

Anion-assisted *trans-cis* isomerization of palladium(II) phosphine complexes containing acetanilide functionalities through hydrogen bonding interactions

Xiao-Xia Lu, Hau-San Tang, Chi-Chiu Ko, Jenny Ka-Yan Wong, Nianyong Zhu and Vivian Wing-Wah Yam*

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, P. R. China

Supplementary Information

Synthesis of Ph₂PC₆H₄NHCOMe

To a stirred mixture of (*p*-aminophenyl)diphenylphosphine (6.50 g, 23.4 mmol) and triethylamine (3.5 ml) in dichloromethane (50 ml), cooled in an ice-bath, was added dropwise acetyl chloride (1.84 g, 23.4 mmol) over 10 mins. Stirring continued for 3 hours at this temperature and the resulting mixture was evaporated in vacuo and partitioned between ethyl acetate and water. The organic layer was washed with water and saturated brine solution, dried over anhydrous MgSO₄ and evaporated to dryness. The residue was dissolved in chloroform and purified by column chromatography on silica gel, using chloroform as eluent. Yield 5.00 g, 67%. ¹H NMR (400 MHz, CDCl₃, 298 K, relative to Me₄Si): δ 2.22 (s, 3H, COCH₃), 7.13 (s, br, 1H, NH), 7.28-7.34 (m, 12H, phenyl protons), 7.49-7.52 (d, *J* = 8.1 Hz, 2H, phenyl protons). ³¹P{¹H} NMR (202 MHz, CDCl₃, 298 K, relative to 85 % H₃PO₄): δ -6.22 (s). Positive-ion FAB-MS: *m/z* 319 {M}⁺. Anal. Found: C 75.17, H 5.69, N 4.42; Calcd for C₂₀H₁₈NOP: C 75.22, H 5.68, N 4.39.

Synthesis of Ph₂PC₆H₄NMeCOMe

This reaction was carried out using standard Schlenk technique. To a mixture of *N*-methyl-4-iodoacetanilide (2.75 g, 10 mmol) and PdCl₂(MeCN)₂ (65 mg, 0.25 mmol) in benzene (200 ml), was added dropwise via syringe (trimethylsilyl)diphenylphosphine (2.71 g, 10.5 mmol) over 10 mins. The resulting mixture was heated at 65 °C for 24 hours. After cooling, the benzene was evaporated in vacuo and chloroform added. The organic layer was washed with saturated sodium bicarbonate and saturated brine solution, dried over anhydrous MgSO₄ and evaporated to dryness. The residue was dissolved in chloroform and purified by column chromatography on silica gel, using chloroform as eluent. Yield 2.16 g, 65 %. ¹H NMR (400 MHz, CDCl₃, 298 K, relative to Me₄Si): δ 1.90 (s, 3H, COCH₃), 3.27 (s, 3H, NCH₃), 7.14-7.16 (d, *J* = 7.8, 2H, phenyl H ortho to N) 7.30-7.37 (m, 12H, phenyl protons). ³¹P{¹H} NMR (202 MHz, CDCl₃, 298 K, relative to 85% H₃PO₄): δ -5.80 (s). Positive-ion FAB-MS: *m/z* 333 {M}⁺. Anal. Found: C 75.61, H 6.07, N 4.22; Calcd for C₂₁H₂₀NOP: C 75.66, H 6.05, N 4.20.

Characterization of [Pd(Ph₂PC₆H₄NHCOMe)₂Cl₂] (1)

Yield: 363 mg, 89 %. ¹H NMR (400 MHz, CDCl₃, 298 K, relative to Me₄Si): δ 1.74 (s, 6H, COCH₃), 7.37-7.46 (m, 16H, phenyl protons) 7.61-7.63 (m, 12H, phenyl protons). ³¹P{¹H} NMR (202 MHz, CDCl₃, 298 K, relative to 85% H₃PO₄): δ 23.36 (s). Positive-ion FAB-MS: *m/z* 816 {M}⁺, 780 {M-Cl}⁺. Anal. Found: C 58.90, H 4.47, N 3.41; Calcd. for C₄₀H₃₆Cl₂N₂O₂P₂Pd: C 58.88, H 4.45, N 3.43.

