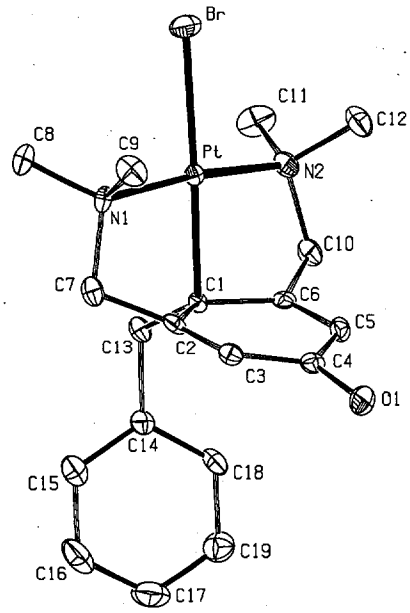
Characterization of $[PtBr(C_6H_2\{CH_2C_6H_5\}\text{-}1\text{-}\{CH_2NMe_2\}_2\text{-}2,6\text{-}OH\text{-}4)][BF_4]$ 5.



Elemental Analysis for $C_{19}H_{26}BBrF_4N_2OPt$ (660.23):

	calcd.	found
C	34.57	34.72
H	3.97	4.03
N	4.24	4.29

^{1}H NMR (δ, acetone-d_6, $SiMe_4$, 293 K, 300 MHz):

7.1-6.8 (m, 5H, C_6H_5), 6.44 (s, 2H, C_6H_2), 4.90 (d, 2H, $^2J_{HH}$ = 13.2 Hz, CH_2N, downfield part of ABq), 4.29 (s, 2H, $^3J_{PtH}$ = 30 Hz, CCH_2Ar), 3.39 (d, 2H, $^2J_{HH}$ = 13.7 Hz, CH_2N, upfield part of ABq), 3.06 (s, 6H, $^3J_{PtH}$ not resolved, NCH_3Me), 2.88 (s, 6H, $^3J_{PtH}$ = 37.2 Hz, $NMeCH_3$); O*H* not observed.

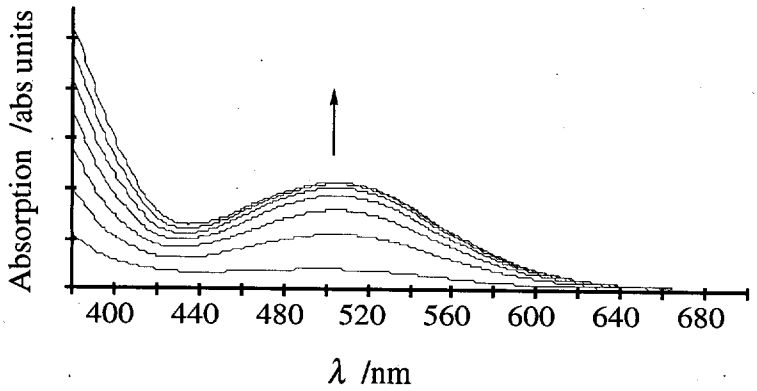
^{13}C {^{1}H} NMR (δ, acetone-d_6, $SiMe_4$, 293 K, 75 MHz):

172.5 (C4), 157.5 (C2, C6),129.3, 127.6, 127.5 (C15-C19), 118.3 (C3, C5), 79.8 (C1), 69.2 (C7, C10), 55.0, 52.9 (C8,C9, C11, C12), 39.3 (C13); C14 not observed.

UV-Vis spectroscopic Data (acetone solution)

λ_{max} (ε) in nm (1000 M^{-1} cm^{-1}) for **4**: 338 (0.25)
B: 505 (0.36)
5: 380 (1.0)

Overlapping UV/Vis spectra during the formation of **B** from *aqua*-complex **4** and BnBr:



Spectra were recorded every 2 minutes in acetone solution; the last spectrum corresponds to the first spectrum shown in Fig. 2.

