Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Isolation of a Lewis Base Stabilized Parent Phosphenium (PH_2^+) and Related Species

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General

All manipulations were performed under an atmosphere of dry argon using standard Schlenk or dry box techniques. Solvents were dried by standard methods and distilled under argon. ^{1}H, ^{31}P, ^{11}B and ^{13}C NMR spectra were recorded on Varian VX 500, Bruker 300 and Jeol 500 spectrometer at 25 °C. NMR multiplicities are abbreviated as follows: *s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *sept* = septet, *m* = multiplet, *br* = broad signal. Chemical shifts are given in ppm. Single crystal X-ray diffraction data were collected on a Bruker Apex II-CCD detector using Mo-Kα radiation (λ = 0.71073 Å). Crystals were selected under oil, mounted on nylon loops then immediately placed in a cold stream of N_2. Structures were solved and refined using Olex2 and SHELXTL. Mass spectra were performed at the UC San Diego Mass Spectrometry Laboratory. Melting points were measured with an electrothermal MEL-TEMP apparatus.

Synthesis and Characterization

NHC-PH adduct 1: [NHC-H][Cl] (1.00 g, 1.05 mmol) and NaPCO•(1,4-dioxane)$_{2.5}$ (0.40 mg, 1.55 mmol) were dissolved in 50 mL of THF and heated to 80 ºC overnight. After cooling to room temperature, the volatiles were removed under vacuum. The residue was extracted with 60 mL of benzene. The solvent was removed under vacuum leading to 0.87 mg (87 %) of an off white solid. Single colourless crystals were grown by slow evaporation of a saturated ether solution. M.p.: 278-280 ºC. IR (solid, cm^{-1}) ν_{max} 2291 (P-H). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.46 (m, 8H), 7.26 (m, 12H), 7.13 (m, 12H), 6.90 (s, 4H), 6.87 (m, 8H), 5.61 (s, 4H), 5.09 (s, 2H), 2.26 (s, 6H), 2.10 (d, J_{PH} = 172 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 177.3 (d, J_{PC} = 81.7 Hz), 143.8, 143.1, 142.4, 139.4, 133.5, 130.7, 130.2, 129.7, 129.5, 128.6, 128.3, 128.1, 126.5, 126.3, 119.0, 51.7, 22.0; ^{31}P NMR (121 MHz, $CDCl_3$): δ = -134.5 (d, J_{PH} = 172 Hz). HRMS: m/z calculated for $[C_{69}H_{58}N_2P]^+$ $(M+H)^+$ 945.4332, found 945.4328.

NHC-PHCPh$_3$ adduct 2a: **1** (100 mg, 0.106 mmol) and [(Ph_3C^+)(BF_4^-)] (35 mg, 0.106 mmol) were dissolved in 5 mL of chloroform. After 5 minutes, the volatiles were removed under vacuum. The residue was washed with 5 mL of diethyl ether and 5 mL of pentane, leading to 120 mg (89 %) of a white solid. Colourless crystals were grown by vapour diffusion of pentane into a saturated THF solution. M.p.: 340-345 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.46-6.24 (br m, 63H), 5.27 (s, 2H), 5.20 (d, J_{PH} = 278 Hz), 2.28 (br s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.5 (d, J_{PC} = 96 Hz), 142.8, 142.7, 141.5, 141.2, 140.7, 132.3, 131.6, 130.8, 130.1-127.2 (broad and overlapping peaks), 67.7 (d, J_{PC} = 39 Hz), 51.9, 22.1; ^{31}P NMR (121 MHz, $CDCl_3$): δ = -49.4 (d, J_{PH} = 278 Hz). HRMS: m/z calculated for $[C_{88}H_{72}N_2P]^+$ $(M)^+$ 1187.5428, found 1187.5431.

