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Syntheses, Reactions, and Molecular Structures of *trans*-Hydrido(phenylamido)bis(triethylphosphine)platinum(II) and *trans*-Hydridophenoxobis(triethylphosphine)platinum(II)

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Abstract: The reaction between *trans*-$PtH(NO_3)(PEt_3)_2$ and NaNHPh in C_6H_6 yields the novel hydridoamido complex *trans*-$PtH(NHPh)(PEt_3)_2$ (1). This compound is stable in solution; however, crystals of I decompose within hours at room temperature. At −100 °C a crystal of I belongs to the monoclinic space group $P2_1/n$ with a = 11.445 (2) Å, b = 13.010 (2) Å, c = 14.888 (2) Å, β = 104.63 (1)°, V = 2144.9 (6) Å^3, and Z = 4. Complex I adopts a trans structure, with Pt–N = 2.125 (5) Å, indicative of a single bond weakened by the *trans*-hydride ligand. The Pt–N–Ph angle of 125.5 (4)° and the observation of the H on N in a position expected for trigonal-planar coordination suggest sp^2 hybridization about nitrogen. SCF–DV–Xα calculations of the model complex $PtH(NH_2)(PH_3)_2$ confirm the expected repulsive nature of the interaction between the nitrogen lone-pair orbital and filled dπ orbitals on the metal. This interaction is minimized when the nitrogen lone pair lies in the coordination plane of Pt. The reaction between *trans*-$PtH(NO_3)(PEt_3)_2$ and excess NaOPh produces *trans*-$PtH(OPh)(PEt_3)_2$ (II). Crystals of II belong to the triclinic space group $P\bar{1}$, and at −50 °C a = 9.477 (3) Å, b = 10.617 (3) Å, c = 11.641 (3) Å, α = 101.61 (2), β = 98.28 (2)°, γ = 104.13 (2), V = 1089.5 (5) Å^3, and Z = 2. This complex is isostructural to I with Pt–O = 2.098 (9) Å and Pt–O–Ph = 123.6 (7)°. Complex 1 undergoes rapid insertion of electrophilic substrates such as CO_2, COS, and PhNCO into the Pt–NHPh bond in preference to the metal hydride bond. These reactions in C_6H_6 solvent do not appear to involve free $NHPh^-$ as evidenced by the reaction between $PtH(^{15}NHPh)(PEt_3)_2$, which exclusively yields $PtH[PhNC(O)^{15}NHPh](PEt_3)_2$ as the initial product. Crossover between $PtH(NHPh)(PEt_3)_2$ and $PtD(^{15}NHPh)(PEt_3)_2$ to form $PtH(^{15}NHPh)(PEt_3)_2$ and $PtD(NHPh)(PEt_3)_2$ occurs slowly ($t_{1/2} \sim$ 48 h) at room temperature. Electrophiles such as CH_3I and H_2O directly attack bound aniline in $PtD(NHPh)(PEt_3)_2$ to produce *trans*-$PtDI(PEt_3)_2$ and *trans*-$PtD(OH)(PEt_3)_2$, along with $NH(CH_3)Ph$ and NH_2Ph, respectively. The electrophilic olefin acrylonitrile inserts into the Pt–N bond to form *trans*-$PtH[CH(CN)(CH_2NHPh)](PEt_3)_2$ (III). Crystals of III belong to the monoclinic space group $P2_1/c$ and at 22 °C a = 14.260 (6) Å, b = 14.021 (6) Å, c = 13.240 (6) Å, β = 107.96 (3)°, V = 2519 (3) Å^3, and Z = 4. The structure shows a 3-anilinopropionitrile ligand trans to hydride σ-bound to platinum (Pt–C = 2.198 (13) Å) by the 2-carbon atom. Complex III undergoes C–H reductive elimination on heating to 70 °C to produce 3-anilinopropionitrile. Methyl acrylate appears to undergo a similar insertion reaction; however, the organic product is unstable toward elimination in the presence of "$Pt(PEt_3)_2$". Although I is kinetically stable toward N–H reductive elimination, ligands such as CO, azobenzene, and PEt_3 promote the elimination process. Hydrogenolysis of I produces $PtH_2(PEt_3)_2$ and NH_2Ph. Substituted furans $\overline{OCHCHCHC}X$, where X = H, COOPh, CHO, and CN, or acetylene induce reductive elimination of aniline followed by C–H oxidative addition of the substrate. Reactions of II resemble those of I but appear to proceed more rapidly. The influence of relative Pt–N and Pt–O bond strengths on these processes is considered.

Amide (NRR'^-) complexes of the late-transition metals are not as common nor as stable as those for the early-transition elements; however, many have been prepared and characterized.[1] Binding of an amide ligand to electron-rich d^8 metals provides a mismatch between the soft π-donor metal and the hard π-donor amide ligand. Bond energy correlations for a series of ligands predict that Pt–N bonds should be much weaker than Pt–O or Pt–C bonds in reactions that involve homolytic dissociation.[2] This may be advantageous for catalytic chemistry since the weakly bound amide can be used as a reactive group for transfer to an organic substrate in an insertion reaction.

Catalysts for the amination of olefins under mild conditions are unknown. For example, ethylamine is commercially prepared from the high-pressure reaction between ammonia and ethanol rather than from the direct reaction between ethylene and ammonia.[3] Development of homogeneous catalytic processes using nitrogen nucleophiles has been limited. Rhodium-, nickel-, and palladium-catalyzed additions of amines to dienes, based on allylic intermediates, are known.[4,5] These reactions yield a multitude of products arising from both dimerization and amination. Amine additions to α,β-unsaturated olefins to yield vinylogous arylamino ketones, esters, and nitriles are catalyzed by Pd.[5] This process requires a sacrificial oxidant to regenerate the catalytic Pd(II) species. Metal salts such as $RhCl_3{\cdot}3H_2O$, $Rh(NO_3)_3$, and $IrCl_3{\cdot}3H_2O$ will catalyze the addition of secondary amines to ethylene.[6] This reaction (restricted to ethylene) is sensitive to the bulkiness of the amine and also to its nucleophilicity. Hegedus et al.[7] have used a hydroquinone/$PdCl_2(CH_3CN)_2$ mixture to catalytically (in Pd) promote intramolecular cyclization of 2-allylanilines.

One model catalytic cycle for olefin amination would proceed by olefin insertion into a hydridoamido complex, followed by reductive elimination of amine product. It is known that tetrafluoroethylene will insert into a Pt–O bond.[8] Recent studies show that Pt–N bonds should be thermodynamically less stable than Pt–C bonds[2] and that these bonds are weaker than Pt–O bonds by about 16.5 kcal/mol.[9] This explains the greater reactivity of late-transition-metal amide complexes compared to analogous alkoxides and implies that the insertion of olefins into Pt–N bonds should be thermodynamically feasible.

Recent research on late-transition-metal amide chemistry includes N–H intramolecular oxidative addition to Rh(I) and Ir(I),[10-14] preparation of an amido-bridged Ir(III) dimer by addition

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of NH$_3$ to Ir(PEt$_3$)$_2$(CH$_2$CH$_2$)$_2$Cl in liquid NH$_3$,[15] and preparation of hydridoamido- and alkylamidoplatinum(II) complexes.[9,16,17] We recently communicated the first example of an insertion reductive elimination sequence for addition of the hydridoamido complex *trans*-PtH(NHPh)(PEt$_3$)$_2$ to an activated olefin.[17] In this paper we describe the synthesis and molecular structure of *trans*-PtH(NHPh)(PEt$_3$)$_2$ and *trans*-PtH(OPh)(PEt$_3$)$_2$, rare examples of isolable late metal hydridoamido and hydrido aryloxido complexes. Experiments characterizing the reactivity of the amide and aryloxide ligands in these complexes are described. The structure of a product derived from olefin insertion into the Pt–N bond has also been determined crystallographically.

Experimental Section

All manipulations were performed under a nitrogen atmosphere using Schlenk techniques. Materials obtained from commercial sources were used without purification except as noted. C$_6$D$_6$ was purged with N$_2$ and dried over 3-Å molecular sieves; THF, pentane, and benzene were all distilled from sodium or potassium benzophenone ketyl; all gases were passed through a dry ice/acetone trap to remove water and other impurities. The complexes *trans*-PtHCl(PEt$_3$)$_2$ and *trans*-PtDCl(PEt$_3$)$_2$ were prepared by literature procedures.[18] The NaNHPh was prepared from NaH and NH$_2$Ph and recrystallized (extremely air- and moisture-sensitive white crystals) from THF/C$_6$H$_6$/pentane. The NaOPh was prepared from NaOH and phenol and recrystallized from acetone/benzene. Elemental analyses were performed by Galbraith Laboratories, Inc.

IR spectra were recorded with the use of an IBM IR/32 FTIR spectrometer. All NMR spectra were recorded on a GE QE 300-MHz NMR spectrometer equipped with a 5-mm broad-band probe. X-ray crystallographic analyses were performed with the use of a Nicolet R3m/V diffractometer with an LT-2 low-temperature accessory. Structure solutions and data workup were performed on a DEC Microvax II computer with SHELX version 2.2 or 3.4 software. The ^{31}P NMR spectra were referenced to the deuteriated lock solvent, which had been previously referenced to 85% H$_3$PO$_4$. All ^{31}P shifts were recorded relative to H$_3$PO$_4$ with downfield shifts being positive. The ^{15}N chemical shifts were referenced to ^{15}NH$_2$Ph in C$_6$D$_6$. For the ^{1}H, ^{2}H, and ^{13}C NMR spectra the chemical shifts were all referenced to natural abundance or residual solvent peaks observed in the spectra.

Synthesis of *trans*-Hydrido(nitrato)bis(triethylphosphine)platinum(II), *trans*-PtH(NO$_3$)(PEt$_3$)$_2$. To a vigorously stirred solution of *trans*-PtHCl(PEt$_3$)$_2$ (2.01 g, 4.29 mmol) dissolved in 10 mL of degassed CH$_3$CN was added TlNO$_3$ (1.15 g, 4.32 mmol) (Caution! Thallium salts are extremely toxic) dissolved in a mixture of H$_2$O and CH$_3$CN (5:1). A white precipitate of TlCl formed instantly. The solution was stirred for 10 min, filtered, and concentrated under vacuum to yield a pale yellow viscous oil, which was extracted with warm petroleum ether (4 × 50 mL). Cooling the solution (−10 °C) overnight resulted in the formation of long white needles of the title complex, yield 1.98 g (94%). ^{1}H NMR (C$_6$D$_6$): δ −23.62 (t, $^1J_{\mathrm{Pt-H}}$ = 1318 Hz, $^2J_{P\text{-}H}$ = 16 Hz, Pt–*H*). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 25.7 (s, $^1J_{\mathrm{Pt-P}}$ = 2818 Hz). IR (KBr, cm^{-1}): 2280 and 2218 (Pt–H); 1449, 1285, 1001 (NO$_3$). IR (pentane, cm^{-1}): 2243 (Pt–H); 1050 (sh), 1034, 992 (NO$_3$). The appearance of two hydride peaks in the KBr spectrum is probably a result of the formation of *trans*-PtHBr(PEt$_3$)$_2$ in the sample.

