Electronic supplementary information

π-Excess aromatic σ^2-P ligands: Synthesis and structure of an unprecedented μ^2-P-1,3-benzazaphosphole bridged tetranuclear copper(I) acetate complex

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Content

1. NMR spectra of complex 1.

Figure S1. ^{31}P NMR spectrum of **1** in CD_2Cl_2.

Acquisition Time (sec)	0.3277						
Comment	Prof.Heinicke:1074NgDCM 31P{1H}-Spektrum Loesungsmittel: CD2Cl2 Ref.: extern, H3PO4 = 0.0 ppm (+/- 0.3)					EMAU Greifswald - Avance II - 300	
Date	26 Mar 2014 10:57:20	***Date Stamp***		***File Name***			
Frequency (MHz)	121.49	***Nucleus***	31P	***Number of Transients***	128	***Origin***	spect
Original Points Count	16384	***Owner***	nmr	***Points Count***	32768	***Pulse Sequence***	zgpg30
Receiver Gain	23100.00	***SW(cyclical) (Hz)***	50000.00	***Solvent***	DICHLOROMETHANE-d2		
Spectrum Offset (Hz)	499.9960	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	49998.47	***Temperature (degree C)***	27.3

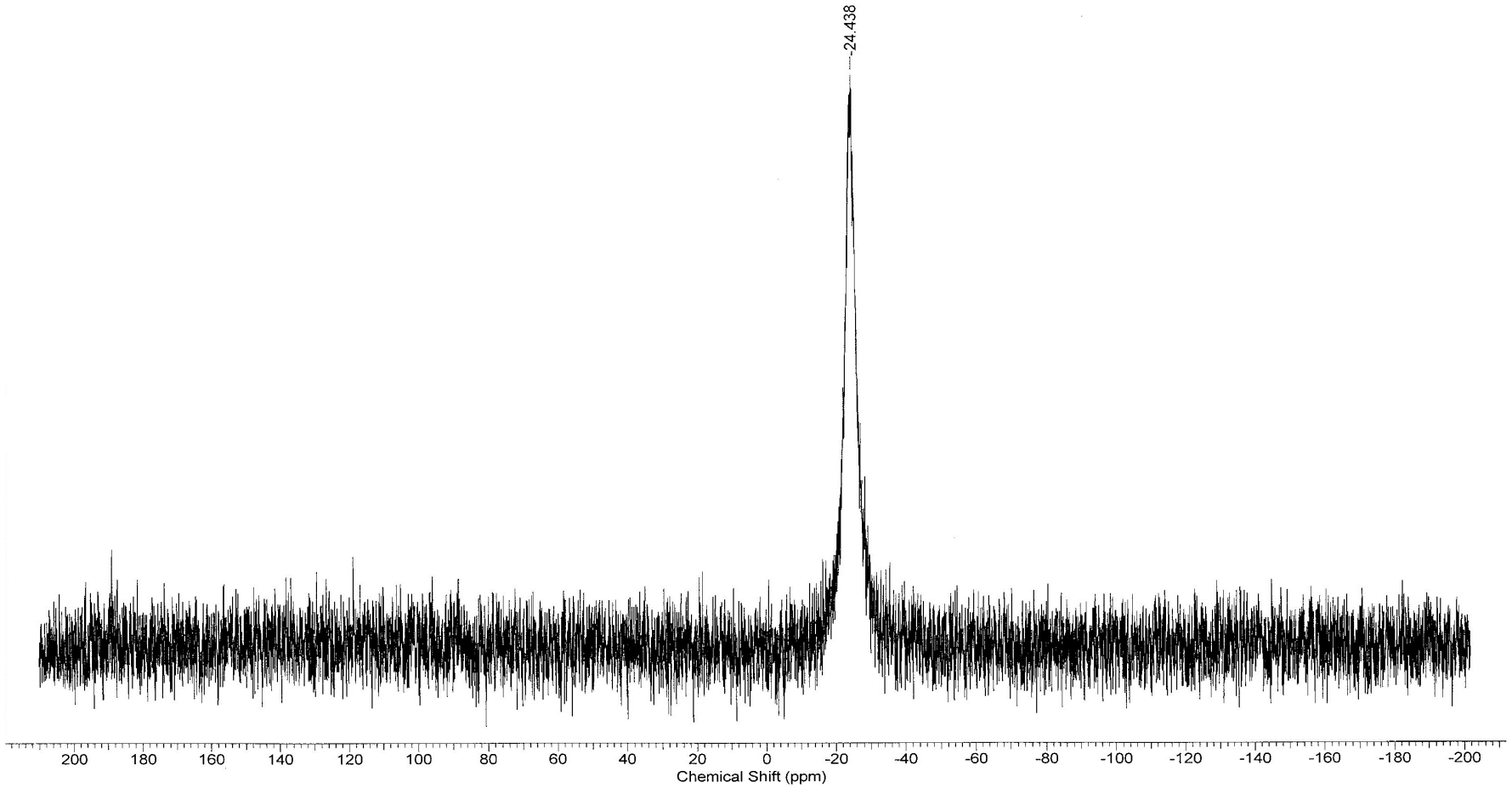
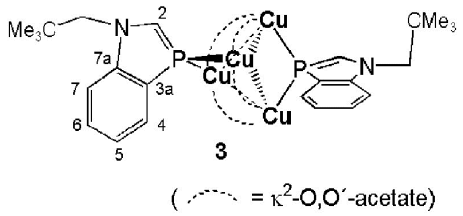