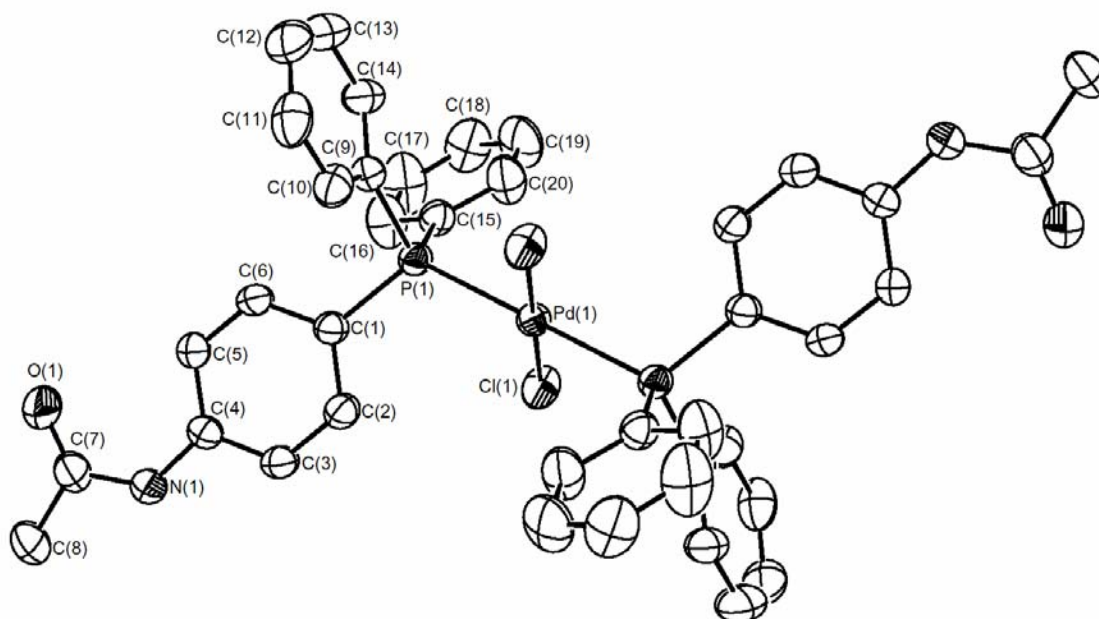
Characterization of [Pd(Ph₂PC₆H₄NMeCOMe)₂Cl₂] (**2**)

Yield: 384 mg, 91 %. ¹H NMR (400 MHz, CDCl₃, 298 K, relative to Me₄Si): δ 1.92 (s, 6H, COCH₃), 3.27 (s, 6H, NCH₃), 7.19-7.21 (d, *J* = 7.3 Hz, 4H, phenyl H ortho to N), 7.41-7.67 (m, 24 H, phenyl protons). ³¹P{¹H} NMR (202 MHz, CDCl₃, 298 K, relative to 85% H₃PO₄): δ 23.13 (s). Positive-ion FAB-MS: *m/z* 844 {M}⁺, 808 {M-Cl}⁺. Anal. Found: C 59.72, H 4.80, N 3.34; Calcd. for C₄₂H₄₀Cl₂N₂O₂P₂Pd: C 59.76, H 4.78, N 3.32.

Crystal data for [Pd(Ph₂PC₆H₄NHCOMe)₂Cl₂] (1)

Table 1. Crystal data and structure refinement.