The determination of the formal oxidation state of platinum in intermediate **B** is, to our opinion, without significant impact on the discussion here. The coupling constants of the nitrogen-bound methyl groups with the platinum center rather point to the formation of a cationic Pt(IV) oxidative addition product than to a Pt(II) Lewis acid – base adduct. For comparisons, see *e.g.*, Albrecht, M.; Gossage, R. A.; Lutz, M.; Spek, A. L.; van Koten, G. *Chem. Eur. J.* submitted for publication; Terheijden, J.; van Koten, G.; de Booys, J. L.; Ubbels, H. J. C.; Stam, C. H. *Organometallics* **1983**, *2*, 1882.

Note the related discussion concerning the catalytic cycle in Pd-mediated Heck chemistry; especially in light of the fact that complexes such as [Pd(PCP)Cl] (*i.e.*, a close structural analogue to **3**) are good Heck catalysts; see *e.g.*, Shaw, B. L. *New J. Chem.* **1998**, 77; Ohff, M.; Ohff, A.; van der Boom, M. E.; Milstein, D. *J. Am. Chem. Soc.* **1997**, *119*, 11687.

Synthesis of 6

A solution of **5** (15.4 mg, 23 μmol) in CH_2Cl_2 (5 mL) was vigorously stirred with an aqueous solution of KCN (0.5 M, 6 mL, 3 mmol) for 4 h. The layers were separated and the inorganic phase was brought to pH > 12 (solid NaOH) and extracted with CH_2Cl_2 (2 × 8 mL). The combined organic fractions were washed with brine (10 mL), dried over $MgSO_4$ and evaporated to dryness to afford a yellowish oil (6.5 mg, 94%).

^{1}H NMR (δ, $CDCl_3$, $SiMe_4$, 293 K, 300 MHz):

7.22-6.95 (m, 5H, C_6H_5), 6.84 (s, 2H, C_6H_2), 4.24 (s, 2H, CCH_2Ar), 3.25 (s, 4H, CH_2N), 2.18 (s, 12H, NCH_3); O*H* not observed.

Crystallographic Data

Crystal Data and Details of the Structure Determination for ***5***

Crystal Data	
Empirical Formula	$C_{19}H_{26}BBrF_4N_2OPt$
Formula Weight	660.21
Crystal System	Monoclinic
Space group	P21/c (No. 14)
Crystal Color, Size [mm]	transparent orange, 0.50 x 0.43 x 0.38
a, b, c [Angstrom]	11.6996(10) 12.3935(11) 15.8708 (13)
beta [deg]	113.340(7)
V [Ang^3]	2112.9(3)
Z	4
D(calc) [g/cm^3]	2.075
F(000)	1264
μ(MoKα) [/mm]	8.58
Data Collection	
Temperature (K)	150
Radiation [Angstrom]	MoKα 0.71073
Theta Min-Max [Deg]	1.40, 26.5
Scan, (Type & Range) [Deg]	0.62 + 0.35 Tan(Theta)
Hor. and vert. aperture [mm]	1.82 4.00
Dataset	-14: 13 ; -15: 15 ; -19: 13
Tot., Uniq. Data, R(int)	8803, 4372, 0.036
Observed data [I > 2.0 sigma(I)]	3750
Refinement	
Nref, Npar	4372, 267
Abs. cor. (min., max. virtual transm.)	DIFABS (0.167, 0.639)
R, wR, GOF	0.0273, 0.0649, 1.06
$w = 1/[\sigma^2(F_o^2)+(0.0317P)^2+1.3330P]$ where $P=(F_o^2+2F_c^2)/3$	
min. and max. residual density [e/Ang^3]	-1.03, 1.15

Final Coordinates and Equivalent Isotropic Displacement Parameters of the non-Hydrogen atoms