Synthesis of *trans*-Hydrido(phenylamido)bis(triethylphosphine)platinum(II), *trans*-PtH(NHPh)(PEt$_3$)$_2$ (I). To *trans*-PtH(NO$_3$)(PEt$_3$)$_2$ (0.41 g, 0.829 mmol) dissolved in 10 mL of benzene under N$_2$ was added quickly (slow addition decreases the yield) with vigorous stirring a solution of NaNHPh (0.145 g, 1.26 mmol) in THF. The solution turned yellow and produced a fine white precipitate. The solvent was removed in vacuo and the residue extracted with pentane (3 × 5 mL). The pentane extracts were concentrated to 5 mL and cooled (−10 °C) overnight to yield yellow crystals, 0.365 g (84%). The complex is thermally unstable and decomposes (yellow crystals to brown oil) over 8 h at room temperature; however, it can be stored at −10 °C for several months. Solutions of the complex in C$_6$H$_6$ are stable at room temperature for days! ^{1}H NMR (C$_6$D$_6$): δ 7.26 (t, J = 8 Hz, *o-H*), 6.83 (d, J = 8 Hz, *m-H*), 6.52 (t, J = 7 Hz, *p-H*), 2.20 (s, $^2J_{\mathrm{Pt-H}}$ = 11 Hz, N–*H*), 1.52 (m, P–C*H*$_2$), 0.93 (m, PCH$_2$C*H*$_3$), −14.71 (t, $^1J_{\mathrm{Pt-H}}$ = 886 Hz, $^2J_{\mathrm{P-H}}$ = 16 Hz, Pt–*H*). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 21.8 (s, $^1J_{\mathrm{Pt-P}}$ = 2775 Hz). IR (pentane, cm^{-1}): 3345 (N–H), 2118 (Pt–H). Mp (uncorrected): 68–68.5 °C.

Table I. Crystal, Data Collection, and Refinement Parameters for I–III

	I	II	III
formula	C$_{18}$H$_{37}$NP$_2$Pt	C$_{18}$H$_{36}$OP$_2$Pt	C$_{21}$H$_{40}$N$_2$P$_2$Pt
cryst syst	monoclinic	triclinic	monoclinic
space gp	$P2_1/n$	$P\bar{1}$	$P2_1/c$
a, Å	11.445 (2)	9.477 (3)	14.260 (6)
b, Å	13.010 (2)	10.617 (3)	14.021 (6)
c, Å	14.888 (2)	11.641 (3)	13.240 (6)
α, deg		101.61 (2)	
β, deg	104.63 (1)	98.28 (2)	107.96 (3)
γ, deg		104.13 (2)	
V, Å^3	2144.9 (6)	1089.5 (5)	2519 (3)
Z	4	2	4
D(calcd), g cm^{-3}	1.62	1.60	1.52
temp, °C	−100	−50	22
cryst dimens, mm	0.38 × 0.40 × 0.43	0.51 × 0.39 × 0.32	0.36 × 0.31 × 0.43
radiatn	Mo Kα	Mo Kα	Mo Kα
diffractometer	Nicolet R3m/V	Nicolet R3m/V	Nicolet R3m/V
abs coeff, cm^{-1}	67.24	66.51	57.6
$T_{\mathrm{max}}/T_{\mathrm{min}}$	0.906/0.542	1.000/0.557	0.933/0.647
scan; speed, deg/min	variable; 1.5–29	variable; 4–29	variable; 5–29
2θ scan range, deg	3–50	3–50	3–50
scan technique	2θ	2θ	2θ
no. of unique data	4305 (4466 coll)	3454 (4125 coll)	5270 (5378 coll)
no. of unique data with (F_o) > $5\sigma(F_o)$	3209	2826	2267
std reflcns	3/100	3/197	3/197
data/param ratio	16.0	21.9	17.4
GOF	1.544	1.29	1.19
R_F, %	2.72	5.35	3.92
R_{wF}, %	4.59	7.20	5.06
weighting factor,[a] g	0.0007	0.001	0.001

[a] $w^{-1} = \sigma^2(F_o) + gF_o^2$.

Synthesis of Labeled Compounds. (a) *trans*-PtD(NO$_3$)(PEt$_3$)$_2$ was synthesized from *trans*-PtDCl(PEt$_3$)$_2$ following the same procedure for I using TlNO$_3$, CD$_3$CN, and D$_2$O. *trans*-PtD(NO$_3$)(PEt$_3$)$_2$ will undergo rapid exchange with moisture in the air, and it should be handled using Schlenk techniques. IR (KBr, cm^{-1}): 1636 and 1591 (Pt–*D*).

(b) *trans*-PtD(NO$_3$)(PEt$_3$)$_2$ was used to synthesize both *trans*-PtD(NHPh)(PEt$_3$)$_2$ (I-*d*) and *trans*-PtD(^{15}NHPh)(PEt$_3$)$_2$ following the procedure for I using either NaNHPh or Na^{15}NHPh. ^{2}H NMR (C$_6$H$_6$): δ −14.7 (s, $^1J_{\mathrm{Pt-D}}$ = 136 Hz, Pt–*D*).

(c) *trans*-PtH(^{15}NHPh)(PEt$_3$)$_2$ was synthesized following the procedure for I using Na^{15}NHPh. ^{1}H NMR (C$_6$D$_6$): δ 7.27 (t, J = 7 Hz, *m-H*), 6.84 (d, J = 8 Hz, *o-H*), 6.53 (t, J = 7 Hz, *p-H*), 2.20 (d, $^1J_{^{15}\mathrm{N-H}}$ = 71 Hz, $^2J_{\mathrm{Pt-H}}$ = 23 Hz, ^{15}N–*H*), 1.52 and 0.93 (m, PC$_2$*H*$_5$), −14.73 (dt, $^1J_{\mathrm{Pt-H}}$ = 885 Hz, $^2J_{\mathrm{P-H}}$ = 16 Hz, $^2J_{^{15}\mathrm{N-H}}$ = 20 Hz, Pt–*H*). ^{15}N{^{1}H} NMR (C$_6$D$_6$): δ −2.25 (s, $^1J_{\mathrm{Pt-^{15}N}}$ = 216 Hz).

Reaction between I and *trans*-PtH(NO$_3$)(PEt$_3$)$_2$. Equal amounts of I and *trans*-PtH(NO$_3$)(PEt$_3$)$_2$ were loaded into a 5-mm NMR tube and sealed with a rubber septum, and C$_6$D$_6$ was injected. After 6 h the hydride resonance for *trans*-PtH(NO$_3$)(PEt$_3$)$_2$ disappeared, while the resonance for I was still visible. A new hydride resonance grew in during the reaction and could be identified as [HPt(PEt$_3$)$_3$]$^+$ by comparison with an authentic sample.[19] ^{1}H NMR (C$_6$D$_6$): δ −6.26 (dt, $^1J_{\mathrm{Pt-H}}$ = 792 Hz, $^2J_{\mathrm{P-H}}$(trans) = 156 Hz, $^2J_{\mathrm{P-H}}$(cis) = 16 Hz, Pt-*H*).

Crystal Structure Determination of *trans*-PtH(NHPh)(PEt$_3$)$_2$ (I). A crystal approximating a cube was cut from a long needle of I. This was

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Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^4$) for *trans*-$PtH(NHPh)(PEt_3)_2$ (I)

	x	y	z	$U(eq)^a$
Pt	2948 (1)	−634 (1)	222 (1)	230 (1)
P(1)	2496 (2)	1070 (1)	112 (1)	266 (5)
C(10)	1117 (6)	1364 (6)	464 (5)	397 (25)
C(11)	1134 (8)	981 (7)	1436 (6)	535 (31)
C(12)	3637 (6)	1915 (5)	821 (5)	329 (22)
C(13)	3370 (8)	3058 (5)	834 (6)	483 (28)
C(14)	2235 (7)	1614 (6)	−1051 (5)	421 (24)
C(15)	1244 (6)	1069 (6)	−1789 (5)	433 (26)
P(2)	3058 (1)	−2378 (1)	230 (1)	263 (5)
C(20)	1799 (7)	−2994 (5)	573 (6)	390 (25)
C(21)	1594 (7)	−2560 (6)	1477 (6)	450 (28)
C(22)	4415 (6)	−2919 (5)	1019 (6)	380 (25)
C(23)	4512 (9)	−4086 (6)	1089 (7)	573 (34)
C(24)	3003 (6)	−2961 (5)	−899 (5)	375 (24)
C(25)	1896 (7)	−2641 (6)	−1662 (5)	402 (25)
N	4749 (5)	−405 (4)	1024 (4)	256 (16)
C(1)	5076 (5)	−176 (4)	1933 (4)	256 (19)
C(2)	4313 (6)	−425 (5)	2527 (5)	315 (22)
C(3)	4657 (7)	−216 (6)	3465 (5)	413 (26)
C(4)	5764 (8)	249 (6)	3876 (5)	482 (28)
C(5)	6505 (8)	506 (5)	3309 (5)	439 (26)
C(6)	6166 (6)	305 (5)	2353 (5)	317 (21)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

sealed into a capillary tube under nitrogen and cooled to −100 °C. Least-squares fitting of 45 centered reflections ($15° < 2\theta < 40°$) determined the cell to be monoclinic with the parameters listed in Table I. Normal low-temperature 2θ data collection was performed from 3 to 50°. An empirical absorption correction from ψ scan data was applied. Analysis of systematic absences uniquely determined the space group to be $P2_1/n$. SHELX version 2.2 software was used in data reduction and refinement. The weighting factor was allowed to refine freely, as was a common isotropic thermal parameter for the hydrogen atoms [final value 0.058 (4)]. The largest peak in the final difference Fourier map corresponded to 1 e/Å^3 and was in the position expected for the metal hydride (Pt–H = 1.63 Å). The largest shift/esd in the final refinement cycle was 0.002 or less for all parameters. Final positional parameters are given in Table II.

Theoretical Studies. Electronic structure calculations were performed with the use of a DEC Micro Vax II computer and employed the self-consistent-field discrete variational Xα (SCF-DV-Xα) method.[20] Numerical atomic orbitals from exact Hartree–Fock–Slater calculations were used assuming the α values of Schwartz.[21] For Pt the orbitals through 6p were used as basis orbitals, and the 1s–4d functions were treated as a frozen core orthogonalized against valence orbitals. Phosphorus orbitals through 3d were included with a 1s–2p frozen core. Hydrogen atoms were treated with a 1s basis, and that for the nitrogen atoms used a 1s, 2s, 2p basis set with a 1s core for the molecular calculations. The molecular Coulomb potential was calculated by a least-squares fit[22] of the model electron density to the numerical density. Seven radial degrees of freedom were allowed in the expansion function, in addition to the radial atomic densities. The idealized C_{2v} model structures of $PtH(NH_2)(PH_3)_2$ assumed the NH_2 group either in the platinum square plane or perpendicular to it. The following angles and distances were used: N–H = 1.03 Å, H–N–H = 120°, Pt–N = 2.118 Å, Pt–P = 2.273 Å, H–P–H = 93.45°, and Pt–H = 1.62 Å.

Reaction between I and Water To Generate *trans*-Hydridohydroxobis(triethylphosphine)platinum(II). Compound I was dissolved in C_6D_6 (0.5 mL) to which 10 μL of H_2O (degassed) was added. The solution was stirred vigorously for 5 min to saturate the solvent with water while undissolved water droplets could still be seen inside the NMR tube. Analysis of the reaction by ^1H NMR spectroscopy showed partial conversion of I to a new hydride species, postulated to be *trans*-$PtH(OH)(PEt_3)_2$, as well as peaks characteristic of free aniline. ^1H NMR (C_6D_6): δ −20.23 (t, $^1J_{Pt-H}$ = 1007 Hz, $^2J_{Pt-H}$ = 16 Hz, Pt-*H*).

Reaction between I and Phenol To Yield *trans*-Hydridophenoxobis(triethylphosphine)platinum(II). Complex I (0.263 g, 0.501 mmol) was dissolved in benzene (10 mL), and excess phenol (0.211 g, 2.24 mmol) was added. Solvent was removed in vacuo to yield an oil. Excess phenol was sublimed away by gentle heating of the oil under vacuum. The residue was extracted with pentane (3 × 5 mL) and cooled (−10 °C) for several days to obtain large colorless crystals of *trans*-$PtH(OPh)(PEt_3)_2$, yield 0.105 g (40%).

