Supporting Information

A Convenient Palladium-catalyzed Arsination: Direct Synthesis of Functionalized Aryl Arsines, Optically Active As,*N* Ligands and Metal Complexes

Fuk Yee Kwong,^a Chi Wai Lai,^a Michael Yu,^a Duan-Ming Tan,^a Fuk Loi Lam,^b Albert S. C. Chan^b and Kin Shing Chan^{a*}

^aDepartment of Chemistry and Open Laboratory of Chirotechnology of the Institute of Molecular Technology for Drug Discovery and Synthesis, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, China; ^bDepartment of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China.

X-ray crystal structure data and refinement for As,*N* ligand **14**.

Table 1. Crystal data and structure refinement for p.

Empirical formula	C ₂₄ H ₂₄ As N O
Formula weight	417.36
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	ORTHORHOMBIC, P2(1)2(1)2(1)
Unit cell dimensions	a = 9.2413(5) Å alpha = 90 deg. b = 14.7410(8) Å beta = 90 deg. c = 15.1499(8) Å gamma = 90 deg.
Volume	2063.81(19) Å ³
Z, Calculated density	4, 1.343 Mg/m ³
Absorption coefficient	1.660 mm ⁻¹
F(000)	864
Crystal size	0.30 x 0.20 x 0.10 mm
Theta range for data collection	1.93 to 28.03 deg.
Limiting indices	-10<=h<=12, -19<=k<=19, -19<=l<=20
Reflections collected / unique	13849 / 4960 [R(int) = 0.0412]
Completeness to theta = 28.03	100.0 %
Absorption correction	SADABS
Max. and min. transmission	1.0000 and 0.440374
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4960 / 0 / 244
Goodness-of-fit on F ²	0.941
Final R indices [I>2sigma(I)]	R1 = 0.0299, wR2 = 0.0645
R indices (all data)	R1 = 0.0375, wR2 = 0.0664
Absolute structure parameter	0.019(8)
Largest diff. peak and hole	0.404 and -0.330 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for p. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
As(1)	13119(1)	8131(1)	-1976(1)	41(1)
C(1)	11944(3)	8222(1)	-3070(1)	47(1)
C(2)	12463(3)	7855(2)	-3851(2)	61(1)
C(3)	11723(4)	7963(2)	-4643(2)	75(1)
C(4)	10454(4)	8430(2)	-4656(2)	78(1)
C(5)	9899(3)	8801(2)	-3894(2)	67(1)
C(6)	10638(3)	8707(2)	-3098(2)	51(1)
C(7)	10024(3)	9115(2)	-2293(2)	51(1)
C(8)	8376(3)	9883(2)	-1522(2)	76(1)
C(9)	9562(3)	9519(2)	-922(2)	55(1)
C(10)	10167(3)	10191(2)	-262(2)	63(1)
C(11)	8963(4)	10511(3)	356(2)	97(1)
C(12)	11403(3)	9771(2)	248(2)	80(1)
C(13)	11884(3)	7316(1)	-1285(1)	40(1)
C(14)	10800(3)	6777(2)	-1635(2)	50(1)
C(15)	9985(3)	6223(2)	-1104(2)	64(1)
C(16)	10240(3)	6197(2)	-211(2)	66(1)
C(17)	11291(3)	6735(2)	151(2)	65(1)
C(18)	12124(3)	7292(2)	-381(2)	51(1)
C(19)	14553(3)	7227(2)	-2387(1)	45(1)
C(20)	14325(3)	6299(2)	-2415(2)	56(1)
C(21)	15416(3)	5718(2)	-2678(2)	72(1)
C(22)	16727(4)	6042(3)	-2918(2)	78(1)
C(23)	16988(3)	6960(2)	-2889(2)	76(1)
C(24)	15903(3)	7550(2)	-2621(2)	58(1)
O(1)	8632(2)	9432(2)	-2361(1)	78(1)
N(1)	10634(2)	9166(1)	-1554(1)	49(1)

Table 3. Bond lengths [$\text{\AA}$] and angles [deg] for p.

