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Preconversion Catalytic Deoxygenation of Phenolic Functional Groups

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Over the course of our studies on catalytic deoxygenation of phenolic residues in coal by carbon monoxide, we performed preliminary investigations into the removal of other heteroatom groups. This report describes our attempted carbonylation of phenyl amido complexes. These studies resulted in the surprisingly facile formation of amidines. The amidine group is the nitrogen analog of carboxylic acids and esters. This functional group combines the properties of an azomethane-like C=N double bond with an amide-like C-N single bond, eq. 1.^{1,2}

This group, like the related allyl (C-C-C), aza-allyl (C-N-C), and carboxylato (O-C-O) groups, form a number of transition metal derivatives, with both early and late transition metals.³ Various bonding modes of the amidino group have been reported.³⁻⁶ However, most isolated complexes have the amidino ligand as a chelating ligand or bridging two metals. This is due to the preference of amidines to bond via the nitrogen lone pairs, in contrast to the $\eta^3 \pi$ bonding observed in metal-allyl complexes.

Experimental Section

General Experimental Descriptions

All reactions and manipulations were carried out under a nitrogen atmosphere using a nitrogen filled glovebox (Vacuum Atmospheres) or by Schlenk line techniques. All glassware was flame dried under an argon purge.

Anhydrous pentane, anhydrous hexane, and anhydrous benzonitrile were purchased from Aldrich Chemical Co. These materials were used without further purification. Aniline was freshly distilled from MgSO_4 and stored under nitrogen. THF was freshly distilled from sodium benzophenone ketyl under a nitrogen atmosphere, and transferred to a septa equipped flask by cannula. Methylene chloride was freshly distilled from calcium hydride. Deuterated acetonitrile (99.9%), purchased from Cambridge Isotope Labs, was stored under nitrogen and used as received.

^1H and ^{31}P NMR spectra were recorded on a Varian XL-200 spectrometer. ^1H NMR spectra were referenced to external TMS via residual solvent peaks. ^{31}P NMR spectra were referenced to external 85% H_3PO_4 and were all proton decoupled. Infrared spectra were obtained using a Perkin Elmer 1710 equipped with a 1700/PC Data Station, or a Mattson Research Series Fourier transform spectrometers.

For these syntheses, the $[\text{Pt}(\text{triphos})(\text{Cl})][\text{Cl}]$ complex was converted to the PF_6 anion by sonicating an acetonitrile suspension of $[\text{Pt}(\text{triphos})(\text{Cl})][\text{Cl}]$ and a large excess of NaPF_6 . After fifteen minutes a white solid was filtered off and the acetonitrile removed under vacuum. This solid was extracted with methylene chloride and the filtrate evaporated to dryness. The white solid was filtered and washed with 20 mL each of water, ethanol, and diethyl ether.

Synthesis of $[\text{Pt}(\text{triphos})\text{N}-(\text{N}'\text{-phenyl-benzamidine})][\text{PF}_6]$ (7)

Lithium phenyl amide was freshly made from aniline (0.0631g, 0.6780 mmol) and butyllithium (1.9M, 0.67 mL) in pentane. The freshly prepared LiNH-Ph was added to a benzonitrile (3 mL) solution of $[\text{Pt}(\text{triphos})(\text{Cl})][\text{PF}_6]$ (0.1543g, 0.1693 mmol). The solution quickly turned yellow, then slowly