Empirical formula	C ₇₂ H ₁₀₈ Cl ₄ N ₄ O ₂ P ₂ Pd	
Formula weight	1371.76	
Temperature	301(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	<i>P</i> 2 ₁ / <i>n</i>	
Unit cell dimensions	<i>a</i> = 13.641(3) Å	$\alpha = 90^\circ$
	<i>b</i> = 18.267(4) Å	$\beta = 92.42(3)^\circ$
	<i>c</i> = 15.156(3) Å	$\gamma = 90^\circ$
Volume	3773.2(14) Å ³	
<i>Z</i>	2	
Density (calculated)	1.207 g cm ⁻³	
Absorption coefficient	0.473 mm ⁻¹	
<i>F</i> (000)	1456	
Crystal size	0.4 mm × 0.25 mm × 0.2 mm	
Theta range for data collection	1.86 to 25.35°	
Index ranges	-13 ≤ <i>h</i> ≤ 15, -22 ≤ <i>k</i> ≤ 22, -17 ≤ <i>l</i> ≤ 17	
Reflections collected	16043	
Independent reflections	5926 [<i>R</i> (int) = 0.0472]	
Completeness to theta = 25.35°	85.8 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	5926 / 0 / 394	
Goodness-of-fit on <i>F</i> ²	0.922	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0427, <i>wR</i> 2 = 0.1177	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0723, <i>wR</i> 2 = 0.1329	
Largest diff. peak and hole	0.457 and -0.511 eÅ ⁻³	



Perspective drawing of [Pd(Ph₂PC₆H₄NHCOMe)₂Cl₂] (**1**) with atomic numbering scheme. Hydrogen atoms are omitted for clarity.

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for mar1109. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	0	0	10000	52(1)
Cl(1)	1072(1)	-962(1)	10210(1)	76(1)
Cl(2)	-762(1)	-4155(1)	8197(1)	79(1)
P(1)	331(1)	-59(1)	8498(1)	54(1)
O(1)	-866(3)	-2603(2)	5240(2)	123(2)
N(1)	-885(3)	-2864(2)	6695(2)	71(1)
N(2)	-3851(3)	-1477(2)	5581(2)	78(1)
C(1)	-129(3)	-878(2)	7941(2)	55(1)
C(2)	-415(3)	-1489(2)	8411(2)	65(1)
C(3)	-684(3)	-2128(2)	7985(2)	67(1)
C(4)	-665(3)	-2186(2)	7070(2)	59(1)
C(5)	-414(3)	-1572(2)	6600(2)	69(1)
C(6)	-167(3)	-931(2)	7031(2)	66(1)
C(7)	-954(4)	-3045(2)	5822(3)	83(1)
C(8)	-1145(4)	-3845(2)	5648(3)	99(2)
C(9)	-137(3)	669(2)	7777(2)	60(1)
C(10)	-1138(4)	752(2)	7651(3)	76(1)
C(11)	-1535(4)	1287(3)	7089(3)	95(2)
C(12)	-897(6)	1741(3)	6657(3)	114(2)
C(13)	89(6)	1663(3)	6770(4)	112(2)
C(14)	461(4)	1137(2)	7333(3)	82(1)
C(15)	1649(3)	-35(2)	8357(2)	63(1)
C(16)	2110(4)	-435(3)	7737(3)	101(2)
C(17)	3104(4)	-330(4)	7615(4)	132(2)
C(18)	3634(4)	148(4)	8091(4)	115(2)
C(19)	3201(4)	538(4)	8732(4)	120(2)
C(20)	2204(4)	433(3)	8874(3)	99(2)
C(21)	-3337(4)	-2043(2)	5018(3)	96(2)
C(22)	-3459(4)	-1926(3)	4042(4)	107(2)
C(23)	-2939(5)	-2540(3)	3568(4)	139(2)
C(24)	-2945(6)	-2444(4)	2628(4)	180(4)

C(25)	-4957(3)	-1527(3)	5452(3)	90(1)
C(26)	-5422(5)	-2240(3)	5656(4)	140(3)
C(27)	-6522(7)	-2153(6)	5586(8)	262(8)
C(28)	-7081(7)	-2530(6)	5216(5)	204(5)
C(29)	-3506(4)	-1634(3)	6535(3)	101(2)
C(30)	-4002(5)	-1204(3)	7232(3)	117(2)
C(31)	-3373(7)	-1243(4)	8097(4)	173(3)
C(32)	-3655(10)	-915(5)	8762(6)	312(9)
C(33)	-3574(4)	-704(2)	5330(3)	84(1)
C(34)	-2499(4)	-539(3)	5368(4)	106(2)
C(35)	-2323(6)	208(3)	4980(4)	137(3)
C(36)	-1275(7)	388(4)	4915(5)	185(4)