Figure S2. ^{13}C NMR spectrum of **1** in CD_2Cl_2.

Acquisition Time (sec)	0.7537	*Comment*	Heinicke: 1074NgDCM 13C{1H}-NMR-Spektrum LM: CD2Cl2 Referenz: LM = 53,8 ppm		EMAU, AVANCE II - 300		
Date	27 Mar 2014 12:35:28	*Date Stamp*					
File Name						*Frequency (MHz)*	75.47
Nucleus	13C	*Number of Transients*	1228	*Origin*	spect	*Original Points Count*	16384
Owner	nmr	*Points Count*	16384	*Pulse Sequence*	zgpg30	*Receiver Gain*	32800.00
SW(cyclical) (Hz)	21739.13	*Solvent*	DICHLOROMETHANE-d2			*Spectrum Offset (Hz)*	8398.3018
Spectrum Type	STANDARD	*Sweep Width (Hz)*	21737.80	*Temperature (degree C)*	26.200		



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(⋯ = κ^2-O,O´-acetate)

Figure S3. Temperature-dependent ^{31}P NMR spectra of kinetically unstable $(npBAP)_xCuOAc$ complexes, obtained from npBAP and CuOAc (molar ratio 2:1) in THF at 20-22 °C (3 d) after separation from insoluble **1**; measurement in CD_2Cl_2 solution.