NHC-PHMe adduct 2b: **1** (60 mg, 0.063mmol) was dissolved in 5 mL of benzene and one drop of MeOTf was added to the solution. After 5 minutes, the volatiles were removed under vacuum. The residue was washed with 5 mL of diethyl ether and 5 mL of pentane, leading to 61 mg (87 %) of a white solid. Colourless crystals were grown by vapour diffusion of pentane into a saturated chloroform solution. M.p.: 330-335 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.30-7.22 (m, 24H), 6.97 (m, 4H), 6.89 (m, 8H), 6.82 (m, 8H), 6.02 (s, 2H), 4.97 (s, 2H), 4.89 (s, 2H), 4.06 (dq, J_{PH}= 241 Hz, J_{HH} = 7.6 Hz, 1H), 2.29 (s, 6H), 0.43 (dd, J_{PH} = 7.4 Hz, J_{HH} = 7.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.6 (d, J_{PC} = 54 Hz), 142.6, 142.2, 142.1, 141.0, 140.3, 140.2, 140.0, 131.6, 131.2, 129.6, 129.4, 129.3, 129.2, 129.1, 129.0, 128.9, 127.9, 127.7, 127.6, 126.7, 51.9, 51.6, 22.0, 0.6 (d, J_{PC} = 16 Hz); ^{31}P NMR (121 MHz, $CDCl_3$): δ = -86.3 (d, J_{PH} = 240 Hz). HRMS: m/z calculated for $[C_{70}H_{60}N_2P]^+$ $(M)^+$ 959.4489, found 959.4488.

NHC-PH$_2$ adduct 2c: **1** (50 mg, 0.053mmol) was dissolved in 5 mL of benzene and one drop of HOTf was added to the solution. After 5 minutes, the volatiles were removed under vacuum. 5 mL of diethyl ether was added to give a clear solution, but upon rigorous stirring a precipitate appeared. The white solid was collected by filtration (49 mg; 85 %). Colourless crystals were grown by vapour diffusion of pentane into a saturated chloroform solution. M.p.: 295-299 ºC. IR (solid, cm^{-1}) ν_{max} 2357, 2302 (P-H). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.29-7.24 (m, 16H), 7.18 (m, 8H), 6.93 (s, 4H), 6.85 (m, 16H), 6.38 (s, 2H), 4.87 (s, 4H), 3.16 (d, J_{PH} = 223 Hz, 2H), 2.30 (s, 6H);

^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.0 (d, J_{PC} = 44 Hz), 142.9, 141.5, 140.6, 140.4, 131.7, 129.8, 129.5, 129.3, 129.1, 128.1, 127.8, 127.6, 51.9, 22.1; ^{31}P NMR (121 MHz, $CDCl_3$): δ = -166.6 (t, J_{PH} = 223 Hz). HRMS: m/z calculated for $[C_{69}H_{58}N_2P]^+$ $(M)^+$ 945.4332, found 945.4333.

Iron complex 3: **1** (50 mg, 0.053 mmol) and $Fe_2(CO)_9$ (15 mg, 0.041 mmol) were dissolved in 5 mL of benzene. After 6 hours, the mixture was filtered and the solvent was removed under vacuum. The residue was washed with 5 mL of pentane, leading to 46 mg (80 %) of an orange solid. Single orange crystals were grown by vapour diffusion of pentane into a saturated THF solution. M.p.: 265-270 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.23 (m, 20H), 7.11 (m, 12H), 6.85 (s, 4H), 6.69 (m, 8H), 5.55 (s, 4H), 5.06 (s, 2H), 3.22 (d, J_{PH} = 208 Hz, 1H), 2.22 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 216.3 (d, J_{PC} = 3 Hz), 143.0, 142.7, 141.8, 140.9, 132.2, 131.6, 130.2, 129.6, 128.4, 128.3, 126.8, 127.7, 50.9, 21.9; ^{31}P NMR (121 MHz, $CDCl_3$): δ = -96.4 (d, J_{PH} = 208 Hz). HRMS: m/z calculated for $[C_{73}H_{58}FeN_2O_4P]^+$ $(M+H)^+$ 1113.3480, found 1113.3470.

