Supplementary Material (ESI) for Chemical Communications

Supplementary Information

"The synthesis, characterisation and electronic structure of *N*-heterocyclic carbene adducts of P(I)"

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This package contains a discussion of Lewis-type bonding models, a summary of DFT and semi-empirical calculation results.

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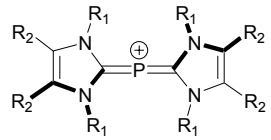
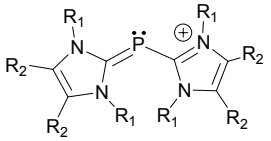
Bonding Models for Phosphamethine Cyanines

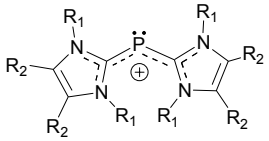
Pictured below are several Lewis-type structures that, despite the known limitations of such drawings, may be possibly used to denote the structural properties (and implied bonding models) of imidazolium-based phosphamethine cyanine cations. Model **A** formally contains a P^V center and is directly analogous to allene; such a model would be consistent with a linear C-P-C framework and NHC rings that are perpendicular to each other. Model **B** formally contains a P^{III} center and, in the delocalized form **B'**, is the model most commonly drawn for such cations; such a model would be consistent with a bent C-P-C unit, shorter-than-single P-C distances and the π-delocalization should be maximized by a planar structure. Model **C** formally contains a P^I center, which is emphasized by the donor-acceptor form **C'**, and appears to the model most consistent with structural features observed in this work; such a model implies a bent C-P-C moiety with single P-C bonds and planar NHC rings that are not necessarily in the C-P-C plane. It should be noted that the electronic structure calculated for **2f** appears to be intermediate between **B'** and **C'**, and is thus consistent with a degree of P→NHC π-backbonding; we have commented previously on the importance of P→ligand π-backbonding in enhancing the stability of P^I centers.[1]



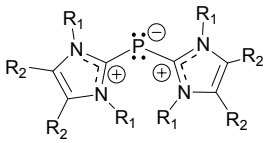
A



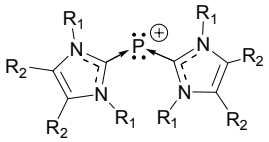
B



B'



C



C'

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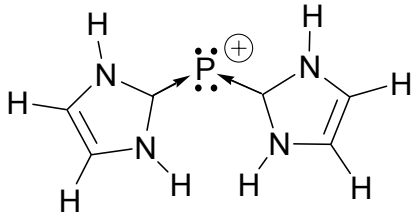
Summary of Density Functional Theory Calculations

Density Functional Theory (DFT) calculations were performed using the Gaussian98[2] suite of programs on a dual Xeon processor Dell Precision workstation. Single point calculations were performed using the B3PW91/6-311+g(3df,2p) level of theory.[3,4] Each model was fully optimized in the point group indicated at the B3PW91/6-31g(d) level of theory; frequency calculations were also performed at the B3PW91/6-31g(d) level to confirm the nature of the stationary points and to obtain the zero point vibrational energy (ZPVE). Absolute energies are reported in hartrees (note: E_{total} = E(B3PW91/6-311+g(3df,2p)) + ZPVE), relative energies are given in units of kJ mol^{-1} bond lengths are reported in Å and angles are given in degrees. Atomic charges (in atomic units) and Wiberg Bond Indices (WBI) were calculated using the NBO[5,6] method as implemented in Gaussian98 and orbital visualizations were done using MOLDEN[7] or Gaussview 3.0. The occupancy of the 3p orbital on the P atom perpendicular to the C-P-C plane (i.e. the orbital that may become part of the potential π system) is given in units of electrons. The "back-bonding" from the central atom to the NHC ligands (π-delocalization) is demonstrated by the decreased occupancy of the 3p (π) orbital and is manifested in the appearance of the third highest occupied molecular orbital (HOMO-3) in the models.



2f

Table S1 – Calculated energies for variants of **2f**.

Model	Symmetry	N_{imag}	E(6-31g(d))	E(6-311+g(3df,2p))	ZPVE	E_{total}	Rel. E
$P(NHC)_2$	D_{2d}	3	-793.2483263	-793.4308977	0.149057	-793.2818407	304.13
	C_{2v} (planar)	2	-793.3572562	-793.5403034	0.149705	-793.3905984	18.58
	C_{2v} (non planar)	2	-793.3563459	-793.5365099	0.151137	-793.3853729	32.30
	C_2	0	-793.3673841	-793.5485113	0.150835	-793.3976763	0.00
	C_s	1	-793.3635832	-793.5446418	0.150805	-793.3938368	10.08

Table S2 – Calculated properties for variants of **2f**.

Model	Symmetry	HOMO	LUMO	P 3p π pop.	q(P)	q(C)	P-C WBI	P-C	C-P-C
$P(NHC)_2$	D_{2d}	-0.32321	-0.21950	1.59212	0.19857	0.10729	1.3162	1.7115	180.00
	C_{2v} (planar)	-0.31751	-0.16711	1.43228	0.33389	0.08650	1.1447	1.7911	106.52
	C_{2v} (non planar)	-0.31234	-0.17184	1.77730	0.08195	0.13080	0.9790	1.8349	97.08
	C_2	-0.31846	-0.17020	1.49223	0.30507	0.08109	1.1088	1.7988	98.12
	C_s	-0.31375	-0.18075	1.58829	0.23336	0.09377	1.1528	1.7935	97.63
						0.10191	0.9754	1.8282	

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Figure S1. DFT Optimized Geometries of **2f**.

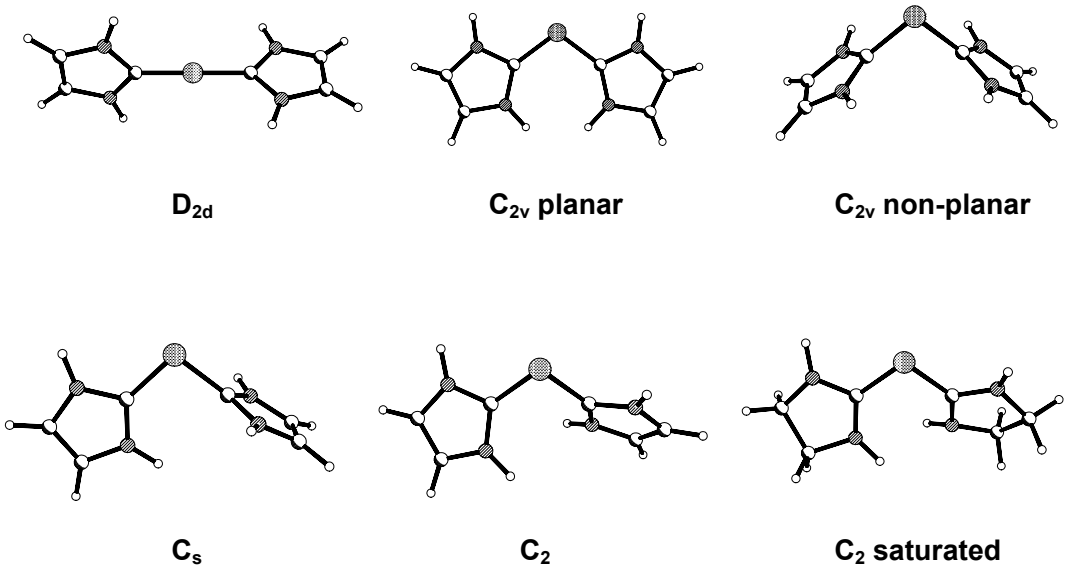
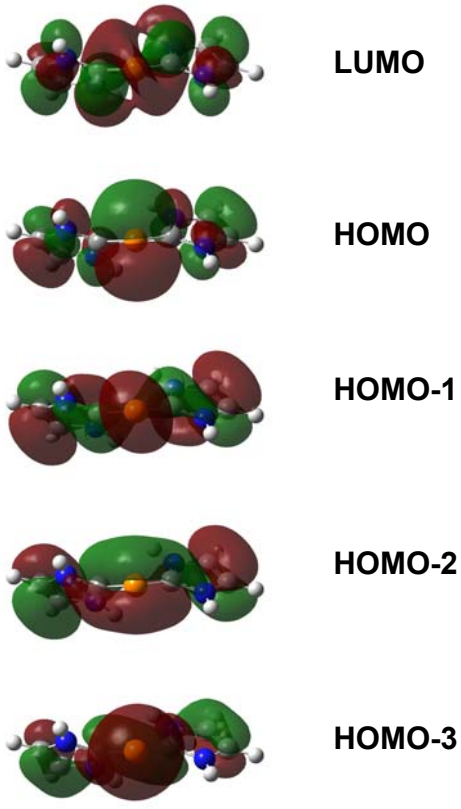


Figure S2. Gaussview® depiction of the frontier DFT orbitals of **2f** in C_2 symmetry.



