.604106	3.293989	2.227443
33	C	1.287856	2.088124	1.554192
34	C	0.920464	3.399312	-1.013647
35	C	2.328694	3.440431	-1.12587
36	C	2.95256	4.25678	-2.087703
37	C	2.180733	5.050711	-2.956622

38	C	0.774826	5.013947	-2.85835
39	C	0.152684	4.190237	-1.904332
40	C	-1.288998	3.304428	0.837715
41	C	-1.155654	4.70378	1.015009
42	C	-2.196969	5.466971	1.572069
43	C	-3.399955	4.848601	1.965212
44	C	-3.556375	3.463591	1.773326
45	C	-2.513915	2.705839	1.208062
46	C	4.257549	-1.459456	-0.629501
47	C	4.614979	-2.746617	-1.097011
48	C	5.696046	-3.438687	-0.520019
49	C	6.432741	-2.855349	0.530638
50	C	6.087721	-1.569138	0.992392
51	C	5.010957	-0.871677	0.413846
52	H	-1.76892	1.209891	-1.206691
53	H	-4.242567	-2.903321	1.067867
54	H	-6.674014	-2.805233	0.664058
55	H	-7.638173	-1.047238	-0.833529
56	H	-6.115912	0.61931	-1.916296
57	H	-3.660855	0.517918	-1.500963
58	H	-1.461361	0.440555	2.448913
59	H	-1.401545	0.015151	4.881275
60	H	-1.683006	-2.313071	5.763559
61	H	-2.031468	-4.202396	4.15645
62	H	-2.109221	-3.771977	1.723725
63	H	-3.251521	-3.475632	-1.524743
64	H	-2.416248	-5.640129	-2.389057
65	H	-0.043401	-6.327772	-1.961388
66	H	1.489025	-4.782043	-0.745138
67	H	2.684232	-3.305021	0.972126
68	H	1.225758	-3.635586	1.936579
69	H	3.120081	-1.63762	2.510212
70	H	1.459855	-1.650713	3.161682
71	H	3.097595	0.041098	3.651875
72	H	3.552447	2.158436	4.779426
73	H	2.622022	4.30873	3.844646
74	H	1.197431	4.223696	1.847705
75	H	2.943227	2.832924	-0.468397
76	H	4.038163	4.268864	-2.156343
77	H	2.663262	5.68466	-3.696916

78	H	0.165098	5.621103	-3.524195
79	H	-0.933214	4.165718	-1.852065
80	H	-0.255088	5.215824	0.688828
81	H	-2.070095	6.540768	1.692347
82	H	-4.487435	2.973091	2.048358
83	H	-2.662498	1.648768	1.015456
84	H	4.04955	-3.19117	-1.912152
85	H	5.964197	-4.424954	-0.89219
86	H	7.269179	-3.389993	0.974588
87	H	6.660457	-1.105023	1.792228
88	H	4.756036	0.126221	0.75957
89	C	0.783373	1.166957	-4.021774
90	C	-2.004665	0.554326	-4.035871
91	C	-0.079695	-1.544261	-3.814992
92	H	0.615878	2.229701	-3.819321
93	H	0.698124	0.984534	-5.103109
94	H	1.797871	0.913972	-3.694673
95	H	-2.298117	1.587394	-3.813314
96	H	-1.841519	0.448528	-5.117836
97	H	-2.822243	-0.109964	-3.732007
98	H	0.913819	-1.868477	-3.484711
99	H	-0.815986	-2.276274	-3.465265
100	H	-0.098493	-1.505794	-4.913696
101	S	2.913454	-0.554615	-1.418151
102	H	-4.20483	5.438732	2.397736

Table S6. Energy comparisons of **2** and **2*** and **3** and **4.**

Complex	Energy (kcal/mol)	Difference (Kcal/mol)
2	-1364339.88	10.94
2*	-1364328.94	
3	-1323482.06	4.5
4	-1323486.56	

References:

1. *Apex 2: Version 2 User Manual, M86-E01078*, Bruker Analytical X-ray Systems, Madison, WI, 2006.
2. A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Cryst.*, 1994, **27**, 435-436.
3. P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout and D. J. Watkin, *J. Appl. Crystallogr.*, 2003, **36**, 1487.
4. C. K. Prout and L. J. Pearce, *Cameron*, Cambridge Crystallography Laboratory, Oxford, UK, 1996.
5. R. I. Cooper, A. L. Thompson and D. J. Watkin, *J. Appl. Crystallogr.*, 2010, **43**, 1100-1107.
6. C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *J. Appl. Crystallogr.*, 2008, **41**, 466-470.
7. A. Spek, *Acta Crystallographica Section C*, 2015, **71**, 9-18.
8. A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 1998.
9. P. van der Sluis and A. L. Spek, *Acta Crystallogr., Sect. A.*, 1990, **A46**, 194-201.
10. M. J. T. Frisch, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009., *Journal*.