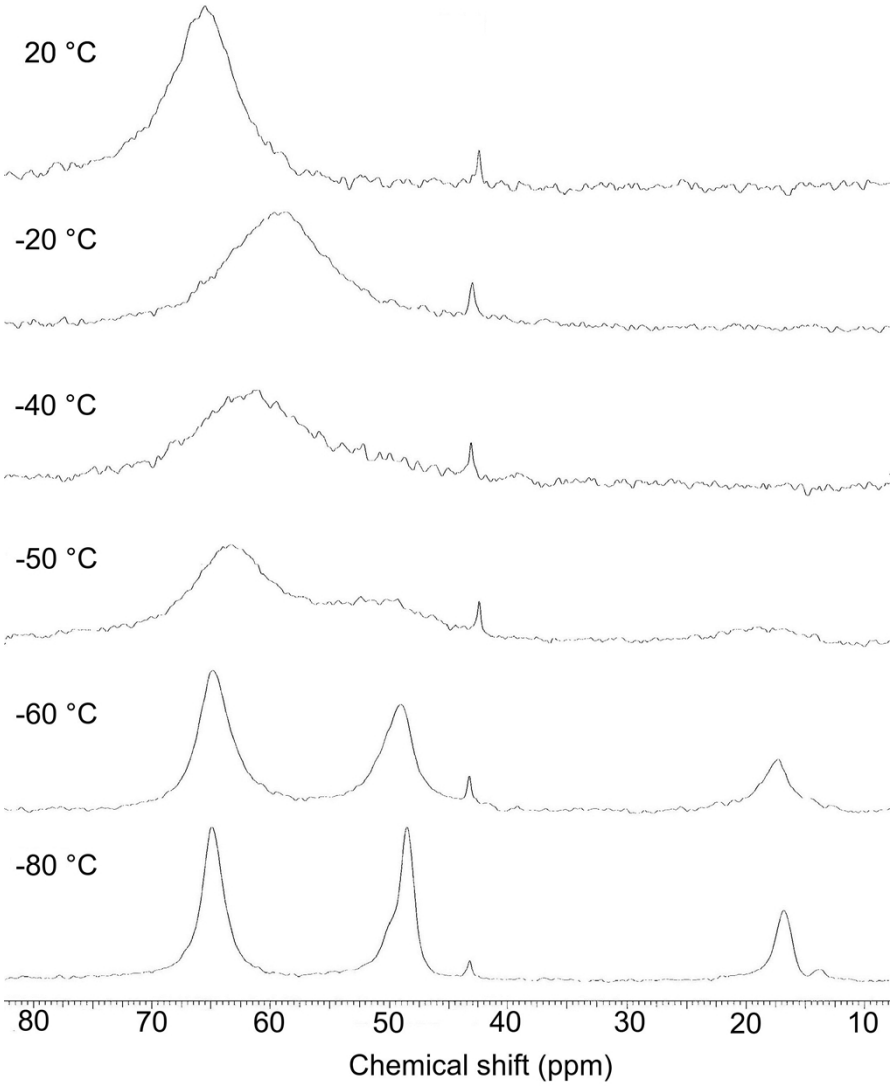