As(1)-C(13)	1.960(2)
As(1)-C(19)	1.980(2)
As(1)-C(1)	1.986(2)
C(1)-C(2)	1.386(3)
C(1)-C(6)	1.404(3)
C(2)-C(3)	1.391(4)
C(3)-C(4)	1.360(5)
C(4)-C(5)	1.377(4)
C(5)-C(6)	1.392(3)
C(6)-C(7)	1.474(4)
C(7)-N(1)	1.255(3)
C(7)-O(1)	1.373(3)
C(8)-O(1)	1.454(4)

C(8)-C(9)	1.522(4)
C(9)-N(1)	1.473(3)
C(9)-C(10)	1.515(4)
C(10)-C(12)	1.511(4)
C(10)-C(11)	1.529(4)
C(13)-C(14)	1.383(3)
C(13)-C(18)	1.389(3)
C(14)-C(15)	1.371(3)
C(15)-C(16)	1.375(4)
C(16)-C(17)	1.368(4)
C(17)-C(18)	1.384(4)
C(19)-C(24)	1.382(4)
C(19)-C(20)	1.385(3)
C(20)-C(21)	1.382(4)
C(21)-C(22)	1.352(4)
C(22)-C(23)	1.376(5)
C(23)-C(24)	1.387(4)

C(13)-As(1)-C(19)	98.34(9)
C(13)-As(1)-C(1)	99.72(9)
C(19)-As(1)-C(1)	98.57(9)
C(2)-C(1)-C(6)	118.1(2)
C(2)-C(1)-As(1)	119.77(19)
C(6)-C(1)-As(1)	121.98(17)
C(1)-C(2)-C(3)	121.4(3)
C(4)-C(3)-C(2)	119.6(3)
C(3)-C(4)-C(5)	120.7(3)
C(4)-C(5)-C(6)	120.2(3)
C(5)-C(6)-C(1)	119.9(2)
C(5)-C(6)-C(7)	119.2(2)
C(1)-C(6)-C(7)	120.9(2)
N(1)-C(7)-O(1)	117.9(2)
N(1)-C(7)-C(6)	126.2(2)
O(1)-C(7)-C(6)	115.9(2)
O(1)-C(8)-C(9)	104.1(2)
N(1)-C(9)-C(10)	114.3(2)
N(1)-C(9)-C(8)	102.7(2)
C(10)-C(9)-C(8)	115.5(2)
C(12)-C(10)-C(9)	110.4(2)
C(12)-C(10)-C(11)	111.3(3)
C(9)-C(10)-C(11)	109.7(2)
C(14)-C(13)-C(18)	118.6(2)
C(14)-C(13)-As(1)	124.70(16)
C(18)-C(13)-As(1)	116.69(18)
C(15)-C(14)-C(13)	121.0(2)
C(14)-C(15)-C(16)	119.9(3)
C(17)-C(16)-C(15)	120.0(3)
C(16)-C(17)-C(18)	120.4(2)
C(17)-C(18)-C(13)	120.0(2)
C(24)-C(19)-C(20)	118.0(2)
C(24)-C(19)-As(1)	116.94(19)
C(20)-C(19)-As(1)	124.9(2)
C(21)-C(20)-C(19)	120.6(3)
C(22)-C(21)-C(20)	120.9(3)
C(21)-C(22)-C(23)	119.7(3)
C(22)-C(23)-C(24)	120.0(3)
C(19)-C(24)-C(23)	120.8(3)