Table III. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for *trans*-$PtH(OPh)(PEt_3)_2$ (II)

	x	y	z	$U(eq)^a$
Pt	703 (1)	2160 (1)	2240 (1)	51 (1)
P(1)	−1065 (4)	2059 (3)	644 (3)	62 (1)
P(2)	2148 (4)	2202 (3)	3980 (3)	63 (1)
C(10)	−2191 (21)	409 (16)	−225 (15)	96 (5)
C(11)	−3130 (22)	−431 (19)	420 (18)	108 (5)
C(12)	−434 (23)	2966 (20)	−426 (18)	116 (6)
C(13)	585 (23)	2359 (19)	−1175 (17)	113 (6)
C(14)	−2493 (25)	2798 (21)	1108 (19)	118 (6)
C(15)	−2131 (30)	4101 (24)	1746 (22)	147 (8)
C(20)	4157 (17)	2894 (15)	4174 (14)	83 (4)
C(21)	4815 (25)	2066 (21)	3277 (18)	120 (6)
C(22)	1832 (20)	514 (16)	4248 (15)	90 (4)
C(23)	2776 (24)	424 (21)	5385 (18)	121 (6)
C(24)	1832 (24)	3381 (21)	5271 (19)	123 (6)
C(25)	319 (26)	3210 (23)	5435 (21)	133 (7)
O	2484 (10)	3220 (8)	1614 (8)	68 (2)
C(1)	3015	4557	1922	59 (3)
C(2)	4199 (10)	5119 (9)	1427 (8)	88 (4)
C(3)	4772	6508	1677	101 (5)
C(4)	4162	7336	2423	96 (4)
C(5)	2978	6774	2918	86 (4)
C(6)	2404	5385	2668	70 (3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Synthesis of *trans*-Hydridophenoxobis(triethylphosphine)platinum(II), *trans*-$PtH(OPh)(PEt_3)_2$ (II). A benzene solution of *trans*-$PtH(NO_3)(PEt_3)_2$ (0.512 g, 1.04 mmol) was stirred with a methanol solution (5 mL) of NaOPh (0.210 g, 2.10 mmol) for 15 min. Solvent was removed in vacuo, and the solid residue was extracted with pentane (5 × 10 mL), concentrated, and cooled (−10 °C) overnight to yield colorless plates of product, 0.307 g (57%). The compound is extremely soluble in most organic solvents including pentane. Crystals of II are thermally sensitive and decompose within 2 h, if warmed slightly above room temperature (~30 °C). The product is not sensitive to oxygen and can be manipulated in the air for short periods of time. ^1H NMR (C_6D_6): δ 7.37 (overlapping d and t, J = 8 Hz, *o*- and *m-H*), 6.76 (t, J = 7 Hz, *p-H*), 1.46 and 0.91 (m, P-C_2H_5), −20.85 (t, $^1J_{Pt-H}$ = 1093 Hz, $^2J_{P-H}$ = 16 Hz, Pt-*H*). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 24.5 (s, $^1J_{Pt-P}$ = 2832 Hz). Mp (uncorrected): 61.5–64 °C.

Crystal Structure Determination of *trans*-$PtH(OPh)(PEt_3)_2$ (II). A rectangular crystal of II was loaded into a capillary tube in the air and sealed with wax. The crystal was cooled to −50 °C (unstable in the beam at 20 °C and tended to shatter below −50 °C) and least-squares fitting of 44 centered random reflections ($15° < 2\theta < 30°$) showed the cell to be triclinic with the parameters listed in Table I. Normal low-temperature 2θ data collection was performed from 3 to 50°. An empirical absorption correction from psi scan data was applied. The generation of a chemically reasonable structure confirmed the space group to be $P\bar{1}$. SHELX version 3.4 software was used in data reduction and refinement. The weighting factor was fixed at 0.001, and the hydrogen atom isotropic thermal parameters were also fixed at 0.12. Only the "heavy" atoms (Pt and P) were allowed to refine anisotropically; all other atoms were left isotropic. The six carbon atoms of the phenoxide ring were refined as a rigid group. The largest peak in the final difference Fourier map was 1.5 e/Å^3, and the final shift/esd was <0.01 for all parameters. Final positional parameters are given in Table III.

Reaction between I and Methyl Iodide. Complex I (~20 mg) contained in a 5-mm NMR tube was dissolved in C_6D_6 (0.5 mL). Methyl iodide was then added by syringe (10 μL). The ^1H NMR spectrum showed the reaction was about 90% complete after 15 min at 75 °C to yield *trans*-$PtHI(PEt_3)_2$.[18] ^1H NMR (C_6D_6): δ −12.69 (t, $^1J_{Pt-H}$ = 1380 Hz, $^2J_{P-H}$ = 13 Hz, Pt-*H*).

Reaction between II and Methyl Iodide. A procedure analogous to that described above was used. The reaction was monitored for products after 72 h at room temperature (22 °C). The ^1H NMR spectrum indicated production of *trans*-$PtHI(PEt_3)_2$[18] (see above) and the organic ether anisole, whose presence was verified by addition of an authentic sample to the reaction tube.

Reaction between I and Carbon Monoxide To Yield *trans*-Dicarbonylbis(triethylphosphine)platinum(0). A benzene-d_6 solution of I

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Table IV. ^{31}P and ^{1}H NMR Parameters for Olefin Adducts of Pt(PEt$_3$)$_2$

olefin	^{31}P, δ	$J_{\mathrm{Pt-P}}$, Hz	$^2J_{\mathrm{P-P}}$, Hz	^{1}H, δ	$^2J_{\mathrm{Pt-H}}$, Hz
diphenylacetylene	12.0 (s)	3301			
ethylene	21.0 (s)	3517		2.11 (s)	57
cis-stilbene	16.5 (s)	3387		4.10 (s)	60
trans-stilbene				4.02 (s)	54
dimethylmaleate				3.71 (d)	55
1-hexene	19.6 (d)	3266	63		
	21.2 (d)	3638	63		
norbornylene	21.0 (s)	3357		2.37	58
styrene	18.2 (d)	3518	73	3.73 (m)	60
	18.9 (d)	3530	73	2.42 (m)	60
				2.52 (m)	60

was injected into a 5-mm NMR tube, which had been capped under nitrogen; carbon monoxide was then bubbled through the solution for 5 min, and the solution changed from bright yellow to reddish orange. Spectroscopic analysis of the product showed it to be *trans*-Pt(CO)$_2$(PEt$_3$)$_2$.[23] ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ −8.3 (s, $^1J_{\mathrm{Pt-P}}$ = 3219 Hz). IR (C$_6$D$_6$, cm^{-1}): 1970 and 1930 (C═O).

Reaction between II and Carbon Monoxide. This reaction followed the procedure outlined for I above with the exception that the color changed from colorless to red. The reaction produced *trans*-Pt(CO)$_2$(PEt$_3$)$_2$ as identified by ^{31}P{^{1}H} NMR spectroscopy (see above); however, a small amount of PtH(PEt$_3$)$_3^+$ also formed.[19]

Reaction between I and Triethylphosphine To Yield Aniline and Tris- or Tetrakis(triethylphosphine)platinum(0). Excess PEt$_3$ was added by syringe to a benzene-d_6 solution of I. Immediate analysis by ^{1}H NMR spectroscopy showed the reaction produced aniline, as identified by its characteristic proton resonances. The ^{31}P{^{1}H} NMR spectrum showed only broad resonances as expected for rapid exchange between excess phosphine and platinum(0) tris- or tetrakis(phosphine) complexes at room temperature.[24]

Reaction between I and Azobenzene To Yield (Azobenzene)bis(triethylphosphine)platinum(0). Complex I (0.329 g, 0.627 mmol) was dissolved in benzene (10 mL). The solution was then treated with solid Ph$_2$N$_2$ (0.133 g, 0.727 mmol), and the resulting orange–red solution was stirred overnight. Solvent was removed and the residue extracted with benzene (2 × 5 mL). The benzene solution was layered with pentane to produce yellow crystals of Pt(PhN═NPh)(PEt$_3$)$_2$, yield 0.185 g (48%). It is important that this compound be recrystallized in the presence of an excess of azobenzene. ^{1}H NMR (CD$_3$CN): δ 7.9, 7.6, 7.3, 7.1, and 6.7 (unresolved, broad features, C$_6$*H*$_5$); 1.6 and 0.9 (m, PC$_2$*H*$_5$). ^{31}P{^{1}H} NMR (CD$_3$CN): δ 6.9 (s, $^1J_{\mathrm{Pt-P}}$ = 4019 Hz). Anal. Calcd for C$_{24}$H$_{40}$N$_2$P$_2$Pt: C, 46.97; H, 6.58; N, 4.56. Found: C, 47.46; H, 6.81; N, 4.21.

Reaction between I and Hydrogen or Deuterium To Yield *trans*-Dihydridobis(triethylphosphine)platinum(II) or Dideuteriobis(triethylphosphine)platinum(II). These reactions were performed in sealed 5-mm NMR tubes with either benzene or benzene-d_6 solvent under an atmosphere of H$_2$ or D$_2$. The samples were allowed to react for about 3 h to reach completion with Vortex stirring. The reactions (monitored by ^{1}H or ^{31}P NMR spectroscopy) were found to yield only *trans*-Pt(H)$_2$(PEt$_3$)$_2$ and aniline or their deuterated analogues.[25]

Reaction between II and Hydrogen. The reaction proceeded analogously to I; however, the reaction time was much shorter, requiring only 30 min to reach completion. The reaction produced *trans*-Pt(H)$_2$(PEt$_3$)$_2$ (the major product),[25] as well as [(PEt$_3$)$_2$Pt(μ-H)$_2$PtH(PEt$_3$)$_2$]$^+$, a species known to arise from combination of *trans*-Pt(H)$_2$(PEt$_3$)$_2$ with PtHX(PEt$_3$)$_2$ where X is any weakly coordinated ligand (i.e. nitrate, triflate, phenoxide, etc.).[26,27]

Reaction between I and Olefins. All reactions (C$_6$D$_6$ solvent) required about 72 h at room temperature to reach completion. Each reaction yielded the corresponding olefin complexes of "PtL$_2$", which have been independently synthesized by reaction of Pt(CH$_2$═CH$_2$)(PEt$_3$)$_2$[28–30] and the corresponding unsaturated hydrocarbon. The unsaturated substrates that we examined are given in Table IV along with their NMR data.

Reaction between I and Phenyl Isocyanate To Yield *trans*-Hydrido-1-(1,3-diphenylureato)bis(triethylphosphine)platinum(II). To *trans*-PtH(NHPh)(PEt$_3$)$_2$ (I) (0.242 g, 0.462 mmol) dissolved in 10 mL of C$_6$H$_6$ was added PhNCO (0.055 mL, 0.050 g, 0.42 mmol) by syringe. The solvent was removed in vacuo and the residue dissolved in 20 mL of pentane to which 6 mL of C$_6$H$_6$ was added. The solution was filtered and cooled (−10 °C) overnight to yield air-stable off-white crystals of *trans*-PtH(NPhCONHPh)(PEt$_3$)$_2$, 0.238 g (80%). ^{1}H NMR (C$_6$D$_6$): δ 8.40 (s, N–*H*), 8.57 (d, J = 8 Hz, *o-H*) 8.10 (d, J = 8 Hz, *o-H*) 7.37 (t, J = 8 Hz, *m-H*), 7.29 (t, J = 8 Hz, *m-H*), 6.92 (t, J = 7 Hz, *p-H*), 6.87 (t, J = 7 Hz, *p-H*), −16.36 (t, J = 1007 Hz, $^2J_{\mathrm{P-H}}$ = 15 Hz, Pt–*H*). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 20.3 (s, $^1J_{\mathrm{Pt-P}}$ = 2688 Hz). IR (KBr, cm^{-1}): 3235 (N–H), 2172 (Pt–H), 1624 (C═O). Anal. Calcd for C$_{25}$H$_{42}$N$_2$OP$_2$Pt: C, 46.64; H, 6.59; N, 4.35. Found: C, 46.88; H, 6.88; N, 4.37.