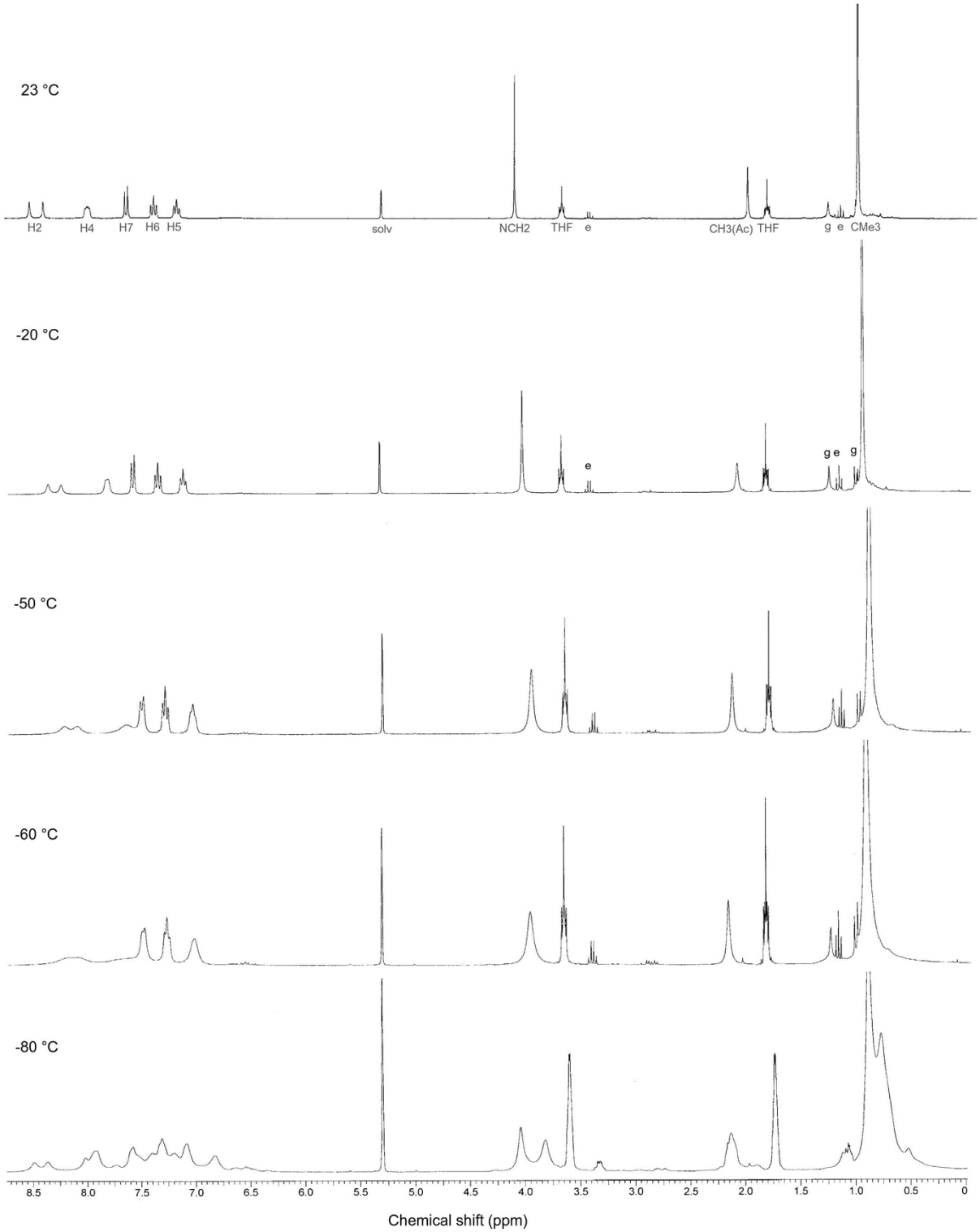