C(7)-O(1)-C(8)	104.0(2)
C(7)-N(1)-C(9)	107.4(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for p.
The anisotropic displacement factor exponent takes the form:
 $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
As(1)	43(1)	39(1)	42(1)	1(1)	-3(1)	-2(1)
C(1)	57(1)	40(1)	45(1)	5(1)	-8(1)	-7(1)
C(2)	81(2)	59(2)	44(1)	0(1)	-8(1)	6(1)
C(3)	111(3)	66(2)	48(1)	-2(1)	-15(2)	-3(2)
C(4)	97(3)	78(2)	58(2)	11(1)	-36(2)	-13(2)
C(5)	65(2)	65(2)	72(2)	15(1)	-27(2)	-4(2)
C(6)	54(1)	45(1)	53(1)	8(1)	-12(1)	-7(1)
C(7)	38(1)	47(1)	68(2)	15(1)	-5(1)	1(1)
C(8)	56(2)	91(2)	82(2)	23(2)	11(2)	23(2)
C(9)	43(1)	55(1)	68(2)	15(1)	10(1)	9(1)
C(10)	64(2)	52(1)	72(2)	-3(1)	22(2)	7(1)
C(11)	97(3)	96(2)	98(2)	-6(2)	35(2)	39(2)
C(12)	69(2)	89(2)	81(2)	-24(2)	-4(2)	12(2)
C(13)	38(1)	39(1)	42(1)	2(1)	2(1)	5(1)
C(14)	49(1)	50(1)	53(1)	-4(1)	1(1)	-4(1)
C(15)	49(2)	57(2)	85(2)	-1(1)	5(2)	-8(1)
C(16)	54(2)	71(2)	74(2)	21(2)	21(2)	2(1)
C(17)	70(2)	78(2)	47(1)	12(1)	11(1)	14(2)
C(18)	48(2)	56(1)	48(1)	2(1)	-2(1)	2(1)
C(19)	43(1)	53(1)	40(1)	1(1)	-3(1)	4(1)
C(20)	53(2)	53(1)	63(2)	0(1)	5(1)	5(1)
C(21)	75(2)	65(2)	74(2)	-5(1)	4(2)	23(2)
C(22)	66(2)	107(2)	63(2)	-2(2)	5(2)	38(2)
C(23)	47(2)	125(3)	58(2)	6(2)	10(1)	7(2)
C(24)	51(2)	72(2)	51(1)	4(1)	2(1)	-4(1)
O(1)	46(1)	101(2)	86(1)	17(1)	-9(1)	13(1)
N(1)	44(1)	45(1)	58(1)	1(1)	-2(1)	9(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for p.

	x	y	z	U(eq)
H(2A)	13325	7529	-3845	73
H(3A)	12094	7717	-5161	90

H(4A)	9956	8499	-5185	93
H(5A)	9027	9116	-3911	81
H(8A)	7426	9733	-1292	92
H(8B)	8449	10536	-1584	92
H(9A)	9167	9004	-592	66
H(10A)	10538	10718	-586	75
H(11A)	9351	10934	776	146
H(11B)	8565	9999	663	146
H(11C)	8216	10801	18	146
H(12A)	12142	9579	-156	119
H(12B)	11055	9257	574	119
H(12C)	11797	10211	649	119
H(14A)	10621	6792	-2239	61
H(15A)	9260	5864	-1349	77
H(16A)	9699	5814	148	79
H(17A)	11446	6727	757	78
H(18A)	12846	7650	-132	61
H(20A)	13429	6064	-2254	67
H(21A)	15247	5097	-2691	86
H(22A)	17450	5645	-3102	94
H(23A)	17890	7186	-3049	92
H(24A)	16087	8170	-2599	70

X-ray crystal structure data and refinement for As,N-Pt complex 18.

Table 1. Crystal data and structure refinement for p.