turned orange over the next five minutes. The solution was stirred for an additional 30 min. Seven volumes of anhydrous diethyl ether were added, the solution then was quickly filtered through a glass microfiber filter and cooled to -20°C overnight. The yellow solid produced was collected and washed with anhydrous diethyl ether and the solid dried overnight *in vacuo*. ^1H NMR (CD_2Cl_2 , 200 MHz, δ , ppm); 2.31 - 2.6 (m, 4H, P- CH_2), 2.60 - 3.38 (m, 4H, P- CH_2), 4.12 (s, 1H, NHC, $^2J(\text{Pt} - \text{H}) = 58.4$ Hz), 5.8 (m, 2H, CH), 6.7 (m, 1H, CH), 6.8 (m, 4H, CH), 7.0 (m, 3H, CH), 7.4-8.1 (m, 25H, triphos phenyl). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 80.98 MHz, δ , ppm): A_2BX , (P_A) = 42.6, $^1J(\text{P}_\text{A}-\text{Pt}) = 2672$ Hz; (P_B) = 81.1, $^1J(\text{P}_\text{B}-\text{Pt}) = 2557$ Hz, $^2J(\text{P}_\text{A}-\text{P}_\text{B}) < 1.0$ Hz. Yield = 0.0623g, 34.4%. IR (KBr): $\nu(\text{NH}) = 3398\text{ cm}^{-1}$, (NH)bend = 1545 cm^{-1} . Anal. Calcd for $\text{C}_{40}\text{H}_{44}\text{N}_2\text{F}_6\text{P}_4\text{Pt}$ C, 52.77; H, 4.15; N, 2.62 Found: C, 52.16; H, 4.11; N, 2.21.

Figure 1. ^1H spectra of $[\text{Pt}(\text{triphos})\text{N}-(\text{N}'\text{-phenyl-benzamidine})][\text{PF}_6]$ (7).
 * indicates CH_2Cl_2 .

Figure 2. $^{31}\text{P}\{^1\text{H}\}$ spectra of $[\text{Pt}(\text{triphos})\text{N}-(\text{N}'\text{-phenyl-benzamidine})][\text{PF}_6]$ (7).

Collection of X-ray Diffraction Data for $[\text{Pt}(\text{triphos})\text{N}-(\text{N}'\text{-phenyl-benzamidine})][\text{PF}_6]$ (7)

Crystals suitable for a single-crystal X-ray diffraction study were grown by layering a methylene chloride solution of $[\text{Pt}(\text{triphos})\text{N}-(\text{N}'\text{-phenyl-benzamidine})][\text{PF}_6]$ with diethyl ether. A yellow needle of $\text{C}_{47}\text{H}_{44}\text{PtF}_6\text{N}_2\text{P}_4$ having approximate dimensions of $0.52 \times 0.25 \times 0.20$ mm was mounted in a glass capillary in a random orientation. The data were collected at a temperature of 295 K using the ω - 2θ scan technique. A total of 8790 reflections were collected, of which 8329 were unique.

The structure was solved using the Patterson heavy-atom method which revealed the position of the Pt atom. The remaining atoms were located in

succeeding difference Fourier syntheses. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. The amino hydrogen, H(4), was located but refined isotropically. The final cycle of refinement included 544 variable parameters and converged with $R = 0.045$ and $R_w = 0.118$.

Low Temperature Synthesis of $[\text{Pt}(\text{triphos})(\text{NHPh})][\text{PF}_6]$ (8)

Lithium phenyl amide was freshly made from aniline (0.02 mL, 0.213 mmol) and butyllithium (1.92M, 0.12 mL) in pentane. The freshly prepared LiNH-Ph was first dissolved in THF (5mL) at -42°C then added to a THF (5mL) solution of $[\text{Pt}(\text{triphos})(\text{Cl})][\text{PF}_6]$ (0.1045g, 0.1148 mmol) also at -42°C . The solution quickly turned yellow and the solution was removed from the dry ice/acetonitrile bath and allowed to come to room temperature. The solution was reduced in volume and a yellow orange solid was precipitated out from an orange brown solution with pentane and collected by filtration. $^{31}\text{P}\{^1\text{H}\}$ NMR (CH_3CN , 80.98 MHz, δ , ppm): A_2BX , (P_A) = 43.4, $^1J(\text{P}_\text{A}\text{-Pt}) = 2635$ Hz; (P_B) = 80.5, $^1J(\text{P}_\text{B}\text{-Pt}) = 2368$ Hz, $^2J(\text{P}_\text{A}\text{-P}_\text{B}) < 1.0$ Hz. $^{31}\text{P}\{^1\text{H}\}$ NMR also showed that reaction did not go to completion and that starting material, 40%, is also seen.