Figure S4. Temperature-dependent ^{1}H NMR spectra of kinetically unstable $(npBAP)_xCuOAc$ complexes, obtained from npBAP and CuOAc (molar ratio 2:1) in THF at 20-22 °C (3 d) after separation from insoluble **1**; measurement in CD_2Cl_2 solution, average $x \approx 2.5$ at 23 °C.



(e, g – signals of minor amounts of diethyl ether and hydrocarbon grease in the filtrate)

2. Tables with atomics coordinates, bond lengths and angles, and anisotropic displacement parameters of 1.

Table S1. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) of **1**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Cu(1)	7097(1)	3713(1)	2565(1)	25(1)
Cu(2)	5276(1)	5688(1)	2777(1)	22(1)
Cu(3)	3679(1)	4915(1)	2116(1)	25(1)
Cu(4)	4900(1)	2832(1)	2927(1)	25(1)
P(1)	5736(1)	4481(1)	1614(1)	23(1)
P(2)	4801(1)	4194(1)	3544(1)	19(1)
O(1)	8408(2)	4507(2)	2757(1)	32(1)
O(2)	6827(2)	6336(2)	2688(1)	28(1)
O(3)	3788(2)	7273(2)	2523(1)	33(1)
O(4)	2395(2)	6581(2)	2046(1)	34(1)
O(5)	2262(2)	4190(2)	2022(1)	29(1)
O(6)	3524(2)	2304(2)	2556(1)	34(1)
O(7)	6430(2)	1258(2)	3057(1)	35(1)
O(8)	8144(2)	2023(2)	3008(1)	33(1)
N(1)	6799(2)	3850(2)	457(1)	21(1)
N(2)	5254(2)	3369(2)	4897(1)	18(1)
C(1)	6006(2)	5616(2)	896(1)	21(1)
C(2)	5685(3)	6868(2)	838(1)	27(1)
C(3)	5894(3)	7585(2)	199(2)	32(1)
C(4)	6414(3)	7069(2)	-379(2)	32(1)
C(5)	6768(3)	5833(2)	-331(1)	25(1)
C(6)	6554(2)	5113(2)	315(1)	21(1)
C(7)	6384(3)	3409(2)	1100(1)	23(1)
C(8)	7506(3)	3080(2)	-36(1)	25(1)
C(9)	9096(3)	2534(2)	62(2)	30(1)
C(10)	9752(3)	3531(3)	-60(2)	47(1)
C(11)	9613(4)	1781(3)	-495(2)	49(1)
C(12)	9482(3)	1713(3)	801(2)	40(1)
C(13)	3443(2)	4712(2)	4141(1)	19(1)
C(14)	2107(3)	5557(2)	4000(1)	25(1)
C(15)	1252(3)	5828(2)	4559(2)	29(1)
C(16)	1697(3)	5275(2)	5260(2)	30(1)
C(17)	3014(3)	4450(2)	5413(1)	25(1)
C(18)	3885(2)	4167(2)	4845(1)	18(1)
C(19)	5868(2)	3323(2)	4270(1)	19(1)
C(20)	5963(3)	2606(2)	5564(1)	21(1)
C(21)	5812(2)	1329(2)	5772(1)	21(1)
C(22)	4310(3)	1402(2)	5941(2)	30(1)
C(23)	6710(3)	664(2)	6437(2)	31(1)
C(24)	6342(3)	641(2)	5183(2)	29(1)
C(25)	8060(3)	5640(2)	2707(2)	28(1)

C(26)	9205(4)	6169(3)	2690(3)	51(1)
C(27)	2669(3)	7397(2)	2247(2)	29(1)
C(28)	1544(4)	8626(3)	2145(2)	49(1)
C(29)	2468(3)	3067(2)	2220(1)	25(1)
C(30)	1367(3)	2613(3)	2027(2)	35(1)
C(31)	7671(3)	1156(2)	3131(2)	28(1)
C(32)	8664(3)	-117(2)	3401(2)	40(1)
C(33)	5678(5)	9520(3)	2013(2)	52(1)
Cl(1)	7165(2)	9704(2)	1575(1)	90(1)
Cl(2)	4319(1)	9853(1)	1405(1)	64(1)
C(34)	516(3)	2217(2)	3881(2)	33(1)
Cl(3)	-197(1)	1484(1)	4628(1)	41(1)
Cl(4)	1659(1)	2870(1)	4116(1)	45(1)

Table S2. Bond lengths [A] and angles [deg] of **1**.