Reaction between II and Phenyl Isocyanate To Yield *trans*-Hydrido(*N*,*O*-diphenylcarbamato)bis(triethylphosphine)platinum(II). A solution of II (0.292 g, 0.590 mmol) in benzene was treated with excess PhNCO (0.15 mL, 0.16 g, 1.4 mmol), which caused a slight darkening of the solution. The solvent was immediately evaporated to dryness and the residue extracted with warm pentane (5 × 10 mL). The solution was concentrated and cooled (−10 °C) overnight to yield colorless crystals of *trans*-PtH(PhNC(O)OPh)(PEt$_3$)$_2$, 0.147 g (47%). ^{1}H NMR (C$_6$D$_6$): δ 8.64 (d, J = 8 Hz, *o-H*), 7.49 (d, J = 8 Hz, *o-H*), 7.35 (t, J = 8 Hz, *m-H*), 7.25 (t, J = 8 Hz, *m-H*), 6.96 and 6.94 (overlapping t, J = 7 Hz, *p-H*), 1.45 and 0.88 (m, PC$_2$*H*$_5$), −17.63 (t, $^1J_{\mathrm{Pt-H}}$ = 1022 Hz, $^2J_{\mathrm{P-H}}$ = 16 Hz, Pt–*H*). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 19.7 (s, $^1J_{\mathrm{Pt-P}}$ = 2833 Hz). IR (KBr, cm^{-1}): 2172 (Pt–H), 1662 (C═O). Anal. Calcd for C$_{25}$H$_{41}$NO$_2$P$_2$Pt: C, 46.57; H, 6.42; N, 2.17. Found: C, 46.90; H, 6.70; N, 2.15.

Reaction between I and Carbon Dioxide To Yield *trans*-Hydrido(*N*-phenylcarbamato)bis(triethylphosphine)platinum(II). Complex I (0.341 g, 0.650 mmol) was dissolved in 20 mL of pentane. Dry CO$_2$ gas was then bubbled through the solution for 10 min causing precipitation of the white carbamato insertion product. The solid is thermally sensitive and turns black within 48 h at room temperature. Attempts to purify this compound led to decomposition since it appears to be thermally sensitive and stable only under an atmosphere of CO$_2$. ^{1}H NMR (C$_6$D$_6$): δ 9.10 (s, N–*H*), 8.20 (d, J = 8 Hz, *o-H*), 7.31 (t, J = 8 Hz, *m-H*), 6.89 (t, J = 8 Hz, *p-H*), 1.61 and 1.01 (m, C$_2$*H*$_5$), −22.02 (t, $^1J_{\mathrm{Pt-H}}$ = 1200 Hz, $^2J_{\mathrm{P-H}}$ = 16 Hz, Pt–*H*). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 25.3 (s, $^1J_{\mathrm{Pt-P}}$ = 2854 Hz). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 160.2 (s, *C*═O); 144.0, 119.9, 117.9, and 115.0 (s, *C*$_6$H$_5$); 18.2 and 8.7 (m, P–*C*$_2$H$_5$). IR (C$_6$D$_6$, cm^{-1}): 2220 (Pt–*H*), 1626 (C═O).

Reaction between II and Carbon Dioxide To Generate *trans*-Hydrido(phenyl carbonato)bis(triethylphosphine)platinum(II). A benzene-d_6 solution of II contained in a 5-mm NMR tube was purged with CO$_2$ for 30 min. During this time the solution darkened gradually. Spectral analysis of the reaction showed that less than 10% of the starting material (II) had reacted to produce the new hydride-containing species assigned to *trans*-PtH(OC(O)OPh)(PEt$_3$)$_2$. This complex was observed only under a CO$_2$ atmosphere. ^{1}H NMR (C$_6$D$_6$): δ −22.91 (t, $^1J_{\mathrm{Pt-H}}$ = 1208 Hz, $^2J_{\mathrm{P-H}}$ = 15 Hz, Pt–*H*). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 25.5 (s, $J_{\mathrm{Pt-P}}$ = 2835 Hz).

Reaction between I and Carbonyl Sulfide To Yield *trans*-Hydrido-(*N*-phenylthiocarbamato)bis(triethylphosphine)platinum(II). Complex I (0.214 g, 0.408 mmol) was dissolved in pentane (10 mL). A stream of COS was bubbled through the solution for 5 min causing the yellow color of the solution to disappear and a white precipitate to form. Addition of 2 mL of C$_6$H$_6$ yielded a clear solution, which was filtered and cooled (−10 °C) overnight to obtain colorless crystals of *trans*-PtH(SCONHPh)(PEt$_3$)$_2$. The supernatant solution was concentrated to yield a second crop of crystals, 0.151 g (63%). ^{1}H NMR (C$_6$D$_6$): δ 7.95 (s, N–*H*), 7.56 (d, J = 8 Hz, *o-H*), 7.08 (t, J = 8 Hz, *m-H*), 6.79 (t, J = 7 Hz, *p-H*), 1.83 and 0.98 (m, C$_2$*H*$_5$), −11.27 (t, $^1J_{\mathrm{Pt-H}}$ = 1096, $^2J_{\mathrm{P-H}}$ = 15 Hz, Pt–*H*). ^{31}P{^{1}H}NMR (C$_6$D$_6$): δ 20.8 (s, $^1J_{\mathrm{Pt-P}}$ = 2675 Hz). IR (KBr, cm^{-1}): 3279 (N–H), 2122 (Pt–H). Anal. Calcd for C$_{19}$H$_{37}$NOP$_2$PtS: C, 39.03; H, 6.39; N, 2.39. Found: C, 39.29; H, 6.84; N, 2.22.

Reaction between I and Carbon Disulfide. To I (0.314 g, 0.598 mmol) dissolved in benzene (10 mL), was added carbon disulfide (0.035 mL, 0.044 g, 0.58 mmol) with vigorous stirring. The initial yellow color darkened to brown within 5 min. After 3 h of stirring, the solution became emerald green. The solvent was removed in vacuo to yield a viscous green oil. Analysis by ^{31}P NMR spectroscopy showed the presence of several products. This was later confirmed by column chromatography (Florisil), which eluted five bands, none of which could be identified as the expected hydrido dithiocarbamate insertion product.

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Reaction between II and Carbonyl Sulfide or Carbon Disulfide. When a benzene-d_6 solution of II was purged with COS gas, the originally colorless solution turned orange, and after 20 min, an orange oil separated from solution. Analysis of the reaction mixture by ^{1}H NMR spectroscopy showed no hydride products. Similar results were obtained on addition of CS_2 to a benzene-d_6 solution of II.[31-33]

Insertion Reaction between I and Methyl Acrylate To Yield *trans*-Hydrido-2-[methyl 3-(phenylamino)propionate]bis(triethylphosphine)-platinum(II). Methyl acrylate (0.10 mL, 0.10 g, 1.2 mmol) was added to a solution of complex I (0.305 g, 0.58 mmol) in benzene (10 mL). After 12 h the solution was evaporated to dryness and the residue extracted with pentane (4 × 10 mL). The filtrate was concentrated and cooled (−10 °C) overnight to yield colorless fibrous crystals of *trans*-$PtH[CH(COOMe)CH_2NHPh](PEt_3)_2$, 0.275 g (78%). ^{1}H NMR (C_6D_6): δ 7.20 (t, *m-H*), 6.72 and 6.71 (overlapping t and d, *o-* and *p-H*), 4.44 (pseudo t, N–*H*), 4.26 and 3.74 (m, diastereotopic protons CH_2NHPh), 3.58 (s, OCH_3), 3.31 (m, $^2J_{Pt-H}$ = 84 Hz, Pt–C–*H*), −10.10 (t, $^1J_{Pt-H}$ = 901 Hz, $^2J_{P-H}$ = 18 Hz, Pt–*H*). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 18.4 (s, $^1J_{Pt-P}$ = 2776 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 181.2 (s, $^2J_{Pt-C}$ = 39 Hz, *C*=O); 149.9, 129.4, 116.4, and 113.1 (s, C_6H_5); 49.3 (s, OCH_3); 47.9 (s, $^2J_{Pt-C}$ = 17 Hz, CH_2NHPh); 28.1 (t, $^1J_{Pt-C}$ = 383 Hz, $^2J_{P-C}$ = 5 Hz, Pt–*C*); 19.0 and 8.7 (quint, t, PC_2H_5). IR (KBr, cm^{-1}): 3304 (N–H), 2027 (Pt–H), 1662 (C=O). Anal. Calcd for $C_{22}H_{43}NO_2P_2Pt$: C, 43.27; H, 7.11; N, 2.29. Found: C, 42.82; H, 7.29; N, 2.20.

Insertion Reaction between I and Acrylonitrile To Yield *trans*-Hydrido-2-[3-(phenylamino)propionitrilo]bis(triethylphosphine)platinum(II) (III). Excess acrylonitrile (0.5 mL, 24 equiv) was added to **I** (0.167 g, 0.318 mmol) dissolved in pentane (10 mL). The solution was allowed to react until the initial yellow color faded (12 h at room temperature). Solvent was removed under vacuum until the residue solidified. The solid was extracted with pentane (3 × 5 mL) and filtered, and the filtrate, cooled (−10 °C) overnight to yield white microcrystals of *trans*-Pt(H)$[CH(CN)CH_2NHPh](PEt_3)_2$, 0.095 g (52%). One X-ray quality crystal of the complex formed in a THF/pentane solution left undisturbed for 8 months at −10 °C. ^{1}H NMR (C_6D_6): δ 3.97 and 3.46 (m, CH_2CN diastereotopic protons), 4.27 (s, N–*H*), 2.46 (m, $^2J_{Pt-H}$ = 75 Hz, Pt–C*H*), −9.54 (t, $^1J_{Pt-H}$ = 785 Hz, $^2J_{P-H}$ = 18 Hz, Pt–*H*). $^{31}P\{^1H\}$ NMR C_6D_6: δ 11.7 (s, $^1J_{Pt-P}$ = 2740 Hz). IR (KBr, cm^{-1}): 3351 (N–H), 2180 (C≡N), 2039 (Pt–H). Anal. Calcd for $C_{21}H_{40}N_2P_2Pt$: C, 43.66; H, 6.99; N, 4.85. Found: C, 44.04; H, 7.30; N, 4.77.

Crystal Structure Determination of *trans*-PtH[CH(CN)CH$_2$NHPh](PEt$_3$)$_2$ (III). A rectangular crystal of the complex was cut from a long needle and attached to a glass fiber with epoxy. Data were collected at room temperature. Least-squares fitting of 24 centered reflections (15° < 2θ < 30°) determined the cell to be monoclinic with the parameters listed in Table I. Normal 2θ data collection was performed from 3 to 50°. An empirical absorption correction from psi scan data was applied. Analysis of the systematic absences in the data uniquely determined the cell to be $P2_1/a$, which was transformed to $P2_1/c$. SHELX version 3.4 software was used in data reduction and refinement. During solution of the structure, one ethyl group attached to P(2) was found to be disordered. This was modeled by locating the two disordered orientations in the difference Fourier map and refining them with constrained bond distances (P–C = 1.86 ± 0.02 Å, C–C = 1.55 ± 0.02 Å). The site occupancies of each bonded pair were tied together and allowed to refine to optimum values. The result was a ~2/3:1/3 site occupancy for the two orientations with P–C = 1.86 (4) and 1.88 (4), while C–C = 1.53 (4) and 1.53 (4). The weighting factor was fixed at 0.001, while the hydrogen atoms were allowed to refine to a common isotropic thermal parameter [final value 0.099 (8)]. The largest peak in the final difference Fourier map (~1 e/Å^3) was in the position expected for the metal hydride. The largest shift/esd in the final refinement cycle was 0.02 or less for all parameters. Final positional parameters are given in Table V.

Reaction between II and Acrylonitrile To Yield 3-Phenoxypropionitrile and (Acrylonitrile)bis(triethylphosphine)platinum(0). A benzene-d_6 solution of II was treated with $CH_2{=}CHCN$ (10 μL), and within 30 min the reaction yielded $Pt(CH_2{=}CHCN)(PEt_3)_2$ and $PhOCH_2CH_2CN$. ^{1}H NMR (C_6D_6): δ 3.24 (t, *J* = 6 Hz, $PhOCH_2CH_2CN$), 1.76 (t, *J* = 6 Hz, $PhOCH_2CH_2CN$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 16.8 (d, $^1J_{Pt-P}$ = 3269 Hz, $^2J_{P-P}$ = 36 Hz), 18.4 (d, $^1J_{Pt-P}$ = 3753 Hz, $^2J_{P-P}$ = 36 Hz, Pt($CH_2{=}CHCN$)(PEt_3)$_2$).