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Summary of calculations including optimized geometries (in Cartesian coordinates or Z-matrix format):

$P(NHC)_2$, **2f**, D_{2d} symmetry:

1\1\GINC-NEIL\SP\RB3PW91\6-311+G(3df,2p)\C6H8N4P1(1+)\CHUCK\31-Aug-200
4\0\\# B3PW91/6-311+G(3DF,2P) GEOM=CHECKPOINT SCF=TIGHT #P GFINPUT IOP
(6/7=3) TEST\\Orbitals of carbene-P-carbene+ D2d\\1,1\P,0.,0.,0.\C,0.,
0.,1.7115131466\N,-1.0781997147,0.,2.5399101507\N,1.0781997147,0.,2.53
99101507\C,-0.6776152093,0.,3.8635130555\C,0.6776152093,0.,3.863513055
5\H,-2.0300836626,0.,2.2017038711\H,2.0300836626,0.,2.2017038711\H,-1.
3852697338,0.,4.678221434\H,1.3852697338,0.,4.678221434\C,0.,0.,-1.711
5131466\N,0.,1.0781997147,-2.5399101507\N,0.,-1.0781997147,-2.53991015
07\C,0.,0.6776152093,-3.8635130555\C,0.,-0.6776152093,-3.8635130555\H,
0.,2.0300836626,-2.2017038711\H,0.,-2.0300836626,-2.2017038711\H,0.,1.
3852697338,-4.678221434\H,0.,-1.3852697338,-4.678221434\\Version=x86-L
inux-G98RevA.11.1\HF=-793.4308977\RMSD=1.869e-09\Dipole=0.,0.,0.\PG=D0
2D [O(P1),C2(C1.C1),2SGD(C2H4N2)]\\@

$P(NHC)_2$, **2f**, C_{2v} (planar) symmetry:

1\1\GINC-NEIL\SP\RB3PW91\6-311+G(3df,2p)\C6H8N4P1(1+)\CHUCK\01-Sep-200
4\0\\# B3PW91/6-311+G(3DF,2P) GEOM=CHECKPOINT SCF=TIGHT #P GFINPUT IOP
(6/7=3) TEST\\Orbitals of carbene-P-carbene+ C2v planar\\1,1\P,-1.3407
363707,0.,0.\C,-0.2693162021,0.,1.4353653366\N,-0.8567532597,0.,2.6631
783664\N,1.0600099166,0.,1.7159144752\C,0.0776554646,0.,3.6784291427\C
,1.2927143042,0.,3.0850715002\H,-1.8594105454,0.,2.796809113\H,1.80018
89438,0.,1.0362122799\H,-0.203060136,0.,4.7201149085\H,2.288686519,0.,
3.4996190299\C,-0.2693162021,0.,-1.4353653366\N,-0.8567532597,0.,-2.66
31783664\N,1.0600099166,0.,-1.7159144752\C,0.0776554646,0.,-3.67842914
27\C,1.2927143042,0.,-3.0850715002\H,-1.8594105454,0.,-2.796809113\H,1
.8001889438,0.,-1.0362122799\H,-0.203060136,0.,-4.7201149085\H,2.28868
6519,0.,-3.4996190299\\Version=x86-Linux-G98RevA.11.1\State=1-A1\HF=-7
93.5403034\RMSD=5.881e-09\Dipole=0.9983519,0.,0.\PG=C02V [C2(P1),SGV(C
6H8N4)]\\@

$P(NHC)_2$, **2f**, C_{2v} (non-planar) symmetry:

1\1\GINC-NEIL\SP\RB3PW91\6-311+G(3df,2p)\C6H8N4P1(1+)\CHUCK\01-Sep-200
4\0\\# B3PW91/6-311+G(3DF,2P) GEOM=CHECKPOINT SCF=TIGHT #P GFINPUT IOP
(6/7=3) TEST\\Orbitals of carbene-P-carbene+ C2v not planar\\1,1\P,-1.
5712645031,0.,0.\C,-0.356332492,0.,1.375129318\N,0.1060110622,-1.06336
27663,2.070411406\N,0.1060110622,1.0633627663,2.070411406\C,0.84274612
98,-0.6812271074,3.1666282719\C,0.8427461298,0.6812271074,3.1666282719
\H,-0.1298159144,-2.0131805427,1.8129610918\H,-0.1298159144,2.01318054
27,1.8129610918\H,1.2925010626,-1.3877631163,3.8473318755\H,1.29250106
26,1.3877631163,3.8473318755\C,-0.356332492,0.,-1.375129318\N,0.106011
0622,1.0633627663,-2.070411406\N,0.1060110622,-1.0633627663,-2.0704114
06\C,0.8427461298,0.6812271074,-3.1666282719\C,0.8427461298,-0.6812271
074,-3.1666282719\H,-0.1298159144,2.0131805427,-1.8129610918\H,-0.1298
159144,-2.0131805427,-1.8129610918\H,1.2925010626,1.3877631163,-3.8473
318755\H,1.2925010626,-1.3877631163,-3.8473318755\\Version=x86-Linux-G
98RevA.11.1\State=1-A1\HF=-793.5365099\RMSD=3.539e-09\Dipole=1.7279847
,0.,0.\PG=C02V [C2(P1),SGV(C2),X(C4H8N4)]\\@

$P(NHC)_2$, **2f**, C_2 symmetry:

1\1\GINC-NEIL\SP\RB3PW91\6-311+G(3df,2p)\C6H8N4P1(1+)\BOBBY\09-Jun-200
4\0\\# B3PW91/6-311+G(3DF,2P) SCF=TIGHT #P GFINPUT IOP

(6/7=3) TEST\\Si
ngle Point and Molden carbene-P-carbene+\\1,1\P,0,0.,0.,1.542085\C,0,0
.,1.358756,0.363378\N,0,0.523246,2.576343,0.647515\N,0,-0.582871,1.523
71,-0.85335\C,0,0.253784,3.491294,-0.352253\C,0,-0.441621,2.825358,-1.
305938\H,0,1.063037,2.762605,1.482719\H,0,-1.171943,0.824282,-1.282546
\H,0,0.584955,4.516809,-0.302512\H,0,-0.839021,3.154272,-2.253572\C,0,
0.,-1.358756,0.363378\N,0,-0.523246,-2.576343,0.647515\N,0,0.582871,-1
.52371,-0.85335\C,0,-0.253784,-3.491294,-0.352253\C,0,0.441621,-2.8253
58,-1.305938\H,0,-1.063037,-2.762605,1.482719\H,0,1.171943,-0.824282,-
1.282546\H,0,-0.584955,-4.516809,-0.302512\H,0,0.839021,-3.154272,-2.2
53572\\Version=x86-Linux-G98RevA.11.1\State=1-A\HF=-793.5485113\RMSD=3
.793e-09\Dipole=0.,0.,-1.199182\PG=C02 [C2(P1),X(C6H8N4)]\\@

P(NHC)$_2$, **2f**, C_s symmetry:

1\1\GINC-NEIL\SP\RB3PW91\6-311+G(3df,2p)\C6H8N4P1(1+)\CHUCK\01-Sep-200
4\0\\# B3PW91/6-311+G(3DF,2P) GEOM=CHECKPOINT SCF=TIGHT #P GFINPUT IOP
(6/7=3) TEST\\Orbitals of carbene-P-carbene+ Cs\\1,1\P,-1.5582253831,0
.,-0.0061815184\C,-0.4014521872,0.,1.364431086\N,-0.8157815329,0.,2.65
80063698\N,0.953587581,0.,1.4520631029\C,0.2564180751,0.,3.5342378753\
C,1.3753988344,0.,2.7758380582\H,-1.7889845994,0.,2.9307136083\H,1.568
6335617,0.,0.6533662191\H,0.1244566503,0.,4.6048375766\H,2.4190583837,
0.,3.048350944\C,-0.3301369397,0.,-1.3604645238\N,0.133663307,1.065152
2643,-2.0523907351\N,0.133663307,-1.0651522643,-2.0523907351\C,0.86519
3379,0.6817111685,-3.1512464894\C,0.865193379,-0.6817111685,-3.1512464
894\H,-0.0975706036,2.016716439,-1.7921353666\H,-0.0975706036,-2.01671
6439,-1.7921353666\H,1.312871039,1.388564525,-3.8332939783\H,1.3128710
39,-1.388564525,-3.8332939783\\Version=x86-Linux-G98RevA.11.1\State=1-
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[SG(C4H4N2P1),X(C2H4N2)]\\@

All attempts using the unsaturated NHC (**1f**) to optimize stationary points analogous to the cyclopropylphosphenium intermediate suggested by Schmidpeter resulted only in the acyclic structures tabulated above. Similarly, all attempts using the saturated analogue of **1f** to obtain such a structure resulted in acyclic optimized structure; details of the results are summarized below.

Table S3 – Calculated energies and properties for the saturated analogue of **2f**.

Model	Symm	N_{imag}	E(6-31G(d))	E(6-311g(3df,2p)	ZPVE	E_{total}	HOMO	LUMO
P(satNHC)$_2$	C_2	0	-795.7960787	-795.9767418	0.19856	-795.7781818	-0.34181	-0.17856
			P 3p π pop.	q(P)	q(C)	P-C WBI	P-C	C-P-C
			1.39527	0.37121	0.1488	1.1559	1.7914	99.87

P(saturated NHC)$_2$, C_2 symmetry:

1\1\GINC-NEIL\SP\RB3PW91\6-311+G(3df,2p)\C6H12N4P1(1+)\CHUCK\01-Sep-20
04\0\\#B3PW91/6-311+G(3DF,2P) GEOM=CHECKPOINT SCF=TIGHT #P GFINPUT IOP
(6/7=3) TEST\\Orbitals of saturated carbene-P-carbene+ C2 - close to
C=C\\1,1\P,-1.5520610565,0.,0.\C,-0.3989934704,-0.1653101282,1.3609863
761\N,-0.8327202821,-0.5786635089,2.5583702191\N,0.9229310015,0.121541
4348,1.4551860463\C,0.2457290406,-0.6903617421,3.5404238692\C,1.354353
8282,0.1309255237,2.8633571439\H,-1.7237188923,-1.0424731267,2.6730860

72\H,1.3213861486,0.7897914198,0.807443854\H,0.5318695144,-1.740876417
7,3.6715731578\H,-0.0547885637,-0.2802115527,4.5071498085\H,1.38518322
59,1.1594582972,3.2415641193\H,2.3425150651,-0.3203435732,2.9736937124
\C,-0.3989934704,0.1653101282,-1.3609863761\N,-0.8327202821,0.57866350
89,-2.5583702191\N,0.9229310015,-0.1215414348,-1.4551860463\C,0.245729
0406,0.6903617421,-3.5404238692\C,1.3543538282,-0.1309255237,-2.863357
1439\H,-1.7237188923,1.0424731267,-2.673086072\H,1.3213861486,-0.78979
14198,-0.807443854\H,0.5318695144,1.7408764177,-3.6715731578\H,-0.0547
885637,0.2802115527,-4.5071498085\H,1.3851832259,-1.1594582972,-3.2415
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.,0.\PG=C02 [C2(P1),X(C6H12N4)]\\@

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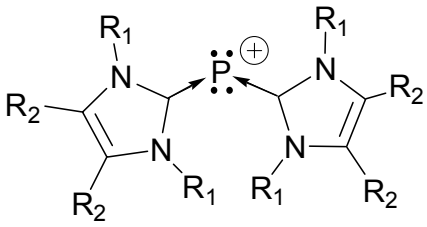
Summary of Semi-Empirical Computational Investigations

Fujitsu's CAChe 6.1 suite of programs[8] was used to perform semi-empirical PM3 calculations on selected fully-substituted model cations. The symmetry of each model was not restricted during the optimization procedure (C_1); selected bond distances are reported in angstroms and angles are reported in degrees. The B88PW91 energies (in a.u.) listed below were obtained from single-point calculations after replacing the R_1 and R_2 substituents in the optimized geometries with H atoms placed in idealized positions. The relative energies ($E_{relative}$) caused by the geometrical influences of the substituents on the "core" heavy atoms (i.e. the distortions of the model **2f**) are reported in kJ mol^{-1}.



R_1	R_2	E(B88-PW91)	$E_{relative}$	P-C(1) dist.	P-C(2) dist.	P-C avg.	C-P-C angle
H	H	-793.5862018	0.00	1.8581	1.8458	1.8520	106.56
Me	H	-793.5804401	15.13	1.8832	1.8838	1.8835	104.90
Me	Me	-793.5802302	15.68	1.8909	1.8622	1.8766	106.29
Et	H	-793.5810631	13.49	1.8862	1.8844	1.8853	104.07
Et	Me	-793.5794749	17.66	1.8909	1.8850	1.8880	104.53
^{i}Pr	H	-793.5776455	22.46	1.8957	1.8785	1.8871	107.11
^{i}Pr	Me	-793.5794041	17.85	1.8950	1.8785	1.8868	105.48
^{t}Bu	H	-793.5683087	46.98	1.9415	1.9302	1.9359	111.94
Mes	H	-793.5754902	28.12	1.8957	1.8967	1.8962	111.08

PM3 optimized atomic positions for R_1 = H, R_2 = H.

1	N	0.00000000	0.00000000	0.00000000
2	C	0.03894400	0.75751900	1.18767800
3	C	1.35607700	1.10033200	1.39667400
4	N	2.09151500	0.56351900	0.32283800
5	C	1.26477000	-0.12384500	-0.53885400
6	P	2.01451000	-1.11700700	-1.90244200
7	C	0.76069600	-1.16708200	-3.27298000
8	N	0.55804200	-2.33532700	-3.97198100
9	C	-0.23757000	-2.10324900	-5.10738400
10	C	-0.55286900	-0.76045800	-5.10406200
11	N	0.07582700	-0.19976000	-3.97759500
12	H	-0.82023000	-0.39874800	-0.38093300
13	H	-0.84195300	0.99311400	1.79274500
14	H	1.79891700	1.67521700	2.21598400
15	H	3.07261900	0.64179700	0.21277600
16	H	0.94775200	-3.21089900	-3.72119000

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17	H	-0.52373100	-2.87680700	-5.82724900
18	H	-1.15956100	-0.19268900	-5.81637000
19	H	0.04321800	0.75875300	-3.73781200

Atomic positions used in the single-point B88PW91 calculation of **2f** from R_1 = H, R_2 = H.

1	N	0.00000000	0.00000000	0.00000000
2	C	0.03793000	0.75821200	1.18709500
3	C	1.35502000	1.10099500	1.39659600
4	N	2.09127400	0.56328400	0.32360700
5	C	1.26466200	-0.12383400	-0.53862500
6	P	2.01415200	-1.11664400	-1.90232300
7	C	0.76153700	-1.16311800	-3.27388400
8	N	0.55992300	-2.33181200	-3.97243400
9	C	-0.23696200	-2.10080600	-5.10727900
10	C	-0.55315700	-0.75823600	-5.10474000
11	N	0.07661100	-0.19634900	-3.97942100
12	H	-0.84538000	-0.40184700	-0.40528000
13	H	-0.81108900	1.02230700	1.81758700
14	H	1.75139300	1.67767100	2.23231900
15	H	3.09848400	0.66801300	0.20129800
16	H	0.93692400	-3.24066300	-3.70362200
17	H	-0.54543500	-2.84001700	-5.84654300
18	H	-1.17134600	-0.23413600	-5.83361600
19	H	0.03273100	0.78943000	-3.72113100

PM3 optimized atomic positions for R_1 = Me, R_2 = H.