Empirical formula	C ₂₄ H ₂₄ As Cl ₂ N O Pt
Formula weight	683.35
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	MONOCLINIC, P2(1)
Unit cell dimensions	a = 10.1250(8) Å alpha = 90 deg. b = 12.9507(11) Å beta = 112.380(2) deg.
	c = 10.6275(9) Å gamma = 90 deg.
Volume	1288.58(19) Å ³

Z, Calculated density	2, 1.761 Mg/m ³
Absorption coefficient	6.941 mm ⁻¹
F(000)	656
Crystal size	0.30 x 0.20 x 0.10 mm
Theta range for data collection	2.07 to 25.00 deg.
Limiting indices	-12<=h<=11, -10<=k<=15, -12<=l<=11
Reflections collected / unique	7003 / 3870 [R(int) = 0.0354]
Completeness to theta = 25.00	100.0 %
Absorption correction	SADABS
Max. and min. transmission	1.0000 and 0.514742
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3870 / 1 / 271
Goodness-of-fit on F ²	1.030
Final R indices [I>2sigma(I)]	R1 = 0.0381, wR2 = 0.0929
R indices (all data)	R1 = 0.0430, wR2 = 0.0966
Absolute structure parameter	0.013(13)
Largest diff. peak and hole	3.086 and -1.258 e.A ⁻³

Table 2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å² x 10³) for p.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Pt(1)	7946(1)	-2385(1)	-103(1)	31(1)
As(1)	6253(1)	-1780(1)	-2108(1)	31(1)
Cl(1)	7134(3)	-1226(2)	1057(3)	47(1)
Cl(2)	9759(3)	-2918(3)	1939(3)	59(1)
C(1)	7007(11)	-1891(9)	-3527(10)	37(2)
C(2)	6579(14)	-1177(10)	-4573(11)	49(3)
C(3)	7154(15)	-1232(12)	-5569(12)	59(3)
C(4)	8111(14)	-1971(13)	-5525(14)	68(4)
C(5)	8559(14)	-2677(10)	-4462(11)	59(4)
C(6)	7990(11)	-2632(8)	-3456(10)	39(3)
C(7)	8478(12)	-3456(10)	-2410(12)	48(3)
C(8)	9477(16)	-4997(12)	-1636(15)	68(4)

C(9)	8986(13)	-4525(10)	-603(13)	49(3)
C(10)	7743(17)	-5087(12)	-388(17)	70(4)
C(11)	8340(20)	-6102(13)	440(20)	92(5)
C(12)	6483(17)	-5310(16)	-1650(20)	92(6)
C(13)	4484(10)	-2574(8)	-2764(11)	43(3)
C(14)	3720(14)	-2751(12)	-4092(13)	73(4)
C(15)	2502(18)	-3357(18)	-4420(20)	104(7)
C(16)	2103(18)	-3777(15)	-3490(20)	92(6)
C(17)	2875(19)	-3631(14)	-2160(20)	87(5)
C(18)	4101(13)	-3025(11)	-1768(15)	60(3)
C(19)	5718(11)	-355(9)	-2151(11)	40(2)
C(20)	4377(15)	-77(12)	-2283(14)	62(3)
C(21)	4071(19)	992(14)	-2207(19)	84(5)
C(22)	5104(18)	1716(11)	-2067(16)	76(4)
C(23)	6404(17)	1427(12)	-1948(14)	66(4)
C(24)	6757(13)	399(11)	-1968(13)	49(3)
N(1)	8510(9)	-3460(7)	-1195(9)	39(2)
O(1)	8945(11)	-4322(8)	-2795(10)	68(3)

Table 3. Bond lengths [Å] and angles [deg] for p.