Reaction of $[\text{Pt}(\text{triphos})\text{N}-(\text{N}'\text{-phenyl-benzamidine})][\text{PF}_6]$ (7) With Carbon Monoxide

A 5 mm J. Young Valve NMR tube (Wilmad), containing a 1:1 d_3 -Acetonitrile : Benzonitrile (1.5 mL) solution of $[\text{Pt}(\text{triphos})\text{N}-(\text{N}'\text{-phenyl-benzamidine})][\text{PF}_6]$ (7, 0.1326, 0.1351 mmol) was pressurized with 50 psig of carbon monoxide. The tube was allowed to stand at room temperature, NMR after 12 hours showed the reaction to be complete. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN ,

80.98 MHz, δ , ppm): A_2BX , (P_A) = 25.8, $^1J(P_A-Pt)$ = 3271.2 Hz; (P_B) = 51.8,
 $^1J(P_B-Pt)$ = 2891 Hz, $^2J(P_A-P_B)$ = 58.2 Hz. IR (Acetonitrile): $\nu(CO)$ = 1643 cm^{-1} .

Table 1. Crystal data and data collection parameters for [Pt(triphos)N-(N'-phenyl-benzamidine)][PF₆] (7).

Formula	PtP ₄ F ₆ N ₂ C ₄₇ H ₄₄
Formula weight	1069.86
Crystal system	triclinic
Space group	P $\bar{1}$ (No. 2)
<i>a</i> , Å	11.294(3)
<i>b</i> , Å	14.790(2)
<i>c</i> , Å	16.939(5)
α , deg	74.163(18)
β , deg	75.57(2)
γ , deg	72.132(17)
<i>V</i> , Å ³	2548.2(11)
<i>Z</i>	2
<i>d</i> _{calc} /g cm ⁻³	1.394
Crystal dimensions, mm	0.52×0.25×0.20
Temperature, K	295
Radiation (wavelength)	Mo K α (0.71073Å)
<i>h, k, l</i> range	-13 to 0 -17 to 15 -19 to 19
Data collected	8790
Unique data	8329
Data used in refinement	8327
Number of variables	544
R(<i>F</i> _o), R _w (<i>F</i> _o ²)	0.045, 0.118
Goodness of fit	1.103

Table 2. Positional parameters and their estimated standard deviations for [Pt(triphos)N-(N'-phenyl-benzamidine)][PF₆] (7).

Atom	x	y	z	U(Å ²)
Pt	0.02934(3)	0.17568(3)	0.20658(2)	0.03656(12)
P(1)	-0.0286(2)	0.0682(2)	0.15671(14)	0.0386(8)
P(2)	0.2110(2)	0.0618(2)	0.21154(14)	0.0416(8)
P(3)	0.1308(2)	0.2742(2)	0.23054(15)	0.0449(8)
N(4)	-0.1294(7)	0.2872(5)	0.1924(5)	0.046(3)
N(40)	-0.2622(7)	0.1970(6)	0.2736(5)	0.053(3)
C(1)	0.1221(8)	0.0173(7)	0.0926(6)	0.049(3)
C(2)	0.2280(9)	-0.0205(8)	0.1440(6)	0.056(4)
C(3)	0.3345(8)	0.1273(8)	0.1756(6)	0.054(4)
C(4)	0.2983(9)	0.2093(8)	0.2245(7)	0.059(4)
C(40)	-0.2477(8)	0.2780(7)	0.2245(6)	0.044(3)
C(41)	-0.3495(8)	0.3608(7)	0.1941(6)	0.049(4)
C(42)	-0.4294(10)	0.3468(9)	0.1508(8)	0.070(5)
C(43)	-0.5198(13)	0.4252(13)	0.1180(10)	0.108(7)
C(44)	-0.5344(14)	0.5152(13)	0.1272(13)	0.122(8)
C(45)	-0.4585(14)	0.5297(10)	0.1695(12)	0.108(7)
C(46)	-0.3643(11)	0.4539(9)	0.2038(9)	0.079(5)
C(111)	-0.1397(8)	0.1187(7)	0.0854(5)	0.044(3)
C(112)	-0.2511(8)	0.0884(7)	0.0979(6)	0.051(3)
C(113)	-0.3327(9)	0.1303(8)	0.0414(7)	0.058(4)
C(114)	-0.3055(10)	0.2031(7)	-0.0254(7)	0.062(4)