Bis(gold) complex 4: **1** (50 mg, 0.053 mmol) and (tht)AuCl (37 mg, 0.115 mmol) were dissolved in 5 mL of benzene. After 5 minutes, 3 mL pentane was added which induced a precipitate. The mixture was filtered and the solid was washed with 2 mL benzene. 37 mg (53 %) of a light yellow solid was obtained. Single crystals were grown by vapour diffusion of pentane into a saturated chloroform solution. M.p.: 270 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.55 (m, 4H), 7.40 (s, 3H), 7.37-7.31 (m, 14H), 7.22-7.08 (m, 12H), 7.01 (m, 4H), 6.78 (m, 4H), 6.70 (m, 4H), 5.51 (m, 3H), 5.29 (d, J_{PH} = 373 Hz, 1H), 5.12 (2, 2H), 2.37 (s, 3H), 2.34 (br s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.0 (d, J_{PC} = 16.5 Hz), 143.0, 142.9, 142.8, 147.8, 141.6, 141.5, 140.4, 140.2, 131.9, 131.8, 131.0, 130.9, 129.4, 129.1, 129.0, 128.8, 128.5, 128.1, 127.9, 127.8, 127.7, 127.4, 127.2, 126.9, 125.9, 52.3, 52.2, 22.2, 22.1; ^{31}P NMR (121 MHz, $CDCl_3$): δ = -91.2 (d, J_{PH} = 373 Hz).HRMS: m/z calculated for $[C_{69}H_{56}Au_2N_2P]^+$ $(M-2HCl+H)^+$ 1337.3507, found 1337.3483.

Bis(borane) complex 5: **1** (50 mg, 0.053mmol) was dissolved in 5 mL of THF and two drops of Me_3S-BH_3 were added to the solution. After 5 minutes, 3 mL of pentane was added which induced a precipitate. The mixture was filtered and the solid was washed with 2 mL pentane. 46 mg (89%) of a colourless solid was obtained. Colourless single crystals were grown by vapour

diffusion of pentane into a saturated THF solution. M.p.: 257 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.35-7.24 (m, 20H), 7.09 (m, 12H), 6.85 (s, 4H), 6.71 (m, 8H), 5.44 (s, 4H), 4.88 (dm, J_{PH} = 330 Hz, 1H), 4.86 (s, 2H), 2.25 (s, 6H), 1.13-0.75 (br, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.1 (d, J_{PC} = 14 Hz), 143.9, 142.1, 142.0, 141.4, 130.9, 130.7, 129.4, 128.5, 127.0, 126.9, 124.8, 51.4, 22.1; ^{11}B NMR (96 MHz, $CDCl_3$): δ = -37.0 (br); ^{31}P NMR (121 MHz, $CDCl_3$): δ = -39.2 (br d, J_{PH} = 330 Hz). HRMS: m/z calculated for $[C_{69}H_{62}B_2N_2P]^+$ $(M\text{-}H^-)^+$ 971.4852, found 971.4841.

Observation of IPr-PH2$^+$: **A** (50 mg, 0.111 mmol) was dissolved in 2 mL of benzene and one drop of HOTf was added to the solution. ^{31}P NMR (121 MHz): δ = -165.3 ppm (t, J_{PH} = 220 Hz).

Tables of Crystallographic Data

	1•Et_2O	**2a**	**2c•H_2O**
Formula	$C_{73}H_{67}N_2OP$	$C_{88}H_{72}BF_4N_2P$	$C_{71}H_{58}F_6N_2O_7PS_2$
wt	1019.26	1275.26	1260.28
Cryst. syst.	Orthorhombic	Triclinic	Triclinic
Space group	Pna21	P-1	P-1
a(Å)	18.9194(13)	13.7202(8)	14.4808(11)
b(Å)	14.8964(11)	16.4329(11)	14.6435(11)
c(Å)	20.0103(14)	19.0854(12)	15.4095(10)
α(deg)	90.00	74.147(2)	83.039(2)
β(deg)	90.00	78.554(2)	84.164(2)
γ(deg)	90.00	81.404(2)	77.715(2)
V(Å^3)	5639.5(7)	4036.3(4)	3159.5(4)
Z	4	2	2
d(calc) gcm^{-3}	1.200	1.049	1.325
R(int)	0.0870	0.0527	0.0398
μ, mm^{-1}	0.097	0.085	0.184
Total data	9816	14228	11126
>2σ(F_O^2)	6953	10958	9434
Variables	699	869	983