Pt(1)-N(1)	2.028(8)
Pt(1)-Cl(1)	2.285(3)
Pt(1)-As(1)	2.3048(9)
Pt(1)-Cl(2)	2.350(3)
As(1)-C(19)	1.919(11)
As(1)-C(1)	1.938(9)
As(1)-C(13)	1.949(10)
C(1)-C(6)	1.364(14)
C(1)-C(2)	1.383(16)
C(2)-C(3)	1.391(18)
C(3)-C(4)	1.35(2)
C(4)-C(5)	1.388(18)
C(5)-C(6)	1.396(14)
C(6)-C(7)	1.483(15)
C(7)-N(1)	1.280(14)
C(7)-O(1)	1.340(15)
C(8)-O(1)	1.438(16)
C(8)-C(9)	1.497(18)
C(9)-N(1)	1.516(14)
C(9)-C(10)	1.544(18)
C(10)-C(12)	1.48(3)
C(10)-C(11)	1.57(2)
C(13)-C(14)	1.346(16)
C(13)-C(18)	1.387(17)
C(14)-C(15)	1.39(2)
C(15)-C(16)	1.32(3)
C(16)-C(17)	1.34(3)
C(17)-C(18)	1.39(2)
C(19)-C(20)	1.359(16)
C(19)-C(24)	1.394(18)
C(20)-C(21)	1.43(2)
C(21)-C(22)	1.37(2)
C(22)-C(23)	1.33(2)

C(23)-C(24)	1.38(2)
N(1)-Pt(1)-Cl(1)	175.5(3)
N(1)-Pt(1)-As(1)	88.7(2)
Cl(1)-Pt(1)-As(1)	88.93(8)
N(1)-Pt(1)-Cl(2)	92.0(3)
Cl(1)-Pt(1)-Cl(2)	90.57(11)
As(1)-Pt(1)-Cl(2)	176.55(10)
C(19)-As(1)-C(1)	104.1(4)
C(19)-As(1)-C(13)	106.6(4)
C(1)-As(1)-C(13)	105.3(5)
C(19)-As(1)-Pt(1)	116.9(3)
C(1)-As(1)-Pt(1)	108.6(3)
C(13)-As(1)-Pt(1)	114.2(3)
C(6)-C(1)-C(2)	120.9(9)
C(6)-C(1)-As(1)	120.3(8)
C(2)-C(1)-As(1)	118.7(8)
C(1)-C(2)-C(3)	118.9(12)
C(4)-C(3)-C(2)	120.8(12)
C(3)-C(4)-C(5)	120.3(12)
C(4)-C(5)-C(6)	119.6(12)
C(1)-C(6)-C(5)	119.5(10)
C(1)-C(6)-C(7)	125.1(8)
C(5)-C(6)-C(7)	115.3(9)
N(1)-C(7)-O(1)	115.4(11)
N(1)-C(7)-C(6)	129.2(11)
O(1)-C(7)-C(6)	115.4(9)
O(1)-C(8)-C(9)	105.0(10)
C(8)-C(9)-N(1)	102.1(9)
C(8)-C(9)-C(10)	115.7(12)
N(1)-C(9)-C(10)	110.0(9)
C(12)-C(10)-C(9)	115.4(13)
C(12)-C(10)-C(11)	110.9(16)
C(9)-C(10)-C(11)	108.5(13)
C(14)-C(13)-C(18)	120.8(12)
C(14)-C(13)-As(1)	123.2(9)
C(18)-C(13)-As(1)	115.8(8)
C(13)-C(14)-C(15)	117.5(15)
C(16)-C(15)-C(14)	122.6(18)
C(15)-C(16)-C(17)	120.6(17)
C(16)-C(17)-C(18)	119.3(17)
C(13)-C(18)-C(17)	119.1(15)
C(20)-C(19)-C(24)	120.0(12)
C(20)-C(19)-As(1)	121.3(10)
C(24)-C(19)-As(1)	118.6(8)
C(19)-C(20)-C(21)	118.7(14)
C(22)-C(21)-C(20)	119.8(14)
C(23)-C(22)-C(21)	120.3(14)
C(22)-C(23)-C(24)	121.6(14)
C(23)-C(24)-C(19)	119.4(12)
C(7)-N(1)-C(9)	107.7(9)
C(7)-N(1)-Pt(1)	132.1(8)
C(9)-N(1)-Pt(1)	120.1(7)
C(7)-O(1)-C(8)	107.9(9)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for p.