Table 2. (continued)

Atom	x	y	z	U(Å ²)
C(115)	-0.1992(11)	0.2349(8)	-0.0376(7)	0.069(5)
C(116)	-0.1152(10)	0.1909(7)	0.0191(6)	0.055(4)
C(121)	-0.0700(9)	-0.0357(7)	0.2306(6)	0.048(3)
C(122)	-0.0905(11)	-0.0384(8)	0.3144(7)	0.065(4)
C(123)	-0.1166(14)	-0.1217(11)	0.3711(8)	0.090(6)
C(124)	-0.1241(15)	-0.1965(11)	0.3439(10)	0.099(7)
C(125)	-0.1003(16)	-0.1961(9)	0.2602(9)	0.098(7)
C(126)	-0.0775(12)	-0.1147(8)	0.2037(7)	0.070(5)
C(211)	0.2379(9)	-0.0119(7)	0.3129(6)	0.048(3)
C(212)	0.1593(10)	0.0113(9)	0.3850(6)	0.062(4)
C(213)	0.1807(14)	-0.0403(10)	0.4615(7)	0.082(6)
C(214)	0.2827(16)	-0.1211(11)	0.4684(9)	0.096(7)
C(215)	0.3615(18)	-0.1460(11)	0.3977(11)	0.112(8)
C(216)	0.3407(12)	-0.0925(8)	0.3199(8)	0.077(5)
C(311)	0.1171(10)	0.3864(7)	0.1538(6)	0.051(4)
C(312)	0.0309(12)	0.4696(8)	0.1701(8)	0.073(5)
C(313)	0.0159(19)	0.5566(9)	0.1081(12)	0.110(8)
C(314)	0.0961(19)	0.5555(12)	0.0330(10)	0.102(8)
C(315)	0.1798(16)	0.4740(11)	0.0152(9)	0.090(7)
C(316)	0.1899(12)	0.3894(9)	0.0763(7)	0.067(5)
C(321)	0.0804(11)	0.3084(8)	0.3303(7)	0.062(4)
C(322)	-0.0261(14)	0.2854(9)	0.3822(7)	0.085(6)

Table 2. (continued)

Atom	x	y	z	U(Å ²)
C(323)	-0.069(2)	0.3124(12)	0.4585(10)	0.122(9)
C(324)	-0.008(3)	0.3640(17)	0.4800(12)	0.140(11)
C(325)	0.095(2)	0.3851(12)	0.4321(13)	0.121(10)
C(326)	0.1415(14)	0.3617(10)	0.3542(9)	0.092(6)
C(411)	-0.3794(9)	0.1853(9)	0.3220(6)	0.060(4)
C(412)	-0.4083(11)	0.0971(10)	0.3338(7)	0.079(5)
C(413)	-0.5162(14)	0.0777(14)	0.3908(9)	0.108(8)
C(414)	-0.5927(15)	0.146(2)	0.4347(9)	0.130(10)
C(415)	-0.5671(13)	0.2327(16)	0.4212(9)	0.107(8)
C(416)	-0.4595(11)	0.2528(10)	0.3670(7)	0.078(5)
H(4)	-0.124(10)	0.337(8)	0.160(7)	0.06000*
P(100)	0.3587(3)	0.1907(2)	0.8884(2)	0.0682(13)
F(1)	0.4968(8)	0.1985(8)	0.8500(7)	0.130(5)
F(2)	0.3610(14)	0.2574(11)	0.9434(8)	0.195(8)
F(3)	0.4080(15)	0.1037(10)	0.9579(10)	0.216(9)
F(4)	0.3714(14)	0.1180(11)	0.8373(10)	0.202(9)
F(5)	0.3094(12)	0.2766(10)	0.8249(9)	0.213(8)
F(6)	0.2219(10)	0.1809(11)	0.9220(9)	0.196(8)