1	N	0.00000000	0.00000000	0.00000000
2	C	-0.02299600	0.92687600	1.06141600
3	C	1.14199800	1.65795500	0.97879700
4	N	1.84698200	1.17412400	-0.13954200
5	C	1.14921300	0.15284700	-0.75255700
6	P	1.92276900	-0.90758300	-2.10378900
7	C	0.71669900	-0.80920700	-3.54673500
8	N	0.20243100	-1.93824400	-4.15205100
9	C	-0.49157900	-1.59979600	-5.32915000
10	C	-0.41014700	-0.23061400	-5.45948100
11	N	0.34364700	0.23986200	-4.36566500
12	C	0.35798300	-3.31307500	-3.66337300
13	C	0.68605400	1.65361900	-4.17847900
14	C	-1.05910100	-0.99054900	-0.21861000
15	C	3.15152700	1.68965100	-0.57000600
16	H	-0.83471100	1.00091700	1.79152600
17	H	1.50125600	2.46067400	1.62984400
18	H	-0.98072700	-2.32839900	-5.98261100
19	H	-0.82014400	0.41418600	-6.24268400

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20	H	0.90592900	-3.29906600	-2.70389000
21	H	0.92573200	-3.92015700	-4.38376300
22	H	-0.62543700	-3.78032200	-3.51361000
23	H	1.60901500	1.74716200	-3.58481200
24	H	0.84592900	2.13794900	-5.15314800
25	H	-0.12333100	2.18561500	-3.65758500
26	H	-0.66822200	-1.84822300	-0.78757900
27	H	-1.44164100	-1.35629000	0.74566600
28	H	-1.89720700	-0.54892700	-0.77674400
29	H	3.92254200	1.47715100	0.18487900
30	H	3.10364900	2.77659600	-0.72237100
31	H	3.44177600	1.19854900	-1.51645000

Atomic positions used in the single-point B88PW91 calculation of **2f** from R_1 = Me, R_2 = H.

1	N	0.00000000	0.00000000	0.00000000
2	C	-0.02299600	0.92687600	1.06141600
3	C	1.14199800	1.65795500	0.97879700
4	N	1.84698200	1.17412400	-0.13954200
5	C	1.14921300	0.15284700	-0.75255700
6	P	1.92276900	-0.90758300	-2.10378900
7	C	0.71669900	-0.80920700	-3.54673500
8	N	0.20243100	-1.93824400	-4.15205100
9	C	-0.49157900	-1.59979600	-5.32915000
10	C	-0.41014700	-0.23061400	-5.45948100
11	N	0.34364700	0.23986200	-4.36566500
12	H	-0.72972700	-0.68775400	-0.18679300
13	H	-0.81131000	1.04311700	1.80515600
14	H	1.45702700	2.45692900	1.64998800
15	H	2.74988700	1.52956100	-0.45390900
16	H	0.31049400	-2.88769000	-3.79529400
17	H	-0.99618600	-2.28833900	-6.00692600
18	H	-0.84533900	0.37299400	-6.25595100
19	H	0.58085800	1.21817600	-4.20124800

PM3 optimized atomic positions for R_1 = Me, R_2 = Me.

1	N	0.00000000	0.00000000	0.00000000
2	C	0.30786400	-0.29817700	1.35214800
3	C	1.65399300	-0.03256800	1.52504400
4	N	2.14691800	0.40667100	0.27381900
5	C	1.13647200	0.42118100	-0.66989100
6	P	1.53091300	1.09067700	-2.36224200
7	C	0.40806500	0.16868700	-3.57244000
8	N	0.57084800	-1.10055600	-4.09074300
9	C	-0.29429500	-1.30527600	-5.18915100

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10	C	-1.00128600	-0.12451300	-5.36143700
11	N	-0.55848900	0.76380400	-4.35520500
12	C	1.52057800	-2.10741500	-3.60726800
13	C	-1.08234000	2.12719400	-4.20246000
14	C	-1.34654000	-0.11961500	-0.56497500
15	C	3.53401200	0.81267300	0.02483100
16	C	-0.63465100	-0.79247800	2.37128400
17	C	2.43871800	-0.17930400	2.76339400
18	C	-0.37946900	-2.54693700	-5.97880700
19	C	-2.01089500	0.20490900	-6.38491400
20	H	2.26049700	-1.63744700	-2.94041200
21	H	2.05036100	-2.56795700	-4.45489100
22	H	0.99555700	-2.90235200	-3.05745300
23	H	-0.26980300	2.83568300	-3.98104700
24	H	-1.81134500	2.16891000	-3.37934800
25	H	-1.59035000	2.42991900	-5.13584100
26	H	-1.49163300	0.60653300	-1.37858400
27	H	-1.51584600	-1.13156600	-0.96075600
28	H	-2.10094600	0.07391300	0.21275400
29	H	4.22863600	0.03434200	0.37255000
30	H	3.68054300	0.97587000	-1.05881200
31	H	3.76703000	1.74671200	0.55757800
32	H	-0.08170600	-0.96374500	3.31131500
33	H	-1.10255800	-1.74017000	2.07224600
34	H	-1.43451300	-0.06670200	2.57597700
35	H	3.29032100	-0.86079600	2.62962500
36	H	1.78639600	-0.59229900	3.55167900
37	H	2.82803600	0.78666200	3.11426400
38	H	0.56421500	-2.75193100	-6.50575900
39	H	-0.60712600	-3.41556700	-5.34463200
40	H	-1.17300000	-2.46485900	-6.73455900
41	H	-1.65268900	-0.07491400	-7.38547500
42	H	-2.94559400	-0.34298200	-6.20137600
43	H	-2.24212600	1.28408700	-6.39361200

Atomic positions used in the single-point B88PW91 calculation of **2f** from R_1 = Me, R_2 = Me.

1	N	0.00000000	0.00000000	0.00000000
2	C	0.30786400	-0.29817700	1.35214800
3	C	1.65399300	-0.03256800	1.52504400
4	N	2.14691800	0.40667100	0.27381900
5	C	1.13647200	0.42118100	-0.66989100
6	P	1.53091300	1.09067700	-2.36224200
7	C	0.40806500	0.16868700	-3.57244000
8	N	0.57084800	-1.10055600	-4.09074300
9	C	-0.29429500	-1.30527600	-5.18915100

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10	C	-1.00128600	-0.12451300	-5.36143700
11	N	-0.55848900	0.76380400	-4.35520500
12	H	-0.92616000	-0.08383200	-0.41904800
13	H	-0.38400400	-0.66616000	2.10978100
14	H	2.22493300	-0.14074500	2.44722900
15	H	3.11407400	0.67550400	0.09288100
16	H	1.22543800	-1.79488500	-3.73043800
17	H	-0.38773600	-2.21349300	-5.78455900
18	H	-1.75248500	0.07886100	-6.12461400
19	H	-0.90601600	1.71402300	-4.22594000

PM3 optimized atomic positions for R_1 = Et, R_2 = H.