Table 3. Bond lengths [Å] and angles [°]

Pd(1)-Cl(1)	2.3001(12)	C(22)-C(23)	1.522(7)
Pd(1)-Cl(1)#1	2.3001(12)	C(23)-C(24)	1.435(8)
Pd(1)-P(1)	2.3420(10)	C(25)-C(26)	1.487(7)
Pd(1)-P(1)#1	2.3420(10)	C(26)-C(27)	1.507(11)
P(1)-C(1)	1.817(3)	C(27)-C(28)	1.156(9)
P(1)-C(9)	1.819(4)	C(29)-C(30)	1.500(7)
P(1)-C(15)	1.820(4)	C(30)-C(31)	1.538(7)
O(1)-C(7)	1.205(5)	C(31)-C(32)	1.248(10)
N(1)-C(7)	1.363(5)	C(33)-C(34)	1.496(6)
N(1)-C(4)	1.390(4)	C(34)-C(35)	1.509(7)
N(2)-C(33)	1.514(5)	C(35)-C(36)	1.475(9)
N(2)-C(25)	1.516(5)		
N(2)-C(29)	1.528(5)	Cl(1)-Pd(1)-Cl(1)#1	180.0
N(2)-C(21)	1.531(5)	Cl(1)-Pd(1)-P(1)	87.25(4)
C(1)-C(6)	1.380(5)	Cl(1)#1-Pd(1)-P(1)	92.75(4)
C(1)-C(2)	1.390(5)	Cl(1)-Pd(1)-P(1)#1	92.75(4)
C(2)-C(3)	1.376(5)	Cl(1)#1-Pd(1)-P(1)#1	87.25(4)
C(3)-C(4)	1.392(5)	P(1)-Pd(1)-P(1)#1	180.0
C(4)-C(5)	1.380(5)	C(1)-P(1)-C(9)	102.49(17)
C(5)-C(6)	1.376(5)	C(1)-P(1)-C(15)	106.78(18)
C(7)-C(8)	1.505(6)	C(9)-P(1)-C(15)	103.63(18)
C(9)-C(14)	1.378(5)	C(1)-P(1)-Pd(1)	114.36(12)
C(9)-C(10)	1.379(5)	C(9)-P(1)-Pd(1)	118.25(13)
C(10)-C(11)	1.391(6)	C(15)-P(1)-Pd(1)	110.20(13)
C(11)-C(12)	1.387(8)	C(7)-N(1)-C(4)	128.2(4)
C(12)-C(13)	1.356(8)	C(33)-N(2)-C(25)	106.4(3)
C(13)-C(14)	1.368(6)	C(33)-N(2)-C(29)	110.1(3)
C(15)-C(16)	1.365(6)	C(25)-N(2)-C(29)	112.1(4)
C(15)-C(20)	1.367(6)	C(33)-N(2)-C(21)	111.4(4)
C(16)-C(17)	1.389(7)	C(25)-N(2)-C(21)	111.4(3)
C(17)-C(18)	1.328(8)	C(29)-N(2)-C(21)	105.7(4)
C(18)-C(19)	1.359(7)	C(6)-C(1)-C(2)	117.1(3)
C(19)-C(20)	1.400(6)	C(6)-C(1)-P(1)	121.3(3)
C(21)-C(22)	1.497(7)	C(2)-C(1)-P(1)	121.5(3)