Cu(1)-O(8)	1.955(2)	C(21)-C(24)	1.528(4)
Cu(1)-O(1)	1.988(2)	C(21)-C(22)	1.529(4)
Cu(1)-P(1)	2.2115(11)	C(25)-C(26)	1.505(4)
Cu(2)-O(3)	1.970(2)	C(27)-C(28)	1.511(4)
Cu(2)-O(2)	1.9714(18)	C(29)-C(30)	1.509(3)
Cu(2)-P(2)	2.2068(10)	C(31)-C(32)	1.511(4)
Cu(3)-O(4)	1.963(2)	C(33)-Cl(1)	1.746(4)
Cu(3)-O(5)	1.9631(19)	C(33)-Cl(2)	1.768(5)
Cu(3)-P(1)	2.2101(10)	C(34)-Cl(4)	1.747(3)
Cu(4)-O(6)	1.966(2)	C(34)-Cl(3)	1.756(3)
Cu(4)-O(7)	1.977(2)		
Cu(4)-P(2)	2.2131(9)	O(8)-Cu(1)-O(1)	98.92(9)
P(1)-C(7)	1.738(3)	O(8)-Cu(1)-P(1)	130.58(7)
P(1)-C(1)	1.778(2)	O(1)-Cu(1)-P(1)	121.06(7)
P(2)-C(19)	1.738(3)	O(3)-Cu(2)-O(2)	96.80(8)
P(2)-C(13)	1.788(2)	O(3)-Cu(2)-P(2)	117.93(7)
O(1)-C(25)	1.260(3)	O(2)-Cu(2)-P(2)	133.30(6)
O(2)-C(25)	1.256(3)	O(4)-Cu(3)-O(5)	96.08(9)
O(3)-C(27)	1.249(3)	O(4)-Cu(3)-P(1)	123.74(7)
O(4)-C(27)	1.251(3)	O(5)-Cu(3)-P(1)	125.28(7)
O(5)-C(29)	1.253(3)	O(6)-Cu(4)-O(7)	96.94(9)
O(6)-C(29)	1.258(3)	O(6)-Cu(4)-P(2)	134.87(7)
O(7)-C(31)	1.252(3)	O(7)-Cu(4)-P(2)	121.76(7)
O(8)-C(31)	1.254(3)	C(7)-P(1)-C(1)	89.34(11)
N(1)-C(7)	1.335(3)	C(7)-P(1)-Cu(3)	125.65(9)
N(1)-C(6)	1.406(3)	C(1)-P(1)-Cu(3)	116.99(9)
N(1)-C(8)	1.468(3)	C(7)-P(1)-Cu(1)	103.54(9)
N(2)-C(19)	1.333(3)	C(1)-P(1)-Cu(1)	121.99(9)
N(2)-C(18)	1.401(3)	Cu(3)-P(1)-Cu(1)	100.50(4)
N(2)-C(20)	1.471(3)	C(19)-P(2)-C(13)	89.08(11)
C(1)-C(6)	1.398(3)	C(19)-P(2)-Cu(2)	122.14(8)
C(1)-C(2)	1.400(3)	C(13)-P(2)-Cu(2)	113.51(8)
C(2)-C(3)	1.380(3)	C(19)-P(2)-Cu(4)	102.70(8)
C(3)-C(4)	1.395(4)	C(13)-P(2)-Cu(4)	124.66(8)
C(4)-C(5)	1.380(4)	Cu(2)-P(2)-Cu(4)	105.06(3)
C(5)-C(6)	1.392(3)	C(25)-O(1)-Cu(1)	122.56(18)
C(8)-C(9)	1.545(4)	C(25)-O(2)-Cu(2)	120.95(16)
C(9)-C(10)	1.522(4)	C(27)-O(3)-Cu(2)	122.63(17)
C(9)-C(11)	1.523(4)	C(27)-O(4)-Cu(3)	124.52(19)
C(9)-C(12)	1.525(4)	C(29)-O(5)-Cu(3)	122.48(18)
C(13)-C(14)	1.400(3)	C(29)-O(6)-Cu(4)	121.12(16)
C(13)-C(18)	1.402(3)	C(31)-O(7)-Cu(4)	123.32(16)
C(14)-C(15)	1.375(4)	C(31)-O(8)-Cu(1)	124.78(18)
C(15)-C(16)	1.398(4)	C(7)-N(1)-C(6)	113.1(2)
C(16)-C(17)	1.381(4)	C(7)-N(1)-C(8)	123.2(2)
C(17)-C(18)	1.401(3)	C(6)-N(1)-C(8)	123.6(2)
C(20)-C(21)	1.543(3)	C(19)-N(2)-C(18)	113.46(19)
C(21)-C(23)	1.527(3)	C(19)-N(2)-C(20)	121.8(2)