1	N	0.00000000	0.00000000	0.00000000
2	C	-0.04274900	0.94436900	1.04602600
3	C	1.13931500	1.64986500	0.99810000
4	N	1.87639500	1.13632500	-0.08572300
5	C	1.17923900	0.12210900	-0.71095300
6	P	1.97029400	-0.91314200	-2.07236700
7	C	0.71939100	-0.84924900	-3.48261500
8	N	0.23172800	-1.99526900	-4.07626300
9	C	-0.52991300	-1.67634600	-5.21600400
10	C	-0.51452400	-0.30360200	-5.33491200
11	N	0.26897100	0.19115000	-4.27316200
12	C	0.48878600	-3.37403400	-3.59834300
13	C	0.57457500	1.62588400	-4.06599700
14	C	-1.08392600	-0.96984100	-0.27880100
15	C	3.21080400	1.62909200	-0.50166600
16	H	-0.88078400	1.04701500	1.74198800
17	H	1.49328700	2.45572100	1.64834800
18	H	-1.01734800	-2.42049200	-5.85320200
19	H	-0.98961000	0.32825800	-6.09151100
20	H	1.19256300	-3.29060500	-2.73382800
21	H	1.02588600	-3.92200200	-4.40028400
22	C	-0.78049200	-4.10084000	-3.20462900
23	H	1.31270700	1.69209200	-3.23683300
24	C	1.11579800	2.30130500	-5.31052500
25	H	-0.35044800	2.13042600	-3.71809900
26	H	-0.73194000	-1.64796200	-1.08738300
27	C	-1.48954100	-1.77398900	0.94023200
28	H	-1.95222300	-0.40838300	-0.68202600
29	C	4.25252300	1.51221800	0.59158700
30	H	3.09859900	2.68431300	-0.82563800
31	H	3.50289400	1.03596300	-1.40274900
32	H	-0.53845200	-5.12699300	-2.89498400
33	H	-1.49943400	-4.17226800	-4.03277000

34	H	-1.29161400	-3.61951400	-2.35865400
35	H	2.02625500	1.81696000	-5.68953400
36	H	0.38279900	2.32152400	-6.12961500
37	H	1.37420200	3.34533400	-5.08393600
38	H	-0.65464300	-2.35044800	1.36164800
39	H	-2.27288300	-2.49338200	0.66406400
40	H	-1.89771100	-1.14461100	1.74392300
41	H	5.21663600	1.88810900	0.22180500
42	H	4.41253100	0.47419300	0.91269600
43	H	3.99297500	2.10130200	1.48246300

Atomic positions used in the single-point B88PW91 calculation of **2f** from R_1 = Et, R_2 = H.

1	N	0.00000000	0.00000000	0.00000000
2	C	-0.04274900	0.94436900	1.04602600
3	C	1.13931500	1.64986500	0.99810000
4	N	1.87639500	1.13632500	-0.08572300
5	C	1.17923900	0.12210900	-0.71095300
6	P	1.97029400	-0.91314200	-2.07236700
7	C	0.71939100	-0.84924900	-3.48261500
8	N	0.23172800	-1.99526900	-4.07626300
9	C	-0.52991300	-1.67634600	-5.21600400
10	C	-0.51452400	-0.30360200	-5.33491200
11	N	0.26897100	0.19115000	-4.27316200
12	H	-0.73503200	-0.67733000	-0.20335300
13	H	-0.85616500	1.08867600	1.75710300
14	H	1.44519600	2.45164400	1.67017700
15	H	2.79824100	1.46783500	-0.36980300
16	H	0.39984600	-2.94215100	-3.73633600
17	H	-1.03498400	-2.38010100	-5.87761600
18	H	-1.01318900	0.28689500	-6.10351300
19	H	0.47446200	1.17700700	-4.11111200

PM3 optimized atomic positions for R_1 = Et, R_2 = Me.

1	N	0.00000000	0.00000000	0.00000000
2	C	-0.04858800	0.93549700	1.06351100
3	C	1.14697100	1.63405200	1.03579900
4	N	1.89506000	1.11673700	-0.04829000
5	C	1.18974400	0.12049100	-0.69217400
6	P	1.98311400	-0.87505500	-2.08232300
7	C	0.70119800	-0.85386200	-3.47214100
8	N	0.22882000	-2.01730200	-4.04238300
9	C	-0.54114500	-1.72973400	-5.19262400
10	C	-0.54536100	-0.35067900	-5.33325700
11	N	0.23607000	0.16964000	-4.27366800

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12	C	0.49666100	-3.37700300	-3.51832700
13	C	0.52012800	1.61109200	-4.08628200
14	C	-1.07942300	-0.97168300	-0.28742800
15	C	3.24611700	1.57971600	-0.44424100
16	C	-1.17752900	1.09745900	1.99822400
17	C	1.59075100	2.71736300	1.93243500
18	C	-1.18767300	-2.73801800	-6.05284800
19	C	-1.21735600	0.45813000	-6.36723100
20	H	1.23265500	-3.26187800	-2.68480800
21	H	0.99753900	-3.96108400	-4.31825200
22	C	-0.76027500	-4.08237000	-3.04873000
23	H	1.04924300	1.72928400	-3.11723500
24	C	1.34486800	2.19945500	-5.21558600
25	H	-0.45207500	2.13964400	-3.99684000
26	H	-0.84623000	-1.47070000	-1.25223800
27	C	-1.25032200	-2.00253100	0.81249100
28	H	-2.01991000	-0.40041700	-0.43437500
29	C	4.30078400	1.30865900	0.61082400
30	H	3.18074100	2.66611600	-0.66049700
31	H	3.49473900	1.06042800	-1.40207200
32	H	-0.51260700	-5.09783900	-2.71155700
33	H	-1.50848100	-4.17593600	-3.85540600
34	H	-1.24084200	-3.56728700	-2.20484900
35	H	2.33665100	1.73496700	-5.29796800
36	H	0.84115400	2.09044000	-6.19236100
37	H	1.50017900	3.27294400	-5.04428900
38	H	-0.34555200	-2.60503700	0.96977300
39	H	-2.06239700	-2.69489500	0.55266900
40	H	-1.51249600	-1.53205500	1.77667200
41	H	5.27505500	1.67803500	0.26344500
42	H	4.41725800	0.23837100	0.82743600
43	H	4.07302900	1.82110700	1.56192900
44	H	-0.87735500	1.72386300	2.85139200
45	H	-1.51867300	0.12207500	2.38881500
46	H	-2.03404900	1.58225800	1.50778900
47	H	2.64174800	2.58140400	2.24303400
48	H	0.96555800	2.74441200	2.83693100
49	H	1.51004600	3.69649900	1.43897800
50	H	-0.44225000	-3.29632500	-6.63772300
51	H	-1.76146600	-3.46737200	-5.45377400
52	H	-1.87596300	-2.25327600	-6.76012700
53	H	-0.51069900	1.15796900	-6.84801600
54	H	-1.64152300	-0.19247200	-7.14560000
55	H	-2.03818100	1.05117500	-5.93941300

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Atomic positions used in the single-point B88PW91 calculation of **2f** from R_1 = Et, R_2 = Me.

1	N	0.00000000	0.00000000	0.00000000
2	C	-0.04858800	0.93549700	1.06351100
3	C	1.14697100	1.63405200	1.03579900
4	N	1.89506000	1.11673700	-0.04829000
5	C	1.18974400	0.12049100	-0.69217400
6	P	1.98311400	-0.87505500	-2.08232300
7	C	0.70119800	-0.85386200	-3.47214100
8	N	0.22882000	-2.01730200	-4.04238300
9	C	-0.54114500	-1.72973400	-5.19262400
10	C	-0.54536100	-0.35067900	-5.33325700
11	N	0.23607000	0.16964000	-4.27366800
12	H	-0.73843800	-0.66743600	-0.22279800
13	H	-0.86860000	1.07774600	1.76739000
14	H	1.45244800	2.42829500	1.71694600
15	H	2.82601900	1.43578000	-0.31648200
16	H	0.40982100	-2.95497400	-3.68403900
17	H	-1.03535300	-2.45190900	-5.84248700
18	H	-1.05235100	0.22231600	-6.10961900
19	H	0.42821500	1.16008100	-4.12364500

PM3 optimized atomic positions for $R_1 = {}^{i}Pr$, R_2 = H.