Atom	x	y	z	U(eq) [Ang^2]
Pt	0.21047(1)	0.14344(1)	0.07428(1)	0.0106(1)
Br	0.12156(5)	0.14749(4)	-0.09301(3)	0.0230(2)
O1	0.0449(3)	-0.0130(3)	0.3063(2)	0.0204(11)
N1	0.2910(4)	-0.0082(3)	0.0792(3)	0.0141(11)
N2	0.1384(4)	0.2953(3)	0.0859(3)	0.0152(11)
C1	0.2936(4)	0.1400(3)	0.2187(3)	0.0109(12)
C2	0.2881(4)	0.0240(4)	0.2255(3)	0.0146(12)
C3	0.2030(4)	-0.0252(3)	0.2528(3)	0.0145(12)
C4	0.1172(4)	0.0379(4)	0.2725(3)	0.0140(12)
C5	0.1041(4)	0.1475(4)	0.2503(3)	0.0147(12)
C6	0.1900(4)	0.1968(3)	0.2245(3)	0.0118(11)
C7	0.3583(4)	-0.0373(4)	0.1796(3)	0.0169(12)
C8	0.3798(5)	-0.0123(4)	0.0336(3)	0.0227(17)
C9	0.1912(5)	-0.0893(4)	0.0354(3)	0.0214(14)
C10	0.1716(5)	0.3108(3)	0.1874(3)	0.0167(14)
C11	0.1940(6)	0.3833(4)	0.0497(4)	0.0276(18)
C12	0.0013(5)	0.2992(4)	0.0377(3)	0.0242(17)
C13	0.4231(4)	0.1929(4)	0.2569(3)	0.0149(12)
C14	0.4803(4)	0.1840(4)	0.3605(3)	0.0155(12)
C15	0.5861(5)	0.1232(4)	0.4056(4)	0.0282(17)
C16	0.6361(6)	0.1138(5)	0.4999(4)	0.0419(19)
C17	0.5779(6)	0.1630(5)	0.5503(4)	0.0353(19)
C18	0.4235(4)	0.2332(4)	0.4128(3)	0.0193(12)
C19	0.4721(5)	0.2227(4)	0.5065(3)	0.0242(17)
F1	0.6656(3)	0.0480(3)	0.2176(2)	0.0389(11)
F2	0.8582(3)	0.0887(3)	0.3224(2)	0.0317(10)
F3	0.7134(3)	0.2208(2)	0.2643(2)	0.0379(11)
F4	0.8027(3)	0.1424(3)	0.1762(2)	0.0395(11)
B	0.7582(6)	0.1259(4)	0.2429(4)	0.0231(17)

U(eq) = 1/3 of the trace of the orthogonalized U Tensor

Hydrogen Atom Positions and Isotropic Displacement Parameters

Atom	x	y	z	U(iso) [Ang^2]
H1	-0.01480	0.02720	0.30250	0.0310
H3	0.20240	-0.10150	0.25840	0.0170
H5	0.03630	0.18740	0.25310	0.0180
H7A	0.35470	-0.11600	0.18910	0.0200
H7B	0.44650	-0.01430	0.20320	0.0200
H8A	0.41920	-0.08350	0.04310	0.0340
H8B	0.44380	0.04320	0.05990	0.0340
H8C	0.33490	0.00080	-0.03230	0.0340
H9A	0.14700	-0.07200	-0.02980	0.0320
H9B	0.13260	-0.08820	0.06560	0.0320
H9C	0.22840	-0.16130	0.04160	0.0320
H10A	0.10350	0.34740	0.19830	0.0200
H10B	0.24890	0.35370	0.21600	0.0200
H11A	0.17100	0.37260	-0.01610	0.0410
H11B	0.28490	0.38160	0.08170	0.0410
H11C	0.16270	0.45330	0.06000	0.0410
H12A	-0.02860	0.37120	0.04460	0.0360
H12B	-0.03610	0.24530	0.06410	0.0360
H12C	-0.02220	0.28370	-0.02760	0.0360
H13A	0.47740	0.15680	0.23100	0.0180
H13B	0.41560	0.26990	0.23870	0.0180
H15	5/8	0.08730	0.37110	0.0340
H16	0.71030	0.07360	0.53010	0.0510
H17	0.61110	0.15560	0.61520	0.0420
H18	0.35020	0.27470	0.38320	0.0230
H19	0.43220	0.25680	0.54120	0.0290