Starred atoms were refined isotropically $U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$

Table 3. Selected bond distances in angstroms for [Pt(triphos)N-(N'-phenylbenzamidine)][PF₆] (7).

Atom 1 - Atom 2	Distance	Atom 1 - Atom 2	Distance
Pt - N(4)	2.043(7)	C(42) - C(43)	1.38(2)
Pt - P(2)	2.223(2)	C(43) - C(44)	1.34(2)
Pt - P(3)	2.276(2)	C(44) - C(45)	1.34(2)
Pt - P(1)	2.305(2)	C(45) - C(46)	1.40(2)
N(4) - H(4)	0.80(10)	C(411) to C(416)	1.38(2)
N(4) - C(40)	1.345(12)	C(411) - C(412)	1.39(2)
N(40) - C(40)	1.290(12)	C(412) - C(413)	1.41(2)
N(40) - C(411)	1.406(12)	C(413) - C(414)	1.37(3)
C(40) - C(41)	1.474(13)	C(414) - C(415)	1.35(3)
C(41) - C(42)	1.386(14)	C(415) - C(416)	1.39(2)
C(41) - C(46)	1.386(15)		

Table 4. Selected bond angles in degrees for [Pt(triphos)N-(N'-phenylbenzamidine)][PF₆] (7).

Atom 1 - Atom 2 - Atom 3	Angle	Atom 1 - Atom 2 - Atom 3	Angle
N(4) - Pt - P(2)	174.8(2)	C(40) - N(40) - C(411)	123.0(8)
N(4) - Pt - P(3)	91.7(2)	N(40) - C(40) - N(4)	118.3(8)
P(2) - Pt - P(3)	86.19(9)	N(40) - C(40) - C(41)	126.0(8)
N(4) - Pt - P(1)	96.9(2)	N(4) - C(40) - C(41)	115.5(8)
P(2) - Pt - P(1)	84.32(8)	C(42) - C(41) - C(40)	119.5(9)
P(3) - Pt - P(1)	165.47(8)	C(46) - C(41) - C(40)	121.9(9)
H(4) - N(4) - C(40)	116(8)	C(416) - C(411) - N(40)	122.4(11)
H(4) - N(4) - Pt	120(8)	C(412) - C(411) - N(40)	118.6(10)
C(40) - N(4) - Pt	123.9(6)		

Table 5. Selected torsion angles in degrees for [Pt(triphos)N-(N'-phenylbenzamidine)][PF₆] (7).

Atom 1-Atom 2-Atom 3-Atom 4	Angle	Atom 1-Atom 2-Atom 3-Atom 4	Angle
P(1) - Pt - N(4) - C(40)	53.97 (0.76)	Pt - N(4) - C(40) - C(41)	-168.60 (0.65)
P(1) - Pt - N(4) - H(4)	-115.38 (9.20)	H(4) - N(4) - C(40) - N(40)	176.54 (8.79)
P(2) - Pt - N(4) - C(40)	156.59 (2.13)	H(4) - N(4) - C(40) - C(41)	1.12 (8.84)
P(2) - Pt - N(4) - H(4)	-12.76 (9.74)	N(4) - C(40) - C(41) - C(42)	117.72 (1.10)
P(3) - Pt - N(4) - C(40)	-137.83 (0.75)	N(4) - C(40) - C(41) - C(46)	-59.01 (1.38)
P(3) - Pt - N(4) - H(4)	52.81 (9.20)	N(40) - C(40) - C(41) - C(42)	-57.31 (1.48)
Pt - N(4) - C(40) - N(40)	6.83 (1.27)	N(40) - C(40) - C(41) - C(46)	125.97 (1.24)

Results and Discussion

The synthesis of the platinum amidine complex [Pt(triphos)N-(N'-phenyl-benzamidine)][PF₆], **7**, proceeds by a reaction involving [Pt(triphos)(Cl)][Cl] and LiNHPH in benzonitrile, eq. 2.