1	N	0.00000000	0.00000000	0.00000000
2	C	0.01380200	0.69383200	1.23044400
3	C	1.18878500	1.40546400	1.27917300
4	N	1.87653800	1.14089900	0.07783000
5	C	1.15551900	0.26841300	-0.71501600
6	P	1.99010600	-0.43714100	-2.24285100
7	C	0.67909500	-0.51244400	-3.61000500
8	N	0.01546300	-1.62378700	-4.09061100
9	C	-0.62571500	-1.32399100	-5.30630600
10	C	-0.35856300	-0.00004500	-5.58568900
11	N	0.44978000	0.48074500	-4.54111100
12	C	-0.01634100	-2.97155000	-3.44169300
13	C	1.01262800	1.86408300	-4.47904000
14	C	-1.08759100	-0.93735600	-0.41394600
15	C	3.20077500	1.73763500	-0.28162200
16	H	-0.78992000	0.63959300	1.97085900
17	H	1.57292000	2.06143300	2.06634200
18	H	-1.20745200	-2.04774400	-5.88580800
19	H	-0.67888800	0.60527400	-6.43957700
20	H	0.43360000	-2.83281400	-2.41066000
21	C	0.81748900	-3.96983600	-4.23555300
22	C	-1.44900900	-3.47202500	-3.29434000

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23	C	1.85321400	2.16731500	-5.71399200
24	C	-0.09765700	2.89497400	-4.31852800
25	H	1.67606300	1.86583000	-3.56759000
26	C	-0.73000300	-2.37482300	-0.04661500
27	C	-2.43619400	-0.55264400	0.18118300
28	H	-1.15633600	-0.85402400	-1.52964800
29	C	4.27046100	1.34855000	0.73101500
30	C	3.09264400	3.25358600	-0.39308200
31	H	3.45504800	1.29895900	-1.29123700
32	H	1.86961500	-3.66443100	-4.31401300
33	H	0.80120900	-4.94975400	-3.73860200
34	H	0.43195900	-4.11530200	-5.25486400
35	H	-1.45318800	-4.43174700	-2.75795400
36	H	-1.93924300	-3.64264700	-4.26330700
37	H	-2.07571000	-2.77726700	-2.71655700
38	H	1.26171500	2.14217600	-6.64065300
39	H	2.68995300	1.46546200	-5.83196800
40	H	2.28489400	3.17492700	-5.63244800
41	H	-0.78596900	2.90384000	-5.17608000
42	H	-0.69480400	2.72990200	-3.41206900
43	H	0.33721700	3.90145300	-4.24209000
44	H	0.11330000	-2.74985800	-0.65447100
45	H	-1.58443300	-3.03846600	-0.24461100
46	H	-0.46722200	-2.48941900	1.01315400
47	H	-2.48290100	-0.73106900	1.26549100
48	H	-3.22938700	-1.16180200	-0.27589800
49	H	-2.69242400	0.50042000	0.00255800
50	H	5.24203400	1.75861500	0.42174000
51	H	4.39078000	0.26011400	0.81459200
52	H	4.05712800	1.74126100	1.73568200
53	H	4.06251200	3.67523700	-0.69200400
54	H	2.81311600	3.72494400	0.56004900
55	H	2.35735900	3.56224500	-1.14865400

Atomic positions used in the single-point B88PW91 calculation of **2f** from $R_1 = {}^{i}Pr$, $R_2 =$ H.

1	N	0.00000000	0.00000000	0.00000000
2	C	0.01380200	0.69383200	1.23044400
3	C	1.18878500	1.40546400	1.27917300
4	N	1.87653800	1.14089900	0.07783000
5	C	1.15551900	0.26841300	-0.71501600
6	P	1.99010600	-0.43714100	-2.24285100
7	C	0.67909500	-0.51244400	-3.61000500
8	N	0.01546300	-1.62378700	-4.09061100
9	C	-0.62571500	-1.32399100	-5.30630600
10	C	-0.35856300	-0.00004500	-5.58568900

Supplementary Material (ESI) for Chemical Communications

11	N	0.44978000	0.48074500	-4.54111100
12	H	-0.75291900	-0.61101300	-0.31650500
13	H	-0.76108500	0.66947200	1.99664000
14	H	1.52425300	2.05062200	2.09116600
15	H	2.78192500	1.53868100	-0.17205700
16	H	-0.00673000	-2.53332700	-3.62947800
17	H	-1.22037100	-2.00774800	-5.91207900
18	H	-0.70722600	0.56480600	-6.45025700
19	H	0.81584200	1.43080600	-4.47960700

PM3 optimized atomic positions for $R_1 = {}^{i}Pr$, $R_2 = Me$.

1	N	0.00000000	0.00000000	0.00000000
2	C	0.31938800	-0.37431800	1.33123800
3	C	1.67163800	-0.14226100	1.50106900
4	N	2.16243400	0.34364100	0.26568400
5	C	1.14108200	0.41942900	-0.66191300
6	P	1.50533700	1.16520400	-2.34714500
7	C	0.46987500	0.16347300	-3.57816300
8	N	0.65271200	-1.11446000	-4.06440800
9	C	-0.22331100	-1.35051700	-5.14670400
10	C	-0.95392300	-0.18583600	-5.33860400
11	N	-0.50414800	0.73878400	-4.37160700
12	C	1.57771300	-2.13127100	-3.47762700
13	C	-1.04367900	2.11089800	-4.11508800
14	C	-1.37274300	-0.08034100	-0.58371100
15	C	3.58801400	0.71360900	-0.00577900
16	C	-0.61495100	-0.91922000	2.33393600
17	C	2.46725600	-0.35795300	2.72401700
18	C	-0.33451600	-2.60261300	-5.91803600
19	C	-2.00389300	0.01761800	-6.35448600
20	H	2.11668700	-1.60734100	-2.64256400
21	C	2.60236900	-2.60240200	-4.50293200
22	C	0.77836900	-3.30466800	-2.91884100
23	C	-1.04976000	2.97440700	-5.36702500
24	C	-2.43031300	2.01850100	-3.48974100
25	H	-0.32694000	2.55741000	-3.36128300
26	C	-1.83341400	-1.53297200	-0.65112400
27	C	-2.36158100	0.77404000	0.20341300
28	H	-1.32001000	0.34783800	-1.62660000
29	C	4.49714400	-0.49904900	0.16072200
30	C	4.03406700	1.85738700	0.89846000
31	H	3.60651500	1.05381100	-1.08243900
32	H	3.25162700	-1.78452600	-4.84273800
33	H	3.25007500	-3.37210900	-4.06202800
34	H	2.12577300	-3.04383500	-5.39631500
35	H	1.45248900	-4.05236500	-2.48131000

Supplementary Material (ESI) for Chemical Communications

36	H	0.18830900	-3.80987600	-3.70533100
37	H	0.07423100	-2.99109700	-2.12854100
38	H	-1.44572300	3.97083200	-5.12738000
39	H	-1.68229400	2.55402900	-6.16759200
40	H	-0.04130400	3.11420400	-5.77853900
41	H	-3.17431900	1.58305400	-4.17168000
42	H	-2.41567300	1.41018600	-2.56667500
43	H	-2.78787800	3.02016100	-3.21589400
44	H	-1.16778200	-2.15422700	-1.27543200
45	H	-2.84134600	-1.59602500	-1.08157100
46	H	-1.87269900	-1.99569400	0.35182200
47	H	-2.42421100	0.47683600	1.26491800
48	H	-3.36803800	0.67393200	-0.22585400
49	H	-2.09874400	1.84007200	0.17231600
50	H	5.54363900	-0.21215500	-0.00863900
51	H	4.25784300	-1.29482000	-0.55674300
52	H	4.43273100	-0.93073300	1.17561300
53	H	3.45974700	2.77590600	0.71992800
54	H	5.09051200	2.09405200	0.71296500
55	H	3.93413900	1.60150200	1.96825100
56	H	-0.06612100	-1.14802300	3.26138000
57	H	-1.09787600	-1.84091100	1.96495800
58	H	-1.41768700	-0.19809000	2.56594200
59	H	3.28423700	-1.07814300	2.54150300
60	H	1.81816600	-0.74719900	3.52400600
61	H	2.93277500	0.58423400	3.06284700
62	H	0.63582300	-2.88418900	-6.36323500
63	H	-0.65087400	-3.43739100	-5.26827600
64	H	-1.07218200	-2.47237100	-6.72587700
65	H	-1.87175100	0.96680900	-6.90052900
66	H	-1.97311700	-0.81585200	-7.07639100
67	H	-3.00453300	0.03098700	-5.89815100

Atomic positions used in the single-point B88PW91 calculation of **2f** from $R_1 = {}^{i}Pr$, $R_2 =$ Me.