C(3)-C(2)-C(1)	121.0(3)	C(33)-C(34)-C(35)	109.8(5)
C(2)-C(3)-C(4)	121.2(3)	C(36)-C(35)-C(34)	113.4(6)
C(5)-C(4)-N(1)	124.5(3)		
C(5)-C(4)-C(3)	117.8(3)		
N(1)-C(4)-C(3)	117.6(3)		
C(6)-C(5)-C(4)	120.5(3)		
C(5)-C(6)-C(1)	122.2(3)		
O(1)-C(7)-N(1)	122.9(4)		
O(1)-C(7)-C(8)	122.9(4)		
N(1)-C(7)-C(8)	114.2(4)		
C(14)-C(9)-C(10)	117.9(4)		
C(14)-C(9)-P(1)	123.1(3)		
C(10)-C(9)-P(1)	119.0(3)		
C(9)-C(10)-C(11)	121.3(5)		
C(12)-C(11)-C(10)	118.3(5)		
C(13)-C(12)-C(11)	121.1(5)		
C(12)-C(13)-C(14)	119.5(5)		
C(13)-C(14)-C(9)	121.9(5)		
C(16)-C(15)-C(20)	118.0(4)		
C(16)-C(15)-P(1)	123.7(3)		
C(20)-C(15)-P(1)	118.2(3)		
C(15)-C(16)-C(17)	119.9(5)		
C(18)-C(17)-C(16)	122.0(5)		
C(17)-C(18)-C(19)	119.3(5)		
C(18)-C(19)-C(20)	119.5(5)		
C(15)-C(20)-C(19)	121.0(5)		
C(22)-C(21)-N(2)	114.9(4)		
C(21)-C(22)-C(23)	109.0(5)		
C(24)-C(23)-C(22)	113.3(6)		
C(26)-C(25)-N(2)	117.2(5)		
C(25)-C(26)-C(27)	108.9(7)		
C(28)-C(27)-C(26)	127.3(9)		
C(30)-C(29)-N(2)	115.9(4)		
C(29)-C(30)-C(31)	108.9(5)		
C(32)-C(31)-C(30)	119.2(8)		
C(34)-C(33)-N(2)	115.7(4)		

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z+2

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for mar1109. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	59(1)	48(1)	51(1)	-1(1)	7(1)	3(1)
Cl(1)	95(1)	71(1)	64(1)	-1(1)	5(1)	32(1)
Cl(2)	99(1)	62(1)	79(1)	6(1)	19(1)	-2(1)
P(1)	60(1)	51(1)	50(1)	0(1)	8(1)	0(1)
O(1)	211(5)	86(2)	70(2)	-2(2)	-19(2)	-27(2)
N(1)	94(3)	55(2)	64(2)	-1(2)	0(2)	-6(2)
N(2)	89(3)	58(2)	88(2)	-3(2)	3(2)	3(2)
C(1)	62(3)	49(2)	55(2)	1(2)	8(2)	0(2)
C(2)	82(3)	59(2)	54(2)	1(2)	8(2)	1(2)
C(3)	85(3)	53(2)	62(2)	7(2)	8(2)	-4(2)
C(4)	68(3)	48(2)	63(2)	-1(2)	3(2)	-2(2)
C(5)	96(3)	61(2)	51(2)	-5(2)	4(2)	-10(2)
C(6)	87(3)	55(2)	56(2)	6(2)	12(2)	-11(2)
C(7)	97(4)	70(3)	81(3)	-6(2)	-14(3)	-8(2)
C(8)	128(5)	72(3)	94(3)	-18(2)	-11(3)	-12(3)
C(9)	71(3)	54(2)	54(2)	-1(2)	-1(2)	-2(2)
C(10)	86(4)	78(3)	64(2)	-2(2)	1(2)	8(2)
C(11)	99(4)	100(4)	84(3)	-14(3)	-24(3)	37(3)
C(12)	178(7)	71(3)	90(4)	17(3)	-21(4)	13(4)
C(13)	142(6)	81(4)	112(4)	36(3)	-6(4)	-14(4)
C(14)	92(4)	70(3)	84(3)	18(2)	-3(2)	-14(3)
C(15)	58(2)	71(2)	59(2)	3(2)	5(2)	-3(2)
C(16)	69(4)	138(5)	98(3)	-40(3)	13(3)	8(3)
C(17)	68(4)	208(7)	119(5)	-52(5)	20(3)	8(4)
C(18)	59(3)	180(6)	106(4)	-1(4)	15(3)	-3(4)
C(19)	72(4)	163(6)	125(5)	-17(4)	-6(3)	-43(4)
C(20)	84(4)	126(4)	86(3)	-25(3)	12(3)	-20(3)
C(21)	99(4)	66(3)	124(4)	-10(3)	22(3)	0(3)
C(22)	107(5)	97(4)	120(4)	-38(3)	26(3)	-12(3)
C(23)	169(6)	96(4)	157(5)	-27(4)	87(5)	-28(4)
C(24)	245(9)	149(6)	155(6)	-50(5)	97(6)	-90(6)