This complex was characterized by ³¹P{¹H} NMR, Figure 2. The very small ²J(P_A-P_B) coupling of less than 1 Hz is consistent with the expected square planar structure of complex **7**.⁷ Furthermore, retention of the square planar configuration about the platinum is attested to by the minimal changes in the P_A chemical shift. With the platinum *trans* influence, the ¹J(P_B - Pt) coupling constants are very sensitive to the nature of the ligand *trans* to P_B.⁸ For **7** this ¹J(Pt-P_B) coupling constant is 2557 Hz, a decrease of 278 Hz from the platinum triphos phenoxide complex, **2b** in chapter 2, measured at 2835.4 Hz. The ¹J(Pt-P) coupling constants in the related pair of complexes, Pt(dppe)(Me)(NHCH₂Ph) ¹J(Pt-P) = 1685 Hz,⁹ and Pt(dppe)(Me)(OMe) ¹J(Pt-P) = 1852 Hz,¹⁰ show a decrease of 167 Hz. The ¹H NMR, Figure 1, shows the amino N-H chemical shift at 4.12 ppm with platinum coupling, ²J(Pt - H) = 58.4

Hz. For $\text{Pt}(\text{dppe})(\text{Me})(\text{NHCH}_2\text{Ph})$ the amino proton is seen at 4.28 ppm with a $^2J(\text{Pt} - \text{H})$ coupling constant of 33 Hz. The IR of 7 shows the N-H stretch and bend at 3398 and 1545 cm^{-1} , respectively. This complex was further characterized by microanalysis and X-ray crystallography.

Crystal and Molecular Structure of $[\text{Pt}(\text{triphos})\text{N}-(\text{N}'\text{-phenyl-benzamidine})][\text{PF}_6]$, (7)

The crystal and molecular structure of the platinum amidine represents the second structurally characterized monodentate transition metal amidine. Data collection parameters, selected bond distances, and angles are summarized in Tables 1 - 6. The molecular structure of the $[\text{Pt}(\text{triphos})\text{N}-(\text{N}'\text{-phenyl-benzamidine})][\text{PF}_6]$ cation along with the adopted numbering scheme is shown as an ORTEP drawing in Figure 3.

The $[\text{Pt}(\text{triphos})\text{N}-(\text{N}'\text{-phenyl-benzamidine})]$, 7, complex shares several structural features with other structurally characterized organic benzamidine and monodentate metal benzamidine derivatives. The organic derivatives are N^1, N^2 -di-*p*-tolyl-benzamidine,¹¹ 9, and N^1, N^2 -diphenylbenzamidine,¹² 10, while the monodentate metal benzamidine derivatives are a mercury complex, $\text{Hg}(\text{Ph})(\text{N}^2-(\text{N}^1, \text{N}^2\text{-di-}p\text{-tolyl-formamidine}))$,¹³ 11, and the platinum complex, $\text{Pt}(\text{dmamp})(\text{N}^2-(\text{N}^1, \text{N}^2\text{-di-}p\text{-tolyl-formamidine}))$, {dmamp = 2,6-Bis[(dimethylamino)methyl]phenyl}¹⁴ 12. These structures are summarized in Figure 4.

Figure 3. Structurally related molecules to $[Pt(triphos)N-(N'-phenylbenzamidine)][PF_6]$ (7).