The temperature factor has the form of exp(-T) where T = 8*(Pi**2)*U*(sin(Theta)/Lambda)**2 for isotropic atoms

(An)isotropic Displacement Parameters

Atom	U(1,1)	U(2,2)	U(3,3)	U(2,3)	U(1,3)	U(1,2)
Pt	0.0102(1)	0.0103(1)	0.0114(1)	-0.0001(1)	0.0043(1)	-0.0009(1)
Br	0.0261(3)	0.0287(3)	0.0139(2)	0.0016(2)	0.0075(2)	-0.0018(2)
O1	0.0170(19)	0.0243(18)	0.0233(18)	0.0035(14)	0.0117(15)	-0.0028(14)
N1	0.013(2)	0.0127(18)	0.020(2)	-0.0023(15)	0.0103(17)	0.0007(15)
N2	0.015(2)	0.0114(18)	0.0164(19)	0.0019(15)	0.0034(16)	0.0008(15)
C1	0.006(2)	0.014(2)	0.011(2)	-0.0035(17)	0.0015(16)	-0.0036(17)
C2	0.010(2)	0.018(2)	0.011(2)	0.0021(17)	-0.0010(18)	0.0016(17)
C3	0.016(2)	0.011(2)	0.015(2)	0.0017(17)	0.0046(19)	0.0011(18)
C4	0.011(2)	0.018(2)	0.011(2)	-0.0004(17)	0.0022(18)	-0.0043(17)
C5	0.010(2)	0.018(2)	0.015(2)	-0.0025(18)	0.0038(18)	0.0004(18)
C6	0.014(2)	0.012(2)	0.0070(19)	-0.0033(16)	0.0015(17)	-0.0007(17)
C7	0.015(2)	0.011(2)	0.024(2)	-0.0021(18)	0.007(2)	0.0015(18)
C8	0.020(3)	0.030(3)	0.024(3)	0.000(2)	0.015(2)	0.004(2)
C9	0.021(3)	0.015(2)	0.022(2)	-0.0061(19)	0.002(2)	-0.003(2)
C10	0.017(3)	0.011(2)	0.020(2)	0.0011(18)	0.005(2)	0.0029(18)
C11	0.045(4)	0.012(2)	0.029(3)	0.002(2)	0.018(3)	-0.006(2)
C12	0.016(3)	0.025(3)	0.025(3)	-0.004(2)	0.001(2)	0.004(2)
C13	0.010(2)	0.015(2)	0.017(2)	-0.0008(18)	0.0025(18)	-0.0010(18)
C14	0.010(2)	0.018(2)	0.017(2)	-0.0012(18)	0.0036(19)	-0.0056(18)
C15	0.021(3)	0.037(3)	0.023(3)	0.001(2)	0.005(2)	0.011(2)
C16	0.031(3)	0.054(4)	0.031(3)	0.007(3)	0.002(3)	0.025(3)
C17	0.042(4)	0.040(3)	0.019(3)	0.008(2)	0.007(3)	0.010(3)
C18	0.014(2)	0.020(2)	0.019(2)	0.0025(19)	0.0012(19)	0.0050(19)
C19	0.028(3)	0.023(3)	0.021(3)	-0.004(2)	0.009(2)	-0.001(2)
F1	0.0209(17)	0.0322(18)	0.060(2)	-0.0144(16)	0.0121(16)	-0.0069(14)
F2	0.0267(18)	0.0401(19)	0.0302(17)	0.0015(14)	0.0134(14)	0.0045(14)
F3	0.044(2)	0.0176(15)	0.061(2)	0.0016(15)	0.0304(18)	0.0059(15)
F4	0.031(2)	0.060(2)	0.0317(18)	0.0029(16)	0.0168(16)	0.0036(17)
B	0.017(3)	0.019(3)	0.035(3)	-0.004(2)	0.012(3)	0.000(2)

The temperature factor has the form of exp(-T) where T = 8*(Pi**2)*U*(sin(Theta)/Lambda)**2 for isotropic atoms T = 2*(Pi**2)*Sumij(h(i)*h(j)*U(i,j)*Astar(i)*Astar(j)), for anisotropic atoms. Astar(i) are reciprocal axial lengths and h(i) are the reflection indices.