Table V. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for *trans*-$PtH[CH(CN)CH_2NHPh](PEt_3)_2$ (III)

	x	*y*	*z*	*U*(eq)[a]
Pt	2635 (1)	432 (1)	1961 (1)	47 (1)
P(1)	2768 (2)	2003 (2)	2423 (3)	49 (1)
P(2)	2224 (3)	−1127 (3)	1586 (3)	66 (2)
C(1)	4007 (8)	433 (9)	1535 (9)	52 (3)
C(2)	3937 (9)	−131 (9)	635 (11)	61 (3)
N(1)	3869 (9)	−612 (9)	−97 (10)	78 (3)
C(3)	4868 (8)	182 (9)	2480 (10)	56 (3)
N(2)	5824 (7)	380 (8)	2334 (8)	63 (3)
C(4)	6674 (9)	336 (10)	3160 (10)	64 (3)
C(5)	6735 (10)	160 (10)	4176 (11)	68 (4)
C(6)	7626 (11)	153 (11)	4998 (13)	85 (5)
C(7)	8467 (12)	306 (11)	4761 (13)	83 (4)
C(8)	8461 (12)	467 (11)	3731 (12)	87 (4)
C(9)	7546 (8)	477 (10)	2902 (10)	62 (3)
C(10)	4011 (10)	2516 (11)	3036 (11)	81 (4)
C(11)	4482 (13)	2169 (13)	4176 (12)	107 (6)
C(12)	2099 (10)	2323 (10)	3337 (11)	70 (4)
C(13)	2098 (12)	3399 (11)	3646 (13)	91 (5)
C(14)	2268 (9)	2787 (10)	1281 (10)	62 (3)
C(15)	1178 (10)	2636 (12)	722 (12)	87 (5)
C(20)	3229 (11)	−1986 (12)	2052 (11)	85 (5)
C(21)	3676 (14)	−2044 (15)	3244 (14)	126 (7)
C(22)	1772 (11)	−1433 (12)	192 (12)	87 (5)
C(23)	1055 (14)	−770 (14)	−482 (15)	118 (6)
C(24A)	1532 (22)	−1708 (23)	2419 (24)	128 (14)
C(25A)	507 (24)	−1253 (28)	2105 (29)	141 (14)
C(24B)	1148 (21)	−1410 (22)	2047 (28)	51 (11)
C(25B)	825 (29)	−2453 (22)	2001 (32)	79 (16)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Reaction between I and Phenyl 2-Furoate To Yield *trans*-Hydrido-5-(phenyl 2-furoate)bis(triethylphosphine)platinum(II). Complex **I** was generated from *trans*-$PtH(NO_3)(PEt_3)_2$ (1.00 g, 2.03 mmol), and the pentane extract was used without recrystallization. The phenyl 2-furoate was added, and the solution turned dark orange brown on standing overnight. Solvent was removed, and the residual oil was dissolved in a mixture of benzene and pentane. This was then eluted down a Florisil column (2-cm diameter × 30 cm) using 10:1 petroleum ether/benzene. The first pale yellow band eluted contained product. Solvent was removed in vacuo, and the residue was recrystallized from petroleum ether, yield 0.386 g (31%). ^{1}H NMR (C_6D_6): δ 7.74 (d, *J* = 3 Hz, *β-H*) 7.25 (d, *J* = 8 Hz, *o-H*), 7.05 (t, *J* = 8 Hz, *m-H*), 6.89 (t, *J* = 7 Hz, *p-H*), 6.32 (d, *J* = 3 Hz, *β′-H*; shows evidence for weak ^{195}Pt coupling), 1.53 and 0.92 (m, P–C_2H_5), −6.80 (t, $^1J_{Pt-H}$ = 663 Hz, $^2J_{P-H}$ = 18 Hz, Pt–*H*). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 20.4 (s, $^1J_{Pt-P}$ = 2690 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 196.8 (t, $^1J_{Pt-C}$ = 819 Hz, $^2J_{P-C}$ = 10 Hz, Pt–*C*(α')), 157.7 (s, $^4J_{Pt-C}$ = 5 Hz, *C*=O), 152.0 (s, aromatic), 146.5 (s, $^3J_{Pt-C}$ = 39 Hz, *C*(α)), 129.3, 125.0, 122.5 (s, C_6H_5), 121.7 (s, $^3J_{Pt-C}$ = 29 Hz, *C*(β)), 120.0 (s, $^2J_{Pt-C}$ = 91 Hz, *C*(β')), 8.7 and 19.8 (m, P–C_2H_5). IR (CCl_4, cm^{-1}): 1991 (Pt–H), 1719 (C=O). Anal. Calcd for $C_{23}H_{38}O_3P_2Pt$: C, 44.58; H, 6.19. Found: C, 44.48; H, 6.07.

Reaction between I and Acetylene To Yield *trans*-Hydridoacetylidobis(triethylphosphine)platinum(II). Complex I (~20 mg) was dissolved in C_6D_6 (0.5 mL) and acetylene was bubbled through the solution for 30 min. The $^{31}P\{^1H\}$ and ^{1}H NMR spectra showed little reaction after 60 min; however, after 10 h, the reaction had gone to completion to yield exclusively *trans*-Pt(H)(C≡CH)(PEt_3)$_2$. Although the ^{1}H and $^{31}P\{^1H\}$ NMR spectra show quantitative formation of the hydridoacetylido complex, attempts to isolate it led to intractable oils. ^{1}H NMR (C_6D_6): δ 2.60 (s, $^3J_{Pt-H}$ = 39 Hz, C≡C–*H*), 1.78 and 1.01 (m, P–C_2H_5), −7.07 (t, $^1J_{Pt-H}$ = 717 Hz, $^2J_{P-H}$ = 16 Hz, Pt–*H*). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 19.5 (s, $^1J_{Pt-P}$ = 2634 Hz). $^{13}C\{^1H\}$ (C_6D_6): δ 137.8 (t, $^1J_{Pt-C}$ = 1436 Hz, $^2J_{P-C}$ = 19 Hz, Pt–*C*), 96.3 (s, $^2J_{Pt-C}$ = 236 Hz, Pt–C≡*C*), 19.7 and 8.9 (m, P–C_2H_5).

Results

Synthesis and Characterization of *trans*-PtH(NHPh)(PEt$_3$)$_2$ (I). Metathesis of *trans*-$PtH(NO_3)(PEt_3)_2$ with sodium anilide cleanly yields the new compound *trans*-$PtH(NHPh)(PEt_3)_2$ (I). A nitrate leaving group is necessary because the analogous reaction with the hydridochloro complex does not proceed to completion. This suggests that anilide is comparable to chloride as a ligand for platinum(II). The addition of sodium anilide must be done rapidly because we have independently determined that I reacts with *trans*-$PtH(NO_3)(PEt_3)_2$ to yield $PtH(PEt_3)_3^+$ according to eq 1. An unusual aspect of the stability of I is that hydrocarbon

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Table VI. Selected Bond Distances and Angles for I and II

	I (X = NH)	II (X = O)		I (X = NH)	II (X = O)
		Bond Lengths (Å)			
Pt-P(1)	2.273 (2)	2.282 (3)	P(1)-C(14)	1.824 (7)	1.815 (25)
Pt-P(2)	2.273 (2)	2.261 (3)	P(2)-C(20)	1.831 (7)	1.828 (16)
Pt-X	2.125 (5)	2.098 (9)	P(2)-C(22)	1.834 (7)	1.841 (18)
P(1)-C(10)	1.825 (7)	1.815 (15)	P(2)-C(24)	1.831 (7)	1.863 (23)
P(1)-C(12)	1.826 (6)	1.803 (23)	X-C(1)	1.343 (8)	1.339 (12)
		Bond Angles (deg)			
P(1)-Pt-P(2)	170.2 (1)	170.7 (1)	C(14)-P(1)-Pt	115.2 (3)	111.8 (7)
P(1)-Pt-X	94.3 (1)	94.9 (3)	C(20)-P(2)-Pt	113.1 (2)	117.8 (6)
P(2)-Pt-X	95.3 (1)	93.7 (3)	C(22)-P(2)-Pt	115.0 (2)	111.1 (5)
C(1)-X-Pt	125.5 (4)	123.6 (7)	C(24)-P(2)-Pt	114.8 (2)	111.5 (8)
C(10)-P(1)-Pt	112.5 (2)	117.4 (6)	X-C(1)-C(2)	121.0 (6)	117.0 (6)
C(2)-P(1)-Pt	115.4 (2)	116.1 (6)	X-C(1)-C(6)	122.9 (6)	123.0 (6)

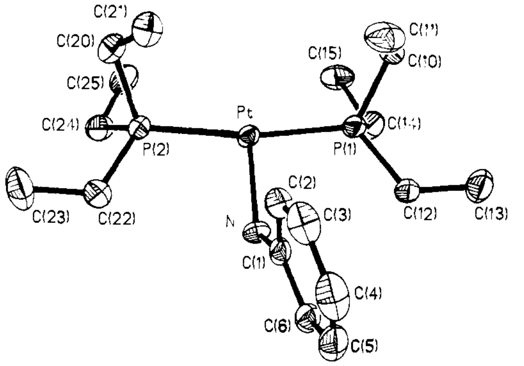

Figure 1. Thermal ellipsoid diagram (50%) and labeling scheme for PtH(NHPh)(PEt$_3$)$_2$ (I).

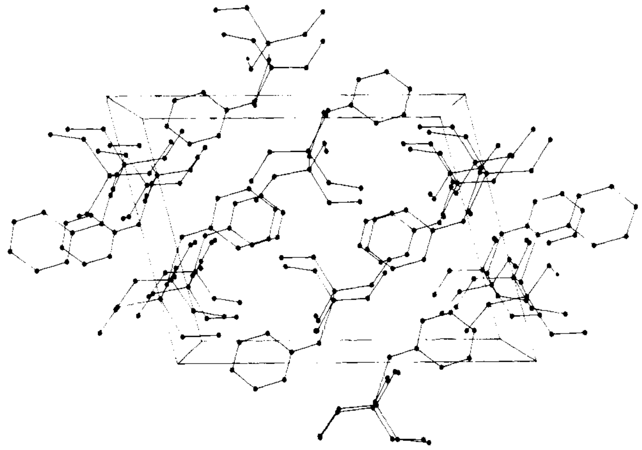

Figure 2. Crystal-packing diagram for I (view along *y* axis).