C(18)-N(2)-C(20)	124.73(19)	C(17)-C(18)-C(13)	121.2(2)
C(6)-C(1)-C(2)	119.8(2)	N(2)-C(18)-C(13)	112.6(2)
C(6)-C(1)-P(1)	110.49(16)	N(2)-C(19)-P(2)	114.40(17)
C(2)-C(1)-P(1)	129.65(19)	N(2)-C(20)-C(21)	114.13(18)
C(3)-C(2)-C(1)	118.8(2)	C(23)-C(21)-C(24)	109.6(2)
C(2)-C(3)-C(4)	120.5(2)	C(23)-C(21)-C(22)	109.5(2)
C(5)-C(4)-C(3)	121.8(2)	C(24)-C(21)-C(22)	109.9(2)
C(4)-C(5)-C(6)	117.5(2)	C(23)-C(21)-C(20)	105.52(19)
C(5)-C(6)-C(1)	121.6(2)	C(24)-C(21)-C(20)	110.78(19)
C(5)-C(6)-N(1)	125.6(2)	C(22)-C(21)-C(20)	111.5(2)
C(1)-C(6)-N(1)	112.71(19)	O(2)-C(25)-O(1)	124.0(2)
N(1)-C(7)-P(1)	114.28(17)	O(2)-C(25)-C(26)	118.8(2)
N(1)-C(8)-C(9)	114.6(2)	O(1)-C(25)-C(26)	117.2(3)
C(10)-C(9)-C(11)	109.3(3)	O(3)-C(27)-O(4)	125.3(2)
C(10)-C(9)-C(12)	109.8(3)	O(3)-C(27)-C(28)	118.1(2)
C(11)-C(9)-C(12)	109.7(3)	O(4)-C(27)-C(28)	116.6(3)
C(10)-C(9)-C(8)	111.2(2)	O(5)-C(29)-O(6)	124.7(2)
C(11)-C(9)-C(8)	105.9(2)	O(5)-C(29)-C(30)	116.8(2)
C(12)-C(9)-C(8)	110.8(2)	O(6)-C(29)-C(30)	118.4(2)
C(14)-C(13)-C(18)	119.5(2)	O(7)-C(31)-O(8)	125.3(2)
C(14)-C(13)-P(2)	130.10(19)	O(7)-C(31)-C(32)	116.8(2)
C(18)-C(13)-P(2)	110.33(17)	O(8)-C(31)-C(32)	118.0(2)
C(15)-C(14)-C(13)	119.2(2)	Cl(1)-C(33)-Cl(2)	111.3(2)
C(14)-C(15)-C(16)	121.0(2)	Cl(4)-C(34)-Cl(3)	111.96(17)
C(17)-C(16)-C(15)	121.0(2)		
C(16)-C(17)-C(18)	118.1(2)		
C(17)-C(18)-N(2)	126.2(2)		

Symmetry transformations used to generate equivalent atoms:

Table S3. Anisotropic displacement parameters (A^2 x 10^3) of **1**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Cu(1)	27(1)	21(1)	25(1)	-1(1)	-2(1)	-9(1)
Cu(2)	20(1)	20(1)	24(1)	-1(1)	1(1)	-7(1)
Cu(3)	25(1)	21(1)	29(1)	-5(1)	2(1)	-9(1)
Cu(4)	26(1)	20(1)	29(1)	-7(1)	-5(1)	-6(1)
P(1)	29(1)	23(1)	16(1)	-3(1)	3(1)	-11(1)
P(2)	21(1)	22(1)	16(1)	-4(1)	3(1)	-9(1)
O(1)	26(1)	25(1)	45(1)	-2(1)	-3(1)	-10(1)
O(2)	25(1)	25(1)	34(1)	-5(1)	2(1)	-12(1)
O(3)	28(1)	23(1)	43(1)	-9(1)	-8(1)	-2(1)
O(4)	31(1)	25(1)	45(1)	-9(1)	-8(1)	-6(1)
O(5)	28(1)	29(1)	31(1)	-4(1)	-2(1)	-12(1)
O(6)	35(1)	27(1)	43(1)	-6(1)	-10(1)	-13(1)