Figure 4. ORTEP Drawing of $[\text{Pt}(\text{triphos})\text{N}-(\text{N}'\text{-phenyl-benzamidino})][\text{PF}_6]$ (7) showing 50% probability ellipsoids and the atomic labeling. Hydrogen atoms are not shown, and ligand phenyl carbons are shown as points for clarity.

In the complex $\text{Pt}(\text{triphos})\text{N}-(\text{N}'\text{-phenyl-benzamidino})][\text{PF}_6]$, **7**, the central d^8 platinum(II) atom has a distorted square planar geometry; the two *trans* angles are $\text{P}(1)\text{-Pt-P}(3) = 165.47(8)^\circ$ and $\text{P}(2)\text{-Pt-C}(40) = 174.8(2)^\circ$. Three of the platinum coordination sites are occupied by the tridentate tripfos ligand. The fourth coordination site is filled by the monodentate $\text{N}-(\text{N}'\text{-phenyl-benzamidino})$ ligand through the amino nitrogen. The $\text{Pt-N}(4)$ bond distance of $2.043(7)\text{\AA}$ is $0.089(7)\text{\AA}$ shorter than the Pt-N bond distance of $2.132(6)\text{\AA}$.

found in the $\text{Pt}(\text{dmamp})(\text{N}^2\text{-(N}^1\text{-(*p*-tolyl)CH=N}^2\text{-(*p*-tolyl))}$, **12**, complex.¹⁴ This can be attributed to the unsubstituted nature of the Pt-bound nitrogen in **7** compared to **12**. Like other N - phenylsubstituted amidines, and aromatic amines in general, the platinum bound nitrogen in **12** is less basic than the unsubstituted benzamidine in **7**.¹

The observed benzamidine N(4) - C(40) bond length of 1.345(12) Å in **7** is 0.12(12) Å shorter than a pure C - N single bond length of 1.465(11) Å.¹⁵ In fact, this distance tends towards the C - N distance in amides of 1.325(9) Å.¹⁵ For both of the organic benzamidine derivatives the C - N single bond distances, 1.351(7) Å for **9** and 1.359(11) Å for **10**, are also shorter than a pure C - N single bond distance of 1.465(11) Å.¹⁵ The C(40) - N(40) double bond in **7** also shows the effects of resonance in the heteroatom backbone. The C(40) - N(40) double bond length of 1.290(12) Å is just slightly longer than the pure C - N double bond distance of 1.279(8).¹⁵ The organic derivatives show greater delocalization of electron density across the heteroatom backbone. In both these organic molecules the C - N double bond distances of 1.351(7) Å and 1.359(11) Å, respectively, are substantially longer than a pure unconjugated C=N double bond 1.279(8).¹⁵

When the $\text{Pt}(\text{triphos})\text{N-(N'-phenyl-benzamidine)}][\text{PF}_6]$, **7**, complex is compared with the other monodentate transition metal amidine, $\text{Pt}(\text{dmamp})(\text{N-(N,N'-di-*p*-tolyl-formamidine)})$ **12**, many similarities are seen. Both of these molecules have tridentate ligands on the platinum, the likely reason for the amidine being monodentate in these cases. This molecule has C - N double and single bond distances identical to those seen in **7**, 1.303(7) Å and 1.345(8) Å respectively.¹⁴ Like all the structurally determined amidines, the platinum N'-phenyl-benzamidine, **7**, has a planar heteroatom skeleton,

with the Pt - N(4) - C(4) - N(40) dihedral being $6.83(1.27)^\circ$. The one difference between **7** and the related platinum complex, **12**, is that in **7** the benzamidine plane is positioned at a $53.97(0.76)^\circ$ angle to the metal coordination plane, while in **12** the amidine group lies at the nearly perpendicular angle of 86.3° . In all these molecules the planarity of the amidine group, the elongation of the double bond and the shortening of the single bond all reflect the effect of the amidine resonance in the π -system, Figure 5.¹

Figure 5. The amidine resonance.