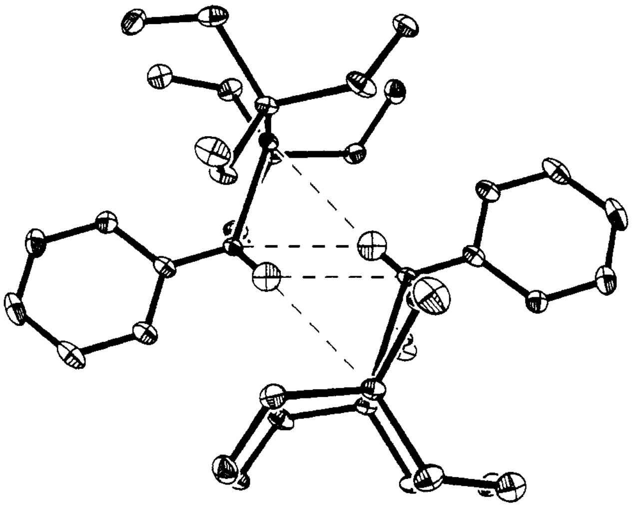

Figure 3. Plot of adjacent molecules in the solid state for I, which show close intermolecular contacts.

solutions of it are stable at room temperature for days, while the solid decomposes within hours.

$$\mathrm{PtH(NHPh)(PEt_3)_2 + 2PtH(NO_3)(PEt_3)_2 \rightarrow 2[PtH(PEt_3)_3]NO_3 + NH_2Ph + Pt(0)} \quad (1)$$

Complex I exhibits ^{31}P{^{1}H} and ^{1}H NMR spectra consistent with a trans square-planar Pt(II) structure. Further spectroscopic characterization of the Pt(NHR) moiety is obtained from an analysis of the ^{15}N NMR spectrum of I prepared from 99% enriched ^{15}N aniline. The proton-decoupled spectrum contains a singlet 2.25 ppm upfield of free aniline flanked by ^{195}Pt satellites ($^1J_{^{15}\mathrm{N-Pt}}$ = 216 Hz). Coupling to cis ^{31}P was not resolved. As the proton-decoupler power was reduced, additional splittings appear from a single directly bound hydrogen ($^1J_{^{15}\mathrm{N-H}}$ = 71 Hz) and the metal hydride ($^2J_{^{15}\mathrm{N-H}}$ = 20 Hz). This assignment is confirmed from the additional ^{15}N splittings that develop in the ^{1}H NMR spectrum of the ^{15}N-enriched complex. The low value of $^1J_{^{15}\mathrm{N-H}}$ suggests sp^3 hybridization and a pyramidal structure about nitrogen;[34] however, this conflicts with results seen in the X-ray structure determination discussed below.

A low-temperature (−100 °C) X-ray structure determination of I revealed the expected trans square-planar geometry about platinum (Figure 1). The bond distances and angles are summarized in Table VI. The Pt-N distance of 2.125 (5) Å resembles that of 2.09 (2) Å reported for *cis*-PtCl(NPh$_2$)(PEt$_3$)$_2$,[35] which confirms the similarity of the trans influence for phosphine and hydride ligands. The hydride ligand, although not refined, could be assigned to the largest peak in the final difference Fourier map with a distance from platinum of 1.63 (2) Å.

The Pt-N-C(1) bond angle of 125.2 (4)° suggests that the hybridization about nitrogen is sp^2 and not sp^3, as suggested by $J_{^{15}\mathrm{N-H}}$ coupling constants. Previous reports of *cis*-PtCl(NPh$_2$)(PEt$_3$)$_2$[35] and Pt(Ph$_2$PCH$_2$CH$_2$PPh$_2$)(CH$_3$)(NCH$_3$Ph)[9] describe the geometry about nitrogen as planar; however, few details of the structure were given. In our structure, the amide proton may be assigned to the largest peak in the final difference Fourier map within bonding distance of nitrogen (N-H = 0.89 (2) Å). If our assignment of this proton is correct, then the geometry about nitrogen is also planar with a least-squares deviation from planarity of 0.06 Å. The bond angles around nitrogen are 126° (Pt-N-C(1)), 115° (Pt-N-H), and 115° (C(1)-N-H). The plane of the benzene ring forms an angle of 14° to the plane of the nitrogen atom. When *p*-nitroaniline hydrogen bonds through both N-*H* atoms, the plane of the benzene ring becomes coplanar with the nitrogen, a situation similar to that we observe.[36,37]

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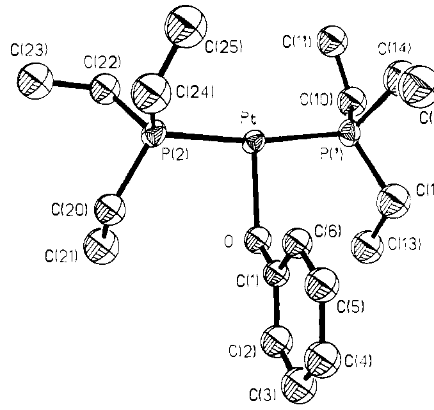

Figure 4. Thermal ellipsoid diagram (30%) and labeling scheme for $PtH(OPh)(PEt_3)_2$ (II).

The packing diagram (Figure 2) shows that I crystallizes as discrete pairs of molecules with each N-H bond directed toward the neighboring platinum atom (Figure 3). The nonbonding distance between the amide proton and the neighboring nitrogen is 2.6 Å, a value that is shorter than the normal hydrogen bonding distance of ~3 Å.[38] Hydrogen bonding of an amine proton bound to tungsten and a neighboring chloride ion has been reported recently.[39] The proton to neighboring platinum distance is 2.96 Å, which may reflect a weak attraction (possibly dipolar) between the amide proton and the electrons in the filled d_{z^2} orbital on platinum. Alternatively, the anilide proton can be viewed as accepting electron density from the Pt-N bond on an adjacent molecule. Although there appears to be unusual hydrogen-platinum bonding between discrete pairs of molecules in the solid state, a lack of network hydrogen bonding throughout the entire crystal is evident by the structure and the melting point of I (68-68.5 °C), which resembles that of other hydridobis(triethylphosphine)platinum complexes.[18]

Synthesis and Characterization of *trans*-$PtH(OPh)(PEt_3)_2$ (II). Complex II can be synthesized from *trans*-$PtH(NO_3)(PEt_3)_2$ by metathesis with an excess of NaOPh in a procedure analogous to the synthesis of I. The product is air stable but thermally sensitive. It can be recrystallized from warm pentane (in which it is very soluble) to yield colorless crystalline blocks suitable for X-ray analysis. The hydridophenoxo complex has NMR spectral parameters consistent with a trans square-planar platinum(II) geometry, and this was confirmed by an X-ray structure determination.

The structure of II (see Figure 4) displays the expected square-planar geometry around platinum with a Pt–O bond length of 2.10 (1) Å. This distance resembles that observed in *trans*-$PtH[OC{=}CHC(Me)(COOEt)OCO](PCy_3)_2$, which has an enolate anion coordinated to platinum through the oxygen while trans to hydride (Pt–O = 2.11 (2) Å).[40] Another similarity between these two structures is the bond angle Pt–O–C(1), which is 124 (1)° for both. Given the tremendous difference in the steric bulk of PCy_3 and PEt_3 its seems unlikely that steric factors determine this angle. Since this angle is 15° larger than expected for idealized sp^3 hybridization and 4° larger than that expected for sp^2 hybridization, this raises the question as to whether rehybridization occurs about oxygen as for nitrogen in the structure of I. The Pt–O–C(1) angle is much smaller than that for early metal complexes where metal-alkoxide π bonding is important.[41-44] For example, $Re(O)(OPh)(MeC{\equiv}CMe)_2$, an early metal phenoxide with a small Re–OPh π-bonding interaction exhibits a Re–O–Ph angle of 124.5 (11)°,[45] similar to the angle we observe and those found in other late metal phenoxides.[1,46]

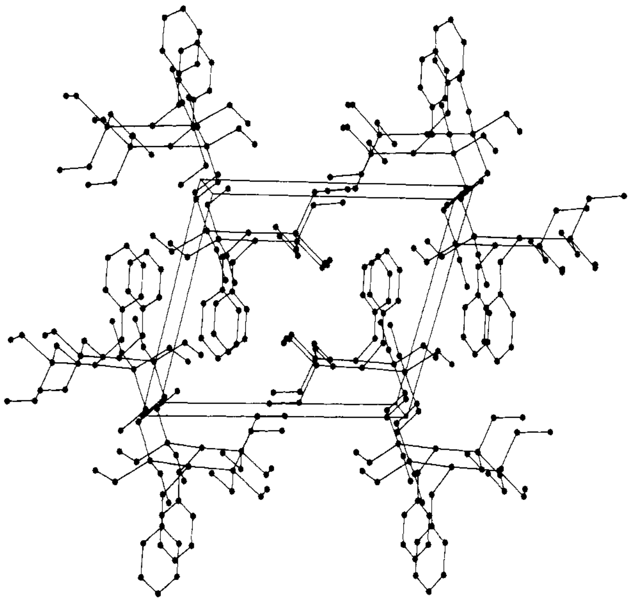

Figure 5. Crystal-packing diagram for II (view along x axis).

The ORTEP drawings for I and II (Figures 1 and 4) and metrical parameters (Table VI) show the similar conformations adopted, in spite of the differing space groups for crystallization. In both cases the metal to heteroatom bond length is equivalent within the standard deviations (2.125 (5) Å for N and 2.098 (9) Å for O) while the Pt–X–C(1) bond angles are also identical within error limits of three esd's (125.5 (4)° for N and 123.6 (7)° for O). Compound I crystallizes in the monoclinic system and packs in units of two molecules with extremely close intermolecular contacts involving Pt–NHPh groups on adjacent molecules ($N\cdots N'$ = 3.42 (1) Å), while II crystallizes in the triclinic system with the molecules alternately stacked with no such close intermolecular contacts ($O\cdots O' > 8$ Å) (see Figures 2 and 5). The lack of protons available for hydrogen-bonding or dipolar interactions in II explains these packing differences.

Associative Reactivity of Coordinated Anilide. Although it is bound to Pt, the anilide ligand displays chemistry consistent with a high electron density at nitrogen. These reactions include the deprotonation of acidic substrates as well as nucleophilic attack at electrophilic substrates. Weak proton donors such as water and phenol both react with I to yield aniline and the complexes *trans*-$PtH(Y)(PEt_3)_2$ [Y = OH, OPh]. The reaction of I in water-saturated C_6D_6 does not go to completion but instead yields a 65:35 mixture of anilide/hydroxide product as determined by ^1H NMR spectroscopy. This supports the recent report that $Pt(CH_3)(NMePh)(dppe)$ undergoes a thermoneutral reaction with water to yield almost equivalent concentrations of amide and hydroxide product.[2,9] The analogous reaction between I and phenol, a stronger acid, goes entirely to phenoxide product.

In addition to simple acid-base chemistry, the bound anilide ligand also behaves as a nucleophile toward methyl iodide to yield $NH(CH_3)Ph$ and $PtHI(PEt_3)_2$. Methyl iodide, in addition to being susceptible to nucleophilic attack, is also capable of oxidative addition at the metal center. If MeI were to oxidatively add then the expected intermediate, $PtH(NHPh)(Me)(I)(PEt_3)_2$, should eliminate methane preferentially[23] to form $PtI(NHPh)(PEt_3)_2$;

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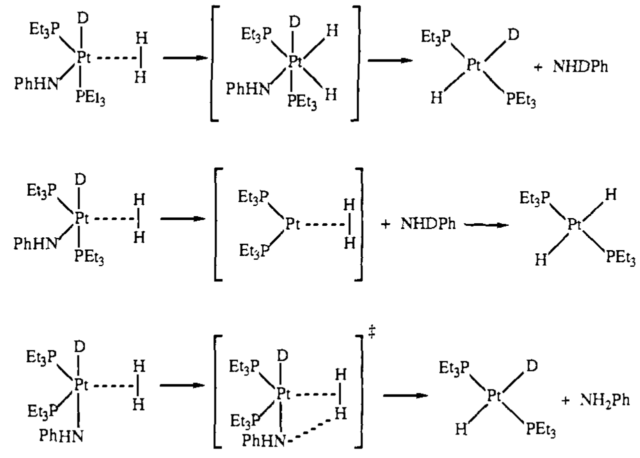
Scheme I



however, this product is not observed.

The reaction between *trans*-PtD(NHPh)(PEt$_3$)$_2$ (I-*d*) and water yields *trans*-PtD(OH)(PEt$_3$)$_2$ (^{2}H NMR analysis), a product which could arise only by protonation of anilide by water followed by platinum trapping the hydroxide anion. The alternative mechanism of N–H reductive elimination followed by O–H oxidative addition is excluded. A similar experiment with methyl iodide substrate showed complete retention of deuterium in the platinum–iodide product. This accords with a mechanism involving the Pt–NHR group or dissociated anilide ion acting directly as a nucleophile.