O(7)	28(1)	21(1)	54(1)	-9(1)	0(1)	-6(1)
O(8)	29(1)	22(1)	42(1)	0(1)	-5(1)	-8(1)
N(1)	22(1)	23(1)	19(1)	-5(1)	-1(1)	-7(1)
N(2)	22(1)	17(1)	17(1)	-4(1)	1(1)	-9(1)
C(1)	23(1)	21(1)	17(1)	-1(1)	1(1)	-7(1)
C(2)	34(1)	22(1)	24(1)	-5(1)	5(1)	-8(1)
C(3)	38(1)	22(1)	32(1)	-1(1)	4(1)	-9(1)
C(4)	34(1)	31(1)	25(1)	4(1)	3(1)	-11(1)
C(5)	26(1)	30(1)	16(1)	-2(1)	1(1)	-7(1)
C(6)	20(1)	24(1)	16(1)	-2(1)	-2(1)	-8(1)
C(7)	26(1)	23(1)	24(1)	-4(1)	0(1)	-11(1)
C(8)	27(1)	28(1)	24(1)	-12(1)	-1(1)	-9(1)
C(9)	28(1)	29(1)	32(1)	-13(1)	1(1)	-5(1)
C(10)	24(1)	39(2)	75(3)	-11(2)	5(2)	-11(1)
C(11)	46(2)	49(2)	45(2)	-25(2)	6(2)	3(1)
C(12)	37(2)	36(1)	41(2)	-11(1)	-8(1)	-2(1)
C(13)	21(1)	19(1)	21(1)	-6(1)	2(1)	-10(1)
C(14)	24(1)	23(1)	28(1)	-4(1)	0(1)	-9(1)
C(15)	23(1)	24(1)	40(1)	-9(1)	5(1)	-7(1)
C(16)	28(1)	28(1)	35(1)	-14(1)	14(1)	-9(1)
C(17)	31(1)	23(1)	24(1)	-9(1)	7(1)	-11(1)
C(18)	22(1)	15(1)	20(1)	-6(1)	2(1)	-9(1)
C(19)	19(1)	19(1)	22(1)	-5(1)	4(1)	-9(1)
C(20)	26(1)	21(1)	19(1)	-3(1)	-3(1)	-11(1)
C(21)	25(1)	19(1)	21(1)	-3(1)	-1(1)	-10(1)
C(22)	29(1)	25(1)	35(1)	-1(1)	2(1)	-15(1)
C(23)	36(1)	26(1)	27(1)	2(1)	-9(1)	-9(1)
C(24)	38(1)	24(1)	30(1)	-10(1)	2(1)	-13(1)
C(25)	26(1)	27(1)	34(1)	-4(1)	0(1)	-15(1)
C(26)	32(2)	43(2)	90(3)	-19(2)	5(2)	-24(1)
C(27)	29(1)	23(1)	31(1)	-8(1)	-2(1)	-4(1)
C(28)	37(2)	31(1)	73(3)	-22(2)	-17(2)	6(1)
C(29)	26(1)	31(1)	22(1)	-10(1)	3(1)	-14(1)
C(30)	33(1)	44(1)	38(2)	-16(1)	1(1)	-22(1)
C(31)	30(1)	21(1)	31(1)	-7(1)	1(1)	-5(1)
C(32)	31(1)	23(1)	60(2)	-5(1)	-5(1)	-1(1)
C(33)	74(3)	43(2)	42(2)	-9(1)	22(2)	-26(2)
Cl(1)	88(1)	92(1)	97(1)	-28(1)	48(1)	-42(1)
Cl(2)	88(1)	33(1)	60(1)	-1(1)	-1(1)	-14(1)
C(34)	38(1)	26(1)	36(1)	-4(1)	0(1)	-13(1)
Cl(3)	37(1)	34(1)	48(1)	5(1)	0(1)	-17(1)
Cl(4)	35(1)	39(1)	69(1)	-15(1)	7(1)	-20(1)