C(25)	77(4)	110(4)	84(3)	-25(3)	7(2)	4(3)
C(26)	138(6)	124(5)	161(6)	-63(4)	55(5)	-59(4)
C(27)	143(9)	268(12)	385(17)	-215(12)	130(10)	-110(8)
C(28)	164(9)	280(12)	164(7)	-88(7)	-55(6)	89(8)
C(29)	127(5)	75(3)	97(3)	17(3)	-23(3)	1(3)
C(30)	186(6)	85(3)	77(3)	-3(3)	-16(3)	-4(4)
C(31)	289(11)	114(5)	107(5)	0(4)	-78(6)	12(6)
C(32)	540(20)	200(10)	179(9)	-89(7)	-188(12)	177(12)
C(33)	100(4)	66(3)	85(3)	1(2)	-1(3)	7(3)
C(34)	115(5)	81(3)	123(4)	-7(3)	13(3)	-15(3)
C(35)	178(8)	101(4)	136(5)	1(4)	59(5)	-34(4)
C(36)	212(9)	180(7)	171(7)	-38(6)	99(6)	-76(7)

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

	x	y	z	U(eq)
H(2)	-425	-1466	9024	78
H(3)	-882	-2527	8314	80
H(5)	-412	-1592	5987	83
H(6)	-22	-520	6699	79
H(8A)	-1601	-3896	5152	148
H(8B)	-1415	-4065	6159	148
H(8C)	-540	-4084	5521	148
H(10)	-1556	445	7949	91
H(11)	-2211	1338	7004	114
H(12)	-1149	2105	6284	136
H(13)	509	1965	6468	134
H(14)	1138	1094	7418	99
H(16)	1760	-777	7396	122
H(17)	3407	-604	7186	158
H(18)	4295	215	7988	138
H(19)	3565	872	9073	144
H(20)	1914	685	9328	118
H(21A)	-2642	-2039	5181	115
H(21B)	-3588	-2525	5156	115
H(22A)	-3180	-1457	3885	129
H(22B)	-4150	-1923	3865	129
H(23A)	-2265	-2568	3796	166
H(23B)	-3255	-3001	3698	166
H(24A)	-3493	-2702	2359	270
H(24B)	-2346	-2634	2407	270
H(24C)	-2999	-1932	2490	270
H(25A)	-5245	-1154	5817	108
H(25B)	-5129	-1406	4842	108
H(26A)	-5219	-2395	6248	168
H(26B)	-5218	-2610	5243	168
H(27A)	-6729	-2133	6190	314

H(27B)	-6636	-1668	5342	314
H(28A)	-7077	-2431	4594	306
H(28B)	-7725	-2440	5424	306
H(28C)	-6906	-3032	5323	306
H(29A)	-3604	-2151	6650	121
H(29B)	-2807	-1540	6593	121
H(30A)	-4648	-1404	7321	140
H(30B)	-4077	-698	7046	140
H(31A)	-3298	-1756	8252	207
H(31B)	-2726	-1059	7975	207
H(32A)	-3486	-406	8725	468
H(32B)	-3344	-1124	9283	468
H(32C)	-4354	-963	8791	468
H(33A)	-3831	-610	4735	101
H(33B)	-3894	-367	5720	101
H(34A)	-2153	-906	5039	128
H(34B)	-2248	-552	5976	128
H(35A)	-2639	232	4396	164
H(35B)	-2627	575	5344	164
H(36A)	-989	475	5495	278
H(36B)	-1209	818	4560	278
H(36C)	-944	-14	4648	278
H(1)	-930(30)	-3200(20)	7050(20)	61(12)