Associative Reactivity at Platinum. Complex I appears to have little tendency toward spontaneous reductive elimination of the N–H bond at ambient temperature in solution for at least 3 days. However, if CO or PR$_3$ is introduced into the solution an immediate reaction takes place to yield free aniline and the zerovalent platinum addition product of the reagent used, Pt(CO)$_2$(PEt$_3$)$_2$ or Pt(PEt$_3$)$_{3,4}$. Because of the speed with which these reactions occur, taken together with the kinetic stability of the hydridoanilide in solution (see below), these reactions must proceed by associative addition of substrate to induce reductive elimination rather than by trapping of Pt(PEt$_3$)$_2$ generated from spontaneous reductive elimination of aniline. Similar associative ligand-induced reductive elimination has been observed for PtH$_2$L$_2$ (P = PEt$_3$ and PMe$_3$).[47]

We also believe the reaction between azobenzene and I involves associative attack at platinum, since reactions reached completion within 2 h at room temperature and yielded aniline plus the zerovalent platinum complex, Pt(PhN=NPh)(PEt$_3$)$_2$. This complex is unusual in that most reactions between platinum(II) compounds and azobenzene are accompanied by orthometalation of the arene.[48,49] Our product has been characterized by ^{1}H and ^{31}P NMR spectroscopy as well as by crystallographic[50] and elemental analysis.

Another reaction involving coordinate addition is that between I and H$_2$ to initiate loss of aniline and induce formation of *trans*-Pt(H)$_2$(PEt$_3$)$_2$ in benzene solvent. Three possible reaction pathways are outlined in Scheme I. The first reaction mechanism involves oxidative addition of H$_2$ to form a platinum(IV) trihydride intermediate, which eliminates aniline to form the observed products. The second mechanism is similar to the reactions of I with CO or phosphine where hydrogen acts as a ligand to induce reductive elimination of aniline to form "PtL$_2$". It is the PtL$_2$ that then adds hydrogen to form products. The third mechanism requires an η^2-H$_2$ molecule bound to platinum as the key intermediate. This hydrogen molecule is then deprotonated by the anilide ligand (heterolytic cleavage) to yield the expected products.

^{2}H NMR experiments show that the reaction between I-*d* and H$_2$ immediately incorporates ^{2}H into the aniline product, and mechanism 3, anilide deprotonation of η^2-H$_2$, is effectively ruled out. The reaction was also conducted under a H$_2$ purge so free D$_2$ was immediately swept from the reaction to eliminate secondary exchange (see below). To distinguish between the remaining two mechanisms, the reaction between I and D$_2$ was examined. In control experiments *trans*-Pt(D)$_2$(PEt$_3$)$_2$ (produced in this reaction) was found to catalytically enrich aniline with deuterium from D$_2$. Although this complicates the originally intended experiment the observation of catalytic deuteriation of the aniline NH$_2$ group suggests mechanism 1 operates. The microscopic reverse of 1 would yield deuterium incorporation into aniline, whereas 2 would not.

Because reductive elimination of H$_2$ from PtH$_2$(PEt$_3$)$_2$ is favored in the absence of a hydrogen atmosphere (eq 2a)[25,51] and hydrogenolysis of the hydridoanilide complex (eq 2b) is favorable, *trans*-PtH(NHPh)(PEt$_3$)$_2$ must be less thermodynamically stable toward reductive elimination than the dihydride species (eq 2c).

$$\mathrm{PtH_2(PEt_3)_2} \overset{K\sim 1}{\rightleftharpoons} \mathrm{Pt(PEt_3)_2} + \mathrm{H_2} \qquad (2a)$$

$$\mathrm{PtH(NHPh)(PEt_3)_2} + \mathrm{H_2} \overset{K'\gg 1}{\rightleftharpoons} \mathrm{PtH_2(PEt_3)_2} + \mathrm{H_2NPh} \qquad (2b)$$

$$\mathrm{PtH(NHPh)(PEt_3)_2} + \mathrm{H_2} \overset{KK'\gg 1}{\rightleftharpoons} \mathrm{PtH_2(PEt_3)_2} + \mathrm{H_2NPh} \qquad (2c)$$

The equilibrium constant for eq 2b must lie far to the right because addition of a 50-fold excess of aniline to a benzene solution of PtH$_2$(PEt$_3$)$_2$ led to no detectable reaction. This is understandable because Pt–N bonds are weaker than Pt–H bonds toward homolytic cleavage.[2]

The kinetic inertness of the hydridoamido complexes prepared by metathesis may arise from a high barrier to N–H reductive elimination caused by the instability of the cis configuration necessary for reductive elimination. In platinum chemistry, strong trans directors (e.g. H, PR$_3$, and CH$_3$) prefer weak trans influence ligands opposite them (e.g. O and N donors),[52] and this may raise the energetic barrier to isomerization. The facile reductive elimination observed on addition of PR$_3$ or CO ligands can be attributed to associative attack at Pt to form a 5-coordinate 18-electron intermediate, which allows the H and NHPh groups to attain the cis geometry necessary for reductive elimination.

Trapping of N–H Reductive Elimination Products. Addition of olefins or other unsaturated substrates to I produces the complexes Pt(unsaturated)(PEt$_3$)$_2$ (Table IV). Most reactions require about 72 h at room temperature or 4 h at 100 °C in toluene to reach completion. In an attempt to determine the energetics of N–H reductive elimination, a toluene solution of I with *trans*-stilbene was heated to 100 °C, and the slow disappearance of Pt–H was monitored by IR spectroscopy. Zeroth-order kinetics was observed, with several experiments showing a short induction period. As discussed earlier, addition of phosphine to a solution of I results in immediate loss of aniline. Therefore, the observed induction period could result from production of a trace amount of free phosphine. In any event, spontaneous reductive elimination of the N–H bond must be extremely slow.

Since the crystal structure of 1 shows that the amide ligand nitrogen atoms are directed toward each other (N···N = 3.42 (1) Å), we were interested in determining whether the facile decomposition observed in the solid state led to N–N coupled products. Attempts to effect thermal decomposition of I in the solid state were complicated by melting of I at 68 °C. Rapid heating of 1 to 250 °C caused a fast color change from yellow to dark brown, with a liquid fraction distilling out of a solid residue. Analysis of the fractions by ^{31}P{^{1}H} and ^{1}H NMR spectroscopies reveals that the liquid fraction contains PEt$_3$ (the only ^{31}P NMR active

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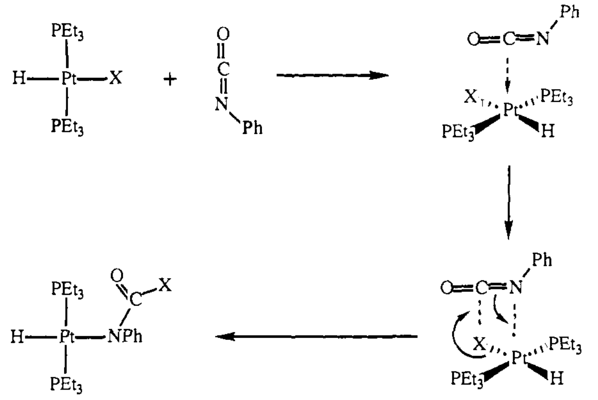
Scheme II



species present) and aniline. The solid residue contains PtH(PEt$_3$)$_3^+$ as the only ^{31}P NMR active species.[19] Reductive elimination therefore appears to be the major process involved in the thermal degradation of I.

Pt-N Insertion Reactions and X-ray Structure of the Acrylonitrile Insertion Product. Complex I reacts with a variety of electrophilic substrates to yield products that result from insertion into the metal-nitrogen bond rather than into the Pt-H bond. Phenyl isocyanate adds cleanly to yield the diphenylurea derivative, *trans*-PtH(PhNC(O)NHPh)(PEt$_3$)$_2$. Both CO$_2$ and COS insert to yield carbamate and thiocarbamate complexes; however, the carbamate complex reversibly inserts CO$_2$ and decomposes in the absence of a CO$_2$ atmosphere. The thiocarbamate product is air stable and has been identified by spectroscopic (^{1}H and ^{31}P NMR, IR) and elemental analyses. Because of the lack of an IR absorption clearly attributable to either a C=O or C=S stretch, the bonding mode of the thiocarbamate ligand is uncertain. The reaction with CS$_2$ yields a complex mixture of products from competing insertion processes.[31-33] Since all of these substrates are electrophiles, the question arose as to whether free NHPh$^-$, generated by dissociation from Pt, might be involved or whether the Pt-NHPh group functioned as a nucleophile.

A sample of I containing ^{15}N-labeled anilide was prepared, and the reaction with PhNCO in C$_6$D$_6$ solvent was monitored using ^{1}H NMR spectroscopy. The spectrum immediately recorded showed retention of the anilide proton on the ^{15}N nucleus from the coupling observed on the N-H resonance (δ 8.38, $^1J_{^{15}\mathrm{N-H}}$ = 85 Hz, $^2J_{\mathrm{Pt-H}}$ = 10 Hz). The position of the proton is not static; within 20 h at room temperature (22 °C) it reaches a statistical distribution between ^{15}N and ^{14}N (the ^{14}N-H resonance grows in at the center of the ^{15}N-H doublet) sites with an integrated intensity of $\sim$1:1. Because the initial product is a single isotopic regioisomer [PtNPhC(O)^{15}NHPh], this requires the reaction to proceed by insertion into the metal-nitrogen bond. If free anilide were to attack PhNCO in solution to generate free PhNC(O)^{15}NHPh$^-$, one would expect fast proton exchange between the nitrogen atoms before recombination with platinum. The "insertion" step probably involves the PtNHR group acting as a nucleophile as depicted in Scheme II.

Another test for free anilide ion, derived by dissociation from I, was performed by mixing a 2-fold excess of *trans*-PtD(^{15}NHPh)(PEt$_3$)$_2$ with *trans*-PtH(NHPh)(PEt$_3$)$_2$ and looking for crossover of ^{15}NHPh to the hydrido complex. The exchange reaction was performed in benzene-d_6 and monitored by ^{1}H NMR spectroscopy, which allowed observation of the ^{15}N-coupled hydride product overlapped with I. At 22 °C exchange of amide ligands between complexes occurs with a half-life of about 48 h. Thus free anilide ion probably does not contribute to the observed nucleophilic reactivity of I, especially for those reactions that occur rapidly. The inefficient exchange process itself may result from a bimolecular process, which transfers the anilide ligand.

Since the anilide ligand underwent insertion with electrophilic substrates, the reaction with olefins activated toward nucleophilic attack (e.g. Michael addition substrates) was explored. All substrates with α-keto protons were too acidic and susceptible to either deprotonation by anilide or C-H oxidative addition at the metal. Acrylonitrile and methyl acrylate insert cleanly into the metal-nitrogen bond to yield the hydridoalkyl products shown in Chart I. These are the expected regioisomers resulting from nucleophilic addition to the terminal carbon of the unsaturated system. In both cases the carbon bound to platinum is chiral, resulting in diastereotopic protons β to Pt. The ^{1}H NMR resonances of these diastereotopic protons are complex multiplets showing resolvable couplings to ^{195}Pt as well as unresolved couplings to each other, the adjacent proton, and the two mutually cis ^{31}P nuclei. The platinum hydride resonance occurs in the region typical for hydrides trans to alkyl groups (δ -9.54 and -10.10, respectively). The ^{31}P{^{1}H} NMR spectra show a singlet for each complex (δ 11.7 and 18.4) as expected for a trans geometry with $^1J_{\mathrm{Pt-P}}$ coupling constants consistent with a Pt(II) hydridoalkyl complex (2740 and 2776 Hz). The acrylonitrile insertion product undergoes C-H reductive elimination when heated to 70 °C overnight. This yields the organic product 3-anilinopropionitrile, which was identified by comparison of its ^{1}H NMR spectrum with that of an authentic sample purchased from Pfaltz and Bauer.