R (>2σ)	0.0589	0.0559	0.0527
R_w	0.1202	0.1498	0.1251
GOF	1.052	1.072	1.068

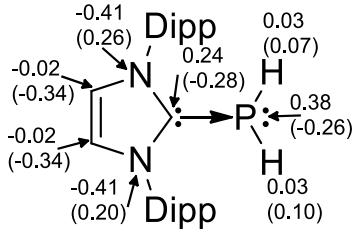
	3	**4**	**5**
Formula	$C_{73}H_{57}FeN_2O_4P$	$C_{69}H_{57}Au_2Cl_2N_2P$	$C_{69}H_{63}B_2N_2P$
wt	1113.03	1409.97	972.80
Cryst. syst.	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
a(Å)	12.6626(8)	15.4817(9)	13.5874(18)
b(Å)	18.3247(11)	18.0766(10)	17.073(2)
c(Å)	25.5405(15)	24.4404(14)	24.447(3)
α(deg)	90.00	90.00	90.00
β(deg)	101.719(2)	98.019(2)	105.718(3)
γ(deg)	90.00	90.00	90.00
V($Å^3$)	5802.8(6)	6772.9(7)	5459.0(12)
Z	4	4	4
d(calc) gcm^{-3}	1.274	1.383	1.184
R(int)	0.0868	0.0520	0.1172
μ, mm^{-1}	0.341	4.467	0.095
Total data	10031	11927	9604
>2σ(F_O^2)	6713	10722	5654
Variables	736	713	697
R (>2σ)	0.0567	0.0447	0.0571
R_w	0.1433	0.1246	0.1231
GOF	1.042	1.106	1.020

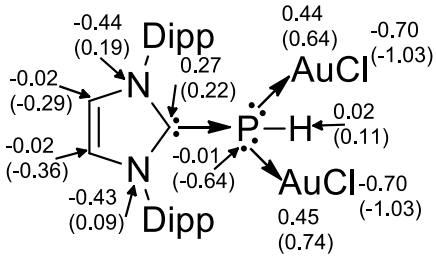
Computational Details

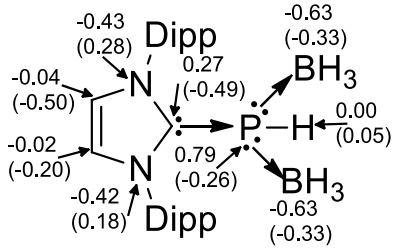
Calculations were carried out with the Gaussian 09 package.[1] To reduce the computational cost, the 2,6-dibenzhydryl-4-methylphenyl groups were replaced by 2,6-diisopropylphenyl groups. Geometry optimizations were performed with the M06-2X

functional because this method was recently established as an excellent functional for describing main group systems.[2] The 6-31G(d) basis set was used for all the atoms except Au and Fe. The LANL2DZ basis set was applied for Au and Fe. Frequency calculations at the same level of theory were performed to identify the number of imaginary frequencies (zero for local minimum) and provide frontier molecular orbitals (HOMO). Natural bond orbital (NBO) calculations were carried out at M06-2X/6-311+G(2d,p)//M06-2X/6-31G(d) or M06-2X/6-311+G(2d,p)+SDD//M06-2X/6-31G(d)+LANL2DZ level.

NBO and Mulliken charges for **2c**, **4** and **5**



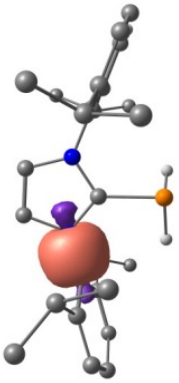


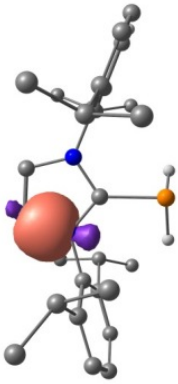


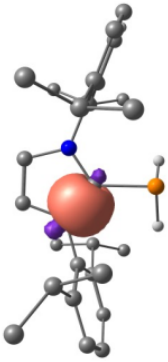
Mulliken charges are given in parantheses

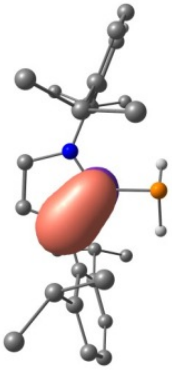
NBO details of **2c**, **4** and **5**.