1	N	0.00000000	0.00000000	0.00000000
2	C	0.31938800	-0.37431800	1.33123800
3	C	1.67163800	-0.14226100	1.50106900
4	N	2.16243400	0.34364100	0.26568400
5	C	1.14108200	0.41942900	-0.66191300
6	P	1.50533700	1.16520400	-2.34714500
7	C	0.46987500	0.16347300	-3.57816300
8	N	0.65271200	-1.11446000	-4.06440800
9	C	-0.22331100	-1.35051700	-5.14670400
10	C	-0.95392300	-0.18583600	-5.33860400
11	N	-0.50414800	0.73878400	-4.37160700

Supplementary Material (ESI) for Chemical Communications

12	H	-0.93370500	-0.03493500	-0.40911500
13	H	-0.36998900	-0.76939900	2.07740800
14	H	2.24897700	-0.30270800	2.41158300
15	H	3.13275600	0.60139800	0.08558200
16	H	1.32247500	-1.78991900	-3.69620700
17	H	-0.30941900	-2.27224200	-5.72212500
18	H	-1.72527900	-0.01793700	-6.09021600
19	H	-0.84844900	1.69381900	-4.27278800

PM3 optimized atomic positions for $R_1 = {}^{t}Bu$, $R_2 = H$.

1	N	0.00000000	0.00000000	0.00000000
2	C	-0.06952800	0.93254300	1.05321100
3	C	1.09417100	1.65849100	1.02966300
4	N	1.86959500	1.17632400	-0.04349100
5	C	1.18024400	0.17409100	-0.71721700
6	P	1.97466500	-0.81997100	-2.16857100
7	C	0.79617900	-0.92236700	-3.70814500
8	N	0.35633300	-2.10858000	-4.27736400
9	C	-0.32212000	-1.84569000	-5.48583900
10	C	-0.27741600	-0.49295300	-5.69663000
11	N	0.42588800	0.07143800	-4.61401300
12	C	0.42197500	-3.56461400	-3.82896800
13	C	0.81648200	1.54200100	-4.62707900
14	C	-1.03771700	-1.09538000	-0.15768600
15	C	3.28516900	1.68189200	-0.28611400
16	H	-0.91133500	1.02872200	1.74688800
17	H	1.39347100	2.46638000	1.70592300
18	H	-0.76229200	-2.63892900	-6.10659300
19	H	-0.69101100	0.06971300	-6.54039400
20	C	1.56679100	-3.83559300	-2.85944400
21	C	0.64120900	-4.45763500	-5.06316400
22	C	-0.92601400	-3.92742400	-3.19378100
23	C	2.33708700	1.62517600	-4.79951900
24	C	0.17339200	2.28003100	-5.81127700
25	C	0.35239800	2.23414700	-3.33907600
26	C	-0.32727800	-2.45314700	-0.12039700
27	C	-2.05528600	-1.07307600	0.99212900
28	C	-1.80791100	-0.89727400	-1.46906500
29	C	4.25216400	0.49298100	-0.28211600
30	C	3.72022200	2.65434500	0.81870400
31	C	3.35161200	2.41318400	-1.62806000
32	H	1.60695700	-4.26325300	-5.54957800
33	H	0.63441600	-5.51518800	-4.76447700
34	H	-0.14919900	-4.32704800	-5.82157100
35	H	-0.91122000	-4.96792100	-2.84064200

36	H	-1.75413000	-3.84027200	-3.91161900
37	H	-1.17751800	-3.29443500	-2.31893000
38	H	2.66701700	1.18975700	-5.75296100
39	H	2.87024200	1.10125200	-3.98336800
40	H	2.66805300	2.67342100	-4.79169600
41	H	0.50724500	1.89207800	-6.78472600
42	H	-0.92528400	2.24865400	-5.78867800
43	H	0.46327000	3.34047900	-5.77781200
44	H	0.60463300	-2.45880200	-0.72396200
45	H	-0.97832300	-3.23998900	-0.53871900
46	H	-0.06223100	-2.75217900	0.90257800
47	H	-1.58881700	-1.24141500	1.97355600
48	H	-2.78559700	-1.88145100	0.84292900
49	H	-2.62374800	-0.13309500	1.04283300
50	H	5.26045700	0.82547700	-0.56467600
51	H	3.95149200	-0.28750900	-1.00685000
52	H	4.32820600	0.02641800	0.70951100
53	H	4.76234000	2.96263600	0.64750300
54	H	3.68824000	2.20148500	1.82001700
55	H	3.11650700	3.57263100	0.83373800
56	H	1.51083200	-4.86980300	-2.49124400
57	H	1.54526400	-3.16345200	-1.97865200
58	H	2.54846800	-3.71594300	-3.34025900
59	H	1.11897000	2.93972400	-2.96735800
60	H	0.16100600	1.52530500	-2.52040300
61	H	-0.57471000	2.80630100	-3.48765300
62	H	-1.19331600	-0.45057600	-2.26310000
63	H	-2.16549000	-1.86935300	-1.85331000
64	H	-2.68604700	-0.24940900	-1.33868900
65	H	4.25315600	3.03861700	-1.68523100
66	H	3.39754700	1.69610700	-2.46840000
67	H	2.48127000	3.06831600	-1.81106700

Atomic positions used in the single-point B88PW91 calculation of **2f** from $R_1 = {}^{t}Bu$, $R_2 = H$.

1	N	0.00000000	0.00000000	0.00000000
2	C	-0.06952800	0.93254300	1.05321100
3	C	1.09417100	1.65849100	1.02966300
4	N	1.86959500	1.17632400	-0.04349100
5	C	1.18024400	0.17409100	-0.71721700
6	P	1.97466500	-0.81997100	-2.16857100
7	C	0.79617900	-0.92236700	-3.70814500
8	N	0.35633300	-2.10858000	-4.27736400
9	C	-0.32212000	-1.84569000	-5.48583900
10	C	-0.27741600	-0.49295300	-5.69663000
11	N	0.42588800	0.07143800	-4.61401300

Supplementary Material (ESI) for Chemical Communications

12	H	-0.71125100	-0.70115500	-0.20713100
13	H	-0.89395000	1.05459800	1.75572900
14	H	1.36846800	2.46056800	1.71488900
15	H	2.80028100	1.51313200	-0.29003300
16	H	0.50236700	-3.03642700	-3.87965300
17	H	-0.79531900	-2.58385100	-6.13337300
18	H	-0.70524200	0.04534300	-6.54238600
19	H	0.63431200	1.06426900	-4.50796900

PM3 optimized atomic positions for R_1 = Mes, R_2 = H.

1	N	0.00000000	0.00000000	0.00000000
2	C	0.08917500	1.15847000	0.79891300
3	C	1.29789700	1.74866600	0.51399500
4	N	1.92487900	0.95121200	-0.46513800
5	C	1.12900300	-0.13494000	-0.79321400
6	P	1.77437500	-1.60823100	-1.79657800
7	C	0.61417300	-2.00946300	-3.24243600
8	N	0.13910500	-3.28863900	-3.48424100
9	C	-0.43265700	-3.37159900	-4.77013100
10	C	-0.32456400	-2.12433800	-5.33866600
11	N	0.32559700	-1.29939100	-4.39779300
12	C	0.21247100	-4.48281000	-2.65661300
13	C	0.66141000	0.06795200	-4.75784600
14	C	-1.13378500	-0.89497900	0.15849800
15	C	3.26577000	1.29163100	-0.91516500
16	C	-0.96614600	-5.00209800	-2.08917800
17	C	-0.89705400	-6.18041000	-1.34804400
18	C	0.31485900	-6.84770100	-1.17065300
19	C	1.47491500	-6.32646700	-1.74003100
20	C	1.44034100	-5.14785800	-2.48518000
21	C	-0.36531800	1.02306000	-4.88596100
22	C	-0.04312900	2.31301200	-5.30073300
23	C	1.27364500	2.65970900	-5.60722900
24	C	2.27925400	1.70275200	-5.49264800
25	C	1.99085500	0.40336900	-5.07123000
26	C	4.36763300	0.53803400	-0.47029300
27	C	5.65188300	0.91611000	-0.86225200
28	C	5.85194500	2.02499200	-1.68161700
29	C	4.75240700	2.76613700	-2.11489100
30	C	3.45654200	2.41644500	-1.73941400
31	C	-2.40301100	-0.49562400	-0.30037700
32	C	-3.49493300	-1.33501000	-0.09010800
33	C	-3.34609700	-2.54871900	0.58202900
34	C	-2.09003700	-2.92155500	1.05652600
35	C	-0.97497400	-2.10689800	0.85496600