The anisotropic displacement factor exponent takes the form:
 $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Pt(1)	36(1)	26(1)	30(1)	4(1)	13(1)	-1(1)
As(1)	40(1)	25(1)	31(1)	3(1)	15(1)	5(1)
Cl(1)	72(2)	37(2)	39(1)	-3(1)	28(1)	0(1)
Cl(2)	60(2)	63(2)	41(2)	6(1)	5(1)	8(2)
C(1)	54(6)	31(6)	32(5)	0(4)	24(5)	-2(5)
C(2)	76(8)	34(7)	39(6)	6(5)	26(6)	7(6)
C(3)	88(9)	61(9)	35(6)	12(6)	30(6)	6(8)
C(4)	73(8)	88(13)	56(7)	12(7)	38(7)	20(7)
C(5)	79(8)	55(10)	49(7)	7(6)	33(7)	15(6)
C(6)	49(5)	38(8)	36(5)	2(4)	24(4)	12(4)
C(7)	49(6)	46(7)	56(7)	9(6)	29(5)	11(5)
C(8)	85(9)	43(8)	98(11)	30(8)	59(9)	29(7)
C(9)	61(7)	32(6)	60(7)	12(5)	28(6)	15(5)
C(10)	113(12)	25(7)	106(11)	9(7)	81(10)	11(7)
C(11)	138(15)	40(9)	117(13)	21(10)	71(12)	0(10)
C(12)	66(10)	61(12)	150(18)	-3(12)	42(11)	-8(8)
C(13)	36(4)	31(8)	57(6)	6(5)	11(4)	9(4)
C(14)	63(7)	76(11)	49(7)	2(6)	-12(6)	-13(7)
C(15)	69(9)	110(18)	95(12)	5(12)	-12(10)	-13(10)
C(16)	59(9)	61(11)	155(18)	13(12)	40(12)	-2(8)
C(17)	78(10)	56(10)	147(17)	11(11)	64(12)	-5(8)
C(18)	58(7)	44(8)	85(9)	4(7)	36(7)	-7(6)
C(19)	51(6)	31(6)	48(6)	5(5)	30(5)	8(5)
C(20)	69(8)	46(8)	80(9)	15(7)	39(7)	14(6)
C(21)	96(12)	51(10)	124(14)	15(9)	61(11)	37(9)
C(22)	109(12)	31(8)	98(11)	3(7)	52(10)	21(8)
C(23)	90(10)	34(8)	73(9)	-1(7)	29(8)	-2(7)
C(24)	48(6)	42(8)	51(7)	-4(6)	13(5)	7(5)
N(1)	48(5)	27(5)	48(5)	7(4)	26(4)	12(4)
O(1)	104(7)	47(6)	78(6)	6(5)	63(6)	32(5)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for p.

	x	y	z	U(eq)
H(2A)	5918	-667	-4610	58
H(3A)	6876	-754	-6276	71
H(4A)	8471	-2007	-6208	82
H(5A)	9234	-3176	-4421	71

H(8A)	10511	-5034	-1289	82
H(8B)	9091	-5687	-1875	82
H(9A)	9796	-4462	269	59
H(10A)	7419	-4640	182	84
H(11A)	7578	-6460	584	138
H(11B)	9071	-5931	1301	138
H(11C)	8731	-6538	-63	138
H(12A)	6128	-4678	-2127	138
H(12B)	5750	-5626	-1409	138
H(12C)	6754	-5771	-2213	138
H(14A)	3997	-2479	-4764	87
H(15A)	1945	-3471	-5334	125
H(16A)	1279	-4177	-3752	110
H(17A)	2594	-3931	-1505	105
H(18A)	4656	-2923	-852	72
H(20A)	3672	-573	-2420	75
H(21A)	3173	1196	-2252	101
H(22A)	4893	2414	-2054	91
H(23A)	7093	1929	-1850	80
H(24A)	7681	211	-1859	59