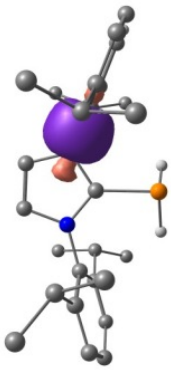
2c


NBO 1


NBO 2


NBO 3


NBO 4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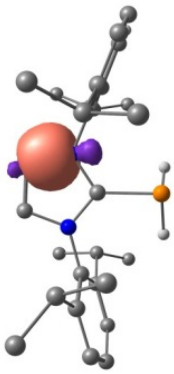
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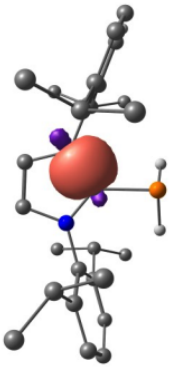
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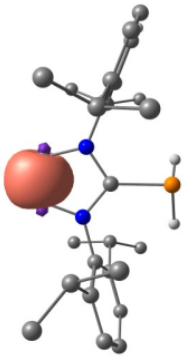
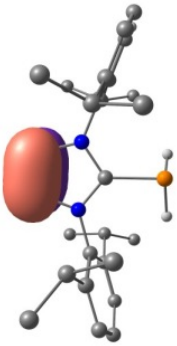
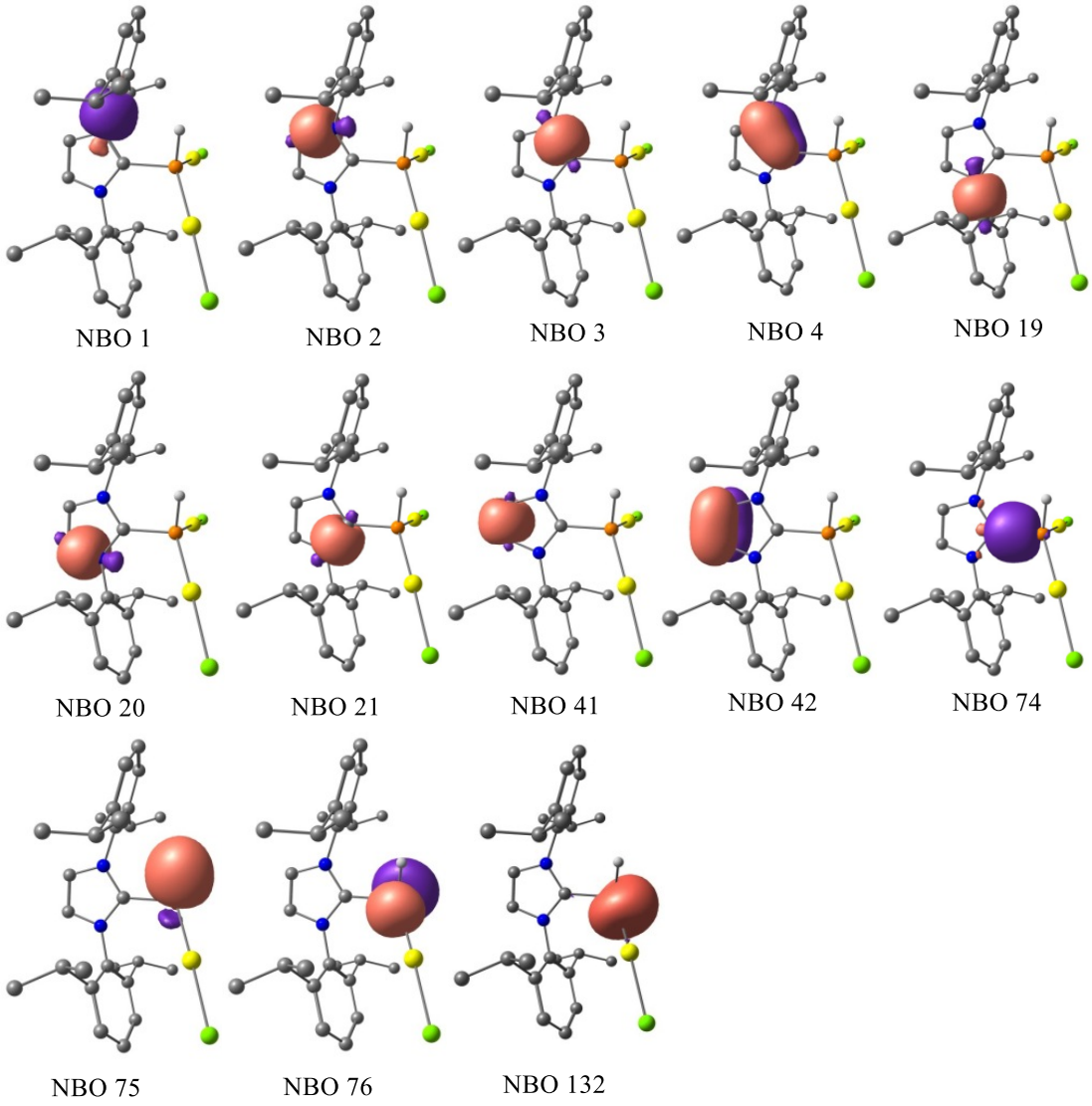