Supplementary Material (ESI) for Chemical Communications

36	C	-2.63122200	0.80789200	-0.97935600
37	H	-4.48933600	-1.03226800	-0.44527800
38	C	-4.51482800	-3.44390600	0.77775800
39	H	-1.97585400	-3.86930400	1.60022400
40	C	0.34069300	-2.54953700	1.38616400
41	C	-2.29184100	-4.34538200	-2.24809400
42	H	-1.81067200	-6.59459900	-0.90104100
43	C	0.36127800	-8.11376200	-0.39623600
44	H	2.42977100	-6.85173600	-1.60141700
45	C	2.70931500	-4.63354600	-3.06674200
46	C	-1.79310200	0.70206500	-4.61924700
47	H	-0.83608300	3.06625200	-5.40279900
48	C	1.59148300	4.03461800	-6.06980000
49	H	3.31460200	1.97070300	-5.74404600
50	C	3.10268400	-0.57796500	-4.97221800
51	C	4.21037500	-0.65751100	0.40079000
52	H	6.51637100	0.33189200	-0.51854500
53	C	7.22192700	2.43158000	-2.08491300
54	H	4.91506700	3.64133200	-2.75781800
55	C	2.33155700	3.25412900	-2.23510800
56	H	-0.68322900	1.47193400	1.50732900
57	H	1.74083900	2.65462100	0.93844700
58	H	-0.86139100	-4.28691600	-5.18880900
59	H	-0.64758800	-1.78596900	-6.32757100
60	H	-2.31567600	1.65018900	-0.34664600
61	H	-3.69241100	0.96507200	-1.21912000
62	H	-2.07262200	0.87038400	-1.92795500
63	H	-4.44068300	-4.01422800	1.71361500
64	H	-4.57178800	-4.16784400	-0.04923400
65	H	-5.46153500	-2.88846000	0.80128000
66	H	0.69608200	-1.87437800	2.17706100
67	H	0.29176400	-3.55817500	1.81885200
68	H	1.10024400	-2.56986000	0.58140300
69	H	-2.48850600	-4.05027100	-3.28816800
70	H	-3.11501200	-5.00819000	-1.94197600
71	H	-2.35882400	-3.44361600	-1.61772600
72	H	1.35649000	-8.30061000	0.02900000
73	H	0.11422100	-8.96486100	-1.04627700
74	H	-0.35994800	-8.11073800	0.43204400
75	H	3.57647000	-5.23376600	-2.75727400
76	H	2.89818100	-3.59315100	-2.73979300
77	H	2.68155800	-4.64783100	-4.16483300
78	H	-2.13735400	-0.14569000	-5.22892000
79	H	-1.95398700	0.44382700	-3.55932800
80	H	-2.45343200	1.55089200	-4.84736200
81	H	2.64542800	4.29313400	-5.89974500

Supplementary Material (ESI) for Chemical Communications

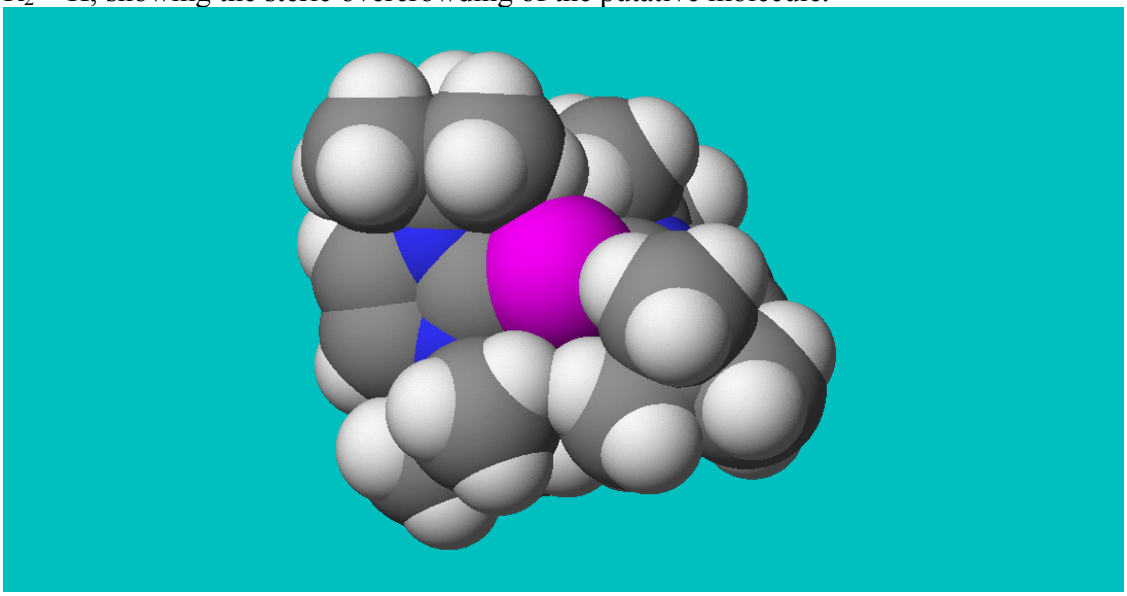
82	H	1.39692000	4.12784400	-7.14746000
83	H	0.97674600	4.78649200	-5.55657900
84	H	4.08036800	-0.11080800	-5.15419200
85	H	2.98710500	-1.38500800	-5.70853900
86	H	3.13534500	-1.03259400	-3.96312700
87	H	5.17171000	-1.15099300	0.60019500
88	H	3.77574600	-0.39079900	1.37409900
89	H	3.54959400	-1.40619100	-0.07674700
90	H	7.97206500	1.66690900	-1.84282200
91	H	7.27779700	2.62321000	-3.16501500
92	H	7.51369800	3.35729000	-1.56930300
93	H	2.68072400	4.23870800	-2.57875600
94	H	1.56963600	3.43733000	-1.46516500
95	H	1.83926400	2.76992400	-3.09448800

Atomic positions used in the single-point B88PW91 calculation of **2f** from R_1 = Mes, R_2 = H.

1	N	0.00000000	0.00000000	0.00000000
2	C	0.08917500	1.15847000	0.79891300
3	C	1.29789700	1.74866600	0.51399500
4	N	1.92487900	0.95121200	-0.46513800
5	C	1.12900300	-0.13494000	-0.79321400
6	P	1.77437500	-1.60823100	-1.79657800
7	C	0.61417300	-2.00946300	-3.24243600
8	N	0.13910500	-3.28863900	-3.48424100
9	C	-0.43265700	-3.37159900	-4.77013100
10	C	-0.32456400	-2.12433800	-5.33866600
11	N	0.32559700	-1.29939100	-4.39779300
12	H	-0.78669200	-0.64922300	0.00499000
13	H	-0.65753800	1.51755100	1.50713600
14	H	1.69581200	2.66000200	0.96034800
15	H	2.83806300	1.14665500	-0.87537900
16	H	0.19537300	-4.06326300	-2.82303600
17	H	-0.87615200	-4.25635300	-5.22688400
18	H	-0.67464600	-1.82949800	-6.32791400
19	H	0.55227500	-0.31610000	-4.54663900

Supplementary Material (ESI) for Chemical Communications

Figure S3. Space-filling picture of the PM3 optimized structure of **2** where R_1 = ^{t}Bu and R_2 = H, showing the steric overcrowding of the putative molecule.



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