In the monodentate platinum amidino complexes, **12**, the *N,N'*-Di-*p*-tolylformamidine ligand is prepared separately, from aniline and ethylorthoformate.¹⁶ The amidine is then introduced to the Pt(dmamp)(H₂O) species to form the Pt(dmamp)N²-(N¹,N²-di-*p*-tolyl-formamidinium) species, which is then converted to the formamidine with base,¹⁷ Figure 6.

Figure 6. Synthesis of $\text{Pt}(\text{dmamp})(\text{N}^2\text{-(N}^1\text{,N}^2\text{-di-}p\text{-tolyl-formamidine)})$, (12).

While it is clear in this system how the amidine ligand was formed, with the platinum triphos species, 7, it is not initially clear whether the ligand is formed in solution or mediated by the metal center. Three mechanisms are proposed. The first, involves insertion of benzonitrile into to a platinum amide bond formed *in situ*, followed by a 1,3 proton shift, Figure 7.

Figure 7. Proposed direct insertion mechanism for the formation of platinum amidine, (7).

The second, involves the direct reaction of lithium phenyl amide with benzonitrile in solution to give a lithioamidine intermediate that attacks the platinum, Figure 8. The third, involves the formation of a benzonitrile solvate which undergoes nucleophilic attack at the nitrile carbon by lithium phenyl amide, followed by a 1,3 proton shift, Figure 9.

Figure 8. Proposed solution formation mechanism for the formation of platinum amidine, (7).

Figure 9. Proposed mechanism for the formation of platinum amidine, (7) via coordinated benzonitrile.

A significant point to be considered about the solution mechanism is the nature of the solvated lithium amidinium intermediate. Mono N-substituted amidines are known to exist as tautomeric pairs.^{1,2} However, NMR studies have shown that N-phenyl amidines exist primarily in the amino form, and that the imino form is not detected in solution, Figure 8.¹⁸⁻²¹ This is due to the electron withdrawing nature of the aryl substituent which is conjugated with the amidine system. For this reason the nitrogen based anion, produced after the nucleophilic attack, is stabilized on the phenyl substituted nitrogen. If this lithioamidine then reacts with the platinum, the resulting product would be substituted on the amino nitrogen, α from platinum, 7', rather than the imino nitrogen, β from platinum, 7, in Figure 8. Thus, benzonitrile insertion is a more logical route to the isolated product than a route involving initial reaction with the solvent. While amidines can be synthesized directly from benzonitrile and

aniline, the reaction is not spontaneous at room temperature. Rather, the reaction occurs at reflux over a period of several hours.^{22,23} The preferred method to synthesize amidines is reaction of amines in the presence of polyphosphoric acid trimethylsilylester at 160°C.²⁴⁻²⁶

If $[\text{Pt}(\text{triphos})(\text{Cl})][\text{PF}_6]$ is reacted with lithium amide at low temperatures in THF, rather than benzonitrile, a yellow product is isolated. The NMR parameters of this product are close to the isolated product, however, the complex is yellow rather than orange. The reaction to produce 7 initially involves a yellow complex, which then gives way to an orange complex. Therefore, this initial yellow color indicates that the platinum amide is formed first. This yellow complex then reacts with the benzonitrile more slowly, to produce the final orange product.

Reaction of $[\text{Pt}(\text{triphos})\text{N}^1\text{-(N}^2\text{-phenyl-benzamidine)}][\text{PF}_6]$ (7) With Carbon Monoxide

When complex 7 is placed under 50 psig of carbon monoxide significant changes in the phosphorus NMR are seen, eq. 3. Unlike the carbon monoxide insertions seen in chapter 3 of this thesis, there is a significant change in the

chemical shift of the *cis* phosphorus nuclei. This indicates that structural changes have occurred around the platinum, such that the complex may not be square planar, Figure 9. The IR spectrum of this complex in acetonitrile shows a new carbonyl stretch at 1643 cm^{-1} . The structure in Figure 10, showing the imino nitrogen bonding to the platinum may explain some of these structural changes.

Figure 10. Possible structure of 8 that would explain the observed $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum.

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