NBO 43


NBO 44

entry	Occupancy	Bond orbital	The percentage of the NBOs
NBO 1	1.98017	BD N1-C10	N1 65.66%; C10 34.34%
NBO 2	1.97442	BD N1-C27	N1 64.47%; C27 35.53%
NBO 3	1.97865	BD N1-C65	N1 63.85%; C65 36.15%
NBO 4	1.89564	BD N1-C65	N1 71.32%; C65 28.68%
NBO 21	1.97983	BD N11-C12	N11 65.57%; C12 34.43%
NBO 22	1.97510	BD N11-C28	N11 64.46%; C28 35.54%
NBO 23	1.97802	BD N11-C65	N11 63.97%; C65 36.03%
NBO 43	1.97476	BD C27-C28	C27 49.97%; C28 50.03%
NBO 44	1.84875	BD C27-C28	C27 50.10%; C28 49.90%
NBO 76	1.97230	BD C65-P66	C65 66.83%; P66 33.17%
NBO 77	1.96356	BD P66-H67	P66 50.78%; H67 49.22%
NBO 78	1.97015	BD P66-H68	P66 50.99%; H68

			49.01%
NBO 114	1.93745	LP P66	P66 100%

4



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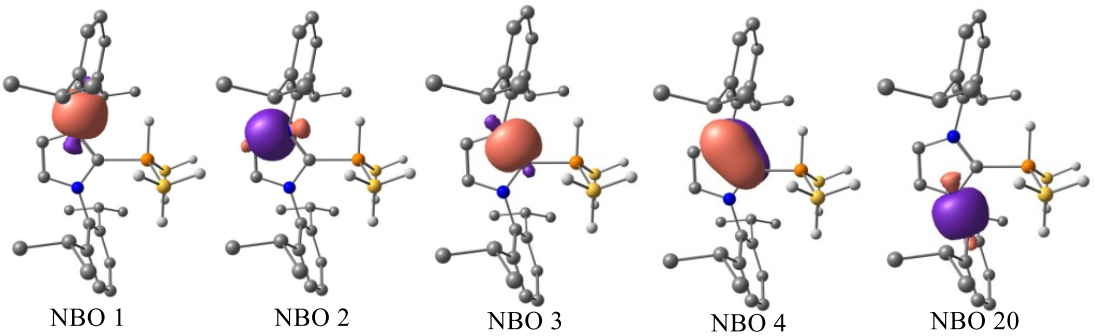
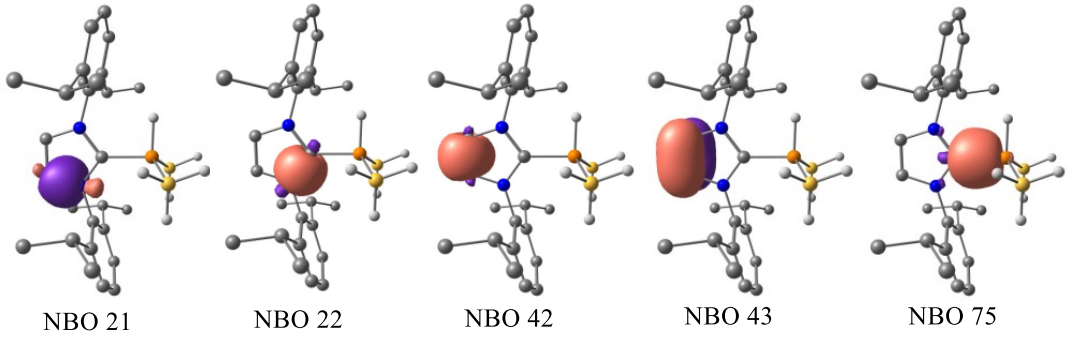
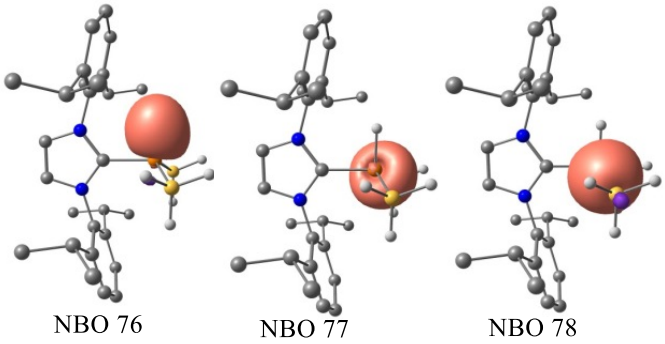
NBO 2	1.97399	BD N1-C27	N1 64.36%; C27 35.64%
NBO 3	1.97795	BD N1-C63	N1 64.63%; C63 35.37%