Selected Bond Distances (Angstrom)

Pt	-Br	2.4383(5)	C1	-C13	1.538(7)
Pt	-N1	2.090(4)	C1	-C6	1.436(7)
Pt	-N2	2.100(4)	C1	-C2	1.445(6)
Pt	-C1	2.106(4)	C2	-C7	1.502(7)
Pt	-C6	2.575(4)	C2	-C3	1.376(7)
F1	-B	1.387(7)	C3	-C4	1.402(7)
F2	-B	1.416(7)	C4	-C5	1.396(7)
F3	-B	1.384(6)	C5	-C6	1.370(7)
F4	-B	1.368(7)	C6	-C10	1.513(5)
O1	-C4	1.327(6)	C13	-C14	1.514(6)
O1	-H1	0.8405			

Selected Contact Distances (Angstrom)

F4	.H1_p	2.6878	F3	.H3_j	2.4964
F4	.H5_p	2.5744	F3	.H7A_j	2.3958
O1	.F2_b	2.621(5)	F3	.H17_a	2.6711
O1	.H10A_c	2.4317	C6	.H18	2.6549
F2	.O1_p	2.621(5)	H7A	.F3_d	2.3958
F1	.H7B	2.5992	C9	.H12B_h	2.6934
F1	.H13A	2.6614	H7B	.F1	2.5992
F1	.H10B_k	2.6599	C10	.H13B	2.6885
F2	.H1_p	1.8057	H1	.F2_b	1.8057
F2	.H11C_k	2.5925	H1	.F4_b	2.6878
H5	.F4_b	2.5744	H10B	.F1_m	2.6599
H12B	.C9_h	2.6934	H13B	.C10	2.6885
H13A	.F1	2.6614	H17	.F3_o	2.6711
H11C	.F2_m	2.5925	H18	.C6	2.6549

Hydrogen Bonds (Angstrom, Deg)

D	-- H	.. A	DH	HA	DA	angle
O1	-- H1	.. F2	0.8405	1.8057	2.621(5)	162.90
C3	-- H3	.. F3	0.9501	2.4964	3.339(5)	147.85
C7	-- H7A	.. F3	0.9904	2.3958	3.328(6)	156.61
C8	-- H8C	.. Br	0.9802	2.9255	3.504(5)	118.75
C9	-- H9A	.. Br	0.9799	2.8738	3.481(5)	120.94
C10	-- H10A	.. O1	0.9898	2.4317	3.376(6)	159.30
C12	-- H12C	.. Br	0.9802	2.8531	3.483(5)	122.81

Translation of Symmetry Code to Equivalent Positions

a =[4554.00] = x,1/2-y,-1/2+z
b =[1455.00] = -1+x,y,z
c =[2545.00] = -x,-1/2+y,1/2-z
d =[2645.00] = 1-x,-1/2+y,1/2-z
e =[3656.00] = 1-x,-y,1-z
f =[4555.00] = x,1/2-y,1/2+z
g =[3655.00] = 1-x,-y,-z
h =[3555.00] = -x,-y,-z
i =[2555.00] = -x,1/2+y,1/2-z
j =[2655.00] = 1-x,1/2+y,1/2-z
l =[3655.00] = 1-x,-y,-z
m =[2655.00] = 1-x,1/2+y,1/2-z
n =[4454.00] = -1+x,1/2-y,-1/2+z
o =[4555.00] = x,1/2-y,1/2+z
p =[1655.00] = 1+x,y,z
q =[4655.00] = 1+x,1/2-y,1/2+z