NBO 4	1.89195	BD N1-C63	N1 72.85%; C63 27.15%
NBO 19	1.97737	BD N11-C12	N11 65.88%; C12 34.12%
NBO 20	1.97748	BD N11-C12	N11 65.65%; C12 34.35%
NBO 21	1.97564	BD N11-C28	N11 64.04%; C28 35.96%
NBO 41	1.97407	BD C27-C28	C27 50.05%; C28 49.95%
NBO 42	1.86577	BD C27-C28	C27 50.12%; C28 49.88%
NBO 74	1.96613	BD C63-P64	C63 66.55%; P64 33.45%
NBO 75	1.96273	BD P64-H65	P64 51.55%; H65 48.45%
NBO 76	1.82078	BD P64-Au68	P64 81.16%; Au68 18.84%
NBO 132	1.68052	LP P64	P64 100%







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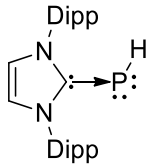
NBO 2	1.97464	BD N1-C27	N1 64.12%; C27 35.88%
NBO 3	1.97875	BD N1-C63	N1 64.60%; C63 35.40%
NBO 4	1.89329	BD N1-C63	N1 73.61%; C63 26.39%
NBO 20	1.97748	BD N11-C12	N11 65.65%; C12 34.35%
NBO 21	1.97564	BD N11-C28	N11 64.04%; C28 35.96%
NBO 22	1.97803	BD N11-C63	N11 64.43%; C63 35.57%
NBO 42	1.97366	BD C27-C28	C27 50.08%; C28

			49.92%
NBO 43	1.87109	BD C27-C28	C27 50.39%; C28 49.61%
NBO 75	1.96650	BD C63-P64	C63 68.60%; P64 31.40%
NBO 76	1.96663	BD P64-H65	P64 50.25%; H65 49.75%
NBO 77	1.95235	BD P64-B68	P64 64.23%; B68 35.77%
NBO 78	1.95482	BD P64-B71	P64 64.31%; B71 35.69%

Cartesian coordinates:



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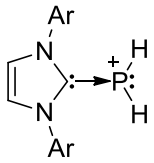

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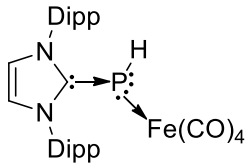

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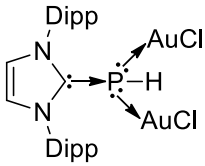

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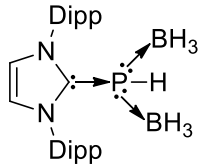

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1	-2.246205	-3.814274	-2.226299
1	-2.323200	-2.094284	-2.642123
5	-0.656760	-1.856619	2.491322
1	-0.196773	-1.986949	3.603007
1	-1.857511	-1.723522	2.483842
5	-0.570335	1.645549	2.653769
1	-0.146224	1.618819	3.786674
1	-0.068631	2.515121	1.970349
1	-0.232131	-2.671308	1.696163
1	-1.775667	1.588252	2.595405

1. Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, **2010**.
2. Y. Zhao and D. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215-241.