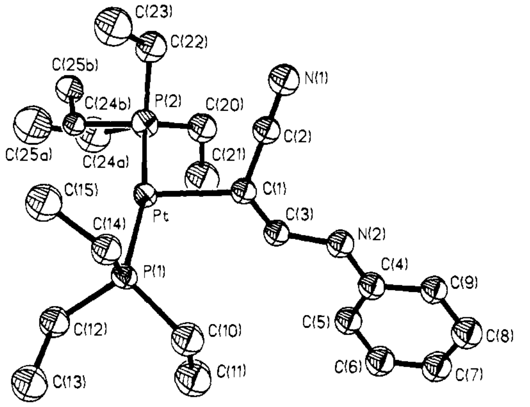
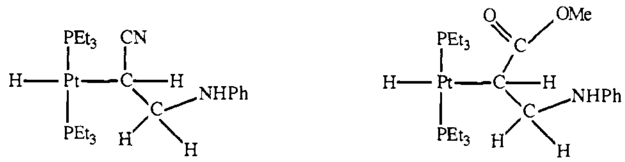


Figure 6. Thermal ellipsoid diagram (30%) and labeling scheme for PtH[CH(CN)(CH$_2$NHPh)](PEt$_3$)$_2$ (II). The two orientations for the C(24)-C(25) ethyl group results from disorder.

Chart I



The product of acrylonitrile insertion was definitively characterized by a single-crystal X-ray structure determination. It has the expected trans square-planar geometry shown in Figure 6. Solution of the structure revealed the site of addition to be the terminal carbon of the olefin as expected for a Michael-type addition, with selected bond lengths and angles provided in Table VII. The hydride ligand was not refined but could be assigned to the only significant peak (>1 e/Å^3) in the final difference Fourier map near Pt (Pt-H $\sim$ 1.01 Å) in the expected position. The alkyl group bound to platinum [(Pt-C(1); 2.198 (3) Å] exhibits a normal tetrahedral geometry about C(1) [Pt-C(1)-C(3), 110.41 (8)°]. The bond distances within the alkyl ligand closely match those previously reported for *trans*-PtH(CH$_2$CN)(PPh$_3$)$_2$.[53,54] The conformation adopted by the 3-anilinopropionitrile ligand places platinum anti to the NHPh group, and the CN group lies in a gauche position when viewed down the C(1)-C(3) bond [N(2)-C(3)-C(1)-C(2) = 66.1°; Pt-C(1)-C(3)-N(2) = -166.6°].

The insertion product obtained with methyl acrylate exhibits an unusually weak carbonyl stretching frequency in the IR

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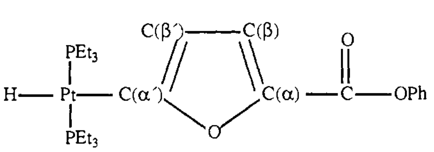
(53) Ros, R.; Michelin, R. A.; Belluco, U.; Zanotti, G.; Del Prã, A.; Bombieri, G. *Inorg. Chim. Acta* **1978**, *29* L187.

(54) Del Prã, A.; Forsellini, E.; Bombieri, G.; Michelin, R. A.; Ros, R. *J. Chem. Soc., Dalton Trans.* **1979**, 1862.

Table VII. Selected Bond Distances and Angles for III

	Bond Lengths (Å)		
Pt-P(1)	2.279 (4)	Pt-P(2)	2.278 (4)
Pt-C(1)	2.198 (13)	C(1)-C(3)	1.500 (14)
C(1)-C(2)	1.407 (18)	C(3)-N(2)	1.462 (17)
C(2)-N(1)	1.160 (19)	C(4)-C(5)	1.344 (20)
N(2)-C(4)	1.360 (14)	C(5)-C(6)	1.394 (18)
C(4)-C(9)	1.402 (20)	C(7)-C(8)	1.380 (24)
C(6)-C(7)	1.347 (25)	C(8)-C(9)	1.423 (17)
	Bond Angles (deg)		
P(1)-Pt-P(2)	168.8 (1)	P(1)-Pt-C(1)	93.5 (3)
P(2)-Pt-C(1)	97.7 (4)	Pt-P(1)-C(10)	118.9 (5)
Pt-P(1)-C(12)	113.6 (5)	C(10)-P(1)-C(12)	104.0 (7)
Pt-P(1)-C(14)	112.4 (4)	C(10)-P(1)-C(14)	101.8 (6)
C(12)-P(1)-C(14)	104.6 (6)	Pt-P(2)-C(20)	115.9 (5)
Pt-P(2)-C(22)	115.9 (6)	Pt-P(2)-C(24B)	108.4 (10)
Pt-P(2)-C(24A)	115.8 (10)	Pt-C(1)-C(2)	112.4 (8)
Pt-C(1)-C(3)	110.4 (8)	C(2)-C(1)-C(3)	113.6 (11)
C(1)-C(2)-N(1)	178.5 (14)	C(1)-C(3)-N(2)	113.7 (11)
C(3)-N(2)-C(4)	121.4 (11)	N(2)-C(4)-C(5)	125.5 (14)
N(2)-C(4)-C(9)	115.7 (12)	C(5)-C(4)-C(9)	118.8 (11)
C(4)-C(5)-C(6)	123.0 (15)	C(5)-C(6)-C(7)	118.7 (16)
C(6)-C(7)-C(8)	121.4 (14)	C(7)-C(8)-C(9)	119.2 (15)
C(4)-C(9)-C(8)	118.8 (13)		

Chart II



atom	δ	J_{Pt-C} (Hz)
C(α′)	196.8	819
C(β′)	120.0	91
C(α)	146.5	39
C(β)	121.7	29
C = O	157.7	5

spectrum. The platinum–hydride stretch at 2027 cm^{-1} is almost the same intensity as the carbonyl stretch at 1663 cm^{-1}! This presented the possibility that anilide may have attacked the carbonyl carbon instead of the terminal olefinic carbon. To definitively determine the site of addition, we recorded ^{13}C NMR spectra of the isolated product. The ^{13}C{^{1}H} spectrum combined with the off-resonance proton-decoupled ^{13}C spectrum definitively characterize the addition product as depicted in Chart I (see the Experimental Section for shifts and coupling constants). It is interesting to note that the $^2J_{Pt-C}$ coupling constant for the carbonyl carbon (39 Hz) is more than double that of the other $^2J_{Pt-C}$ coupling (17 Hz). This may be evidence for a weak carbonyl–platinum interaction in the complex, which could also explain the anomalous IR intensities.

If the methyl acrylate insertion product is heated to 70 °C in C_6D_6 for 12 h, only free methyl acrylate could be observed in the ^{1}H NMR spectrum. The appearance of starting olefin could arise from deinsertion of the alkyl to reform I or from C–H reductive elimination and base-catalyzed (e.g. by PtL$_2$) elimination of aniline from the organic product methyl 3-anilinopropionate. This latter reaction sequence is supported by the use of I-*d*, which leads to predominant incorporation of the deuterium label into the 2 position of methyl acrylate. Formation of the deuteriated olefin must arise from elimination of aniline from the expected C–D reductive elimination product, NHPhCH$_2$CHDC(O)OMe. A deuterium isotope effect on this step would result in most of the label being retained in the olefin product, as observed.

Reductive Elimination Coupled with C–H Oxidative Addition. If phenyl 2-furoate is added to a benzene solution of I and the reaction monitored by ^{1}H NMR spectroscopy, two new hydride species are observed. One is a triplet at δ –6.85, while the second is a doublet of doublets centered at δ –4.04. They are assignable to the cis and trans isomers of the hydridoalkyl complex shown in Chart II. At 70 °C the more thermodynamically stable trans isomer[55] (triplet) becomes the only hydride species produced. The trans product has been isolated as a pure compound by column chromatography (Florisil) of the reaction mixture. The ^{13}C NMR spectrum reveals the site of addition to be the α′-carbon. This was assigned from the progression of decreasing Pt–C coupling constants as one proceeds around the furan ring (see Chart II). This hydridoalkyl complex shows remarkable stability. A toluene solution of it can be heated to 80 °C for over 1 week with little decomposition. It appears that the hydridoalkyl complex is more thermodynamically stable than the corresponding π-olefin complex. In an independent check of this, phenyl 2-furoate was added to a benzene-d_6 solution of Pt(C_2H_4)(PEt$_3$)$_2$ and the reaction monitored by ^{1}H NMR spectroscopy. This experiment showed production of the *cis*- and *trans*-alkyl hydride complexes and no evidence for formation of a π-olefin complex.

This reaction is indeed a C–H activation by platinum and not a simple deprotonation of phenyl 2-furoate by anilide ion followed by carbanion trapping by platinum. For example, I-*d* reacts with phenyl 2-furoate to yield deuterium in the aniline product exclusively; no deuterioalkyl complex of platinum was observed. Furan also reacts with I to yield a similar hydridoalkyl species observed by ^{1}H NMR spectroscopy, and the same species can be generated by reacting Pt(C_2H_4)(PEt$_3$)$_2$ with furan. Activation of a C–H bond after or concomitant with reductive elimination of aniline is also indicated since the reaction between I-*d* and furan yields deuterated aniline and the hydridoalkyl complex. ^{1}H NMR evidence suggests that 2-furonitrile and furfural undergo analogous C–H activation processes. Therefore, it appears that PtL$_2$ is basic enough to oxidatively add C–H bonds at least up to the pK_a of 35.9 measured for furan.[56]

The reaction between I and acetylene yields *trans*-PtH(C≡CH)(PEt$_3$)$_2$. From a pK_a analysis,[57] one might expect this reaction to proceed by deprotonation of acetylene by anilide while platinum traps the carbanion formed. To test for C–H activation, I-*d* was reacted with acetylene under the same conditions as for I, and analysis of the ^{2}H NMR spectrum showed that the deuterium resided in aniline with no detectable amount of deuterioacetylide product formed. This result is consistent with a C–H activation pathway involving Pt(PEt$_3$)$_2$; however, if Pt(C_2H_4)(PEt$_3$)$_2$ is treated with acetylene, only the π-alkyne complex [Pt(C_2H_2)(PEt$_3$)$_2$] forms and no C–H activation is observed. Thus, the nature of the leaving group on platinum apparently influences the reaction path. A reaction where the C–H activated product is an intermediate for the π complex was previously observed with Ir(I) where ethylene reacted to yield a hydridovinyl complex, which was later heated to yield the π adduct.[58]

Reactivity of *trans*-PtH(OPh)(PEt$_3$)$_2$ (II). The chemistry of II resembles that of I in many respects; however, the increased tendency of the phenoxide ligand toward heterolytic dissociation leads to additional chemistry derived from the transient formation of PtH(PEt$_3$)$_2^+$. The reaction with hydrogen yields *trans*-Pt(H)$_2$(PEt$_3$)$_2$ (the major product) and [(PEt$_3$)$_2$Pt(μ-H)$_2$PtH(PEt$_3$)$_2$]OPh, a product known to form from reaction between the dihydride and hydridoalkoxide complexes.[26] The reaction with CO is similar to I since it yields *trans*-Pt(CO)$_2$(PEt$_3$)$_2$ as the major product; however a small amount of PtH(PEt$_3$)$_3^+$ also forms. Phenyl isocyanate inserts cleanly into the platinum–oxygen bond of II to yield a hydrido(*N*-phenylcarbamato) complex of platinum(II). The insertion of carbon dioxide is readily reversible and less than 10% of the insertion product was observed at 1 atm of CO$_2$.

An interesting contrast can be drawn between the reactivity of I and II toward acrylonitrile. In both cases the organic product of Michael addition is obtained; however, in the case of I an

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[55] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 5.

[56] The pK_a for furan is reported as 35.6 in THF. See: Fraser, R. R.; Mansour, T. S.; Savard, S. *Can. J. Chem.* **1985**, *63*, 3505.

[57] The pK_a for NH$_2$Ph is reported as 30.7 in DMSO (Bordwell, F. G. *Pure and Appl. Chem.* **1977**, *49*, 963), acetylene is 25 (Cram, D. J. *Fundamentals of Carbanion Chemistry*; Academic Press: New York, 1965; p 19), phenol is 9.97, and water is 15.74 (Murto, J. In *The Chemistry of the Hydroxyl Group*; Patai, S., Ed.; Interscience: New York, 1971; Part 2, p 1106.

[58] (a) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 5732. (b) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 4581. (c) Wenzel, T. T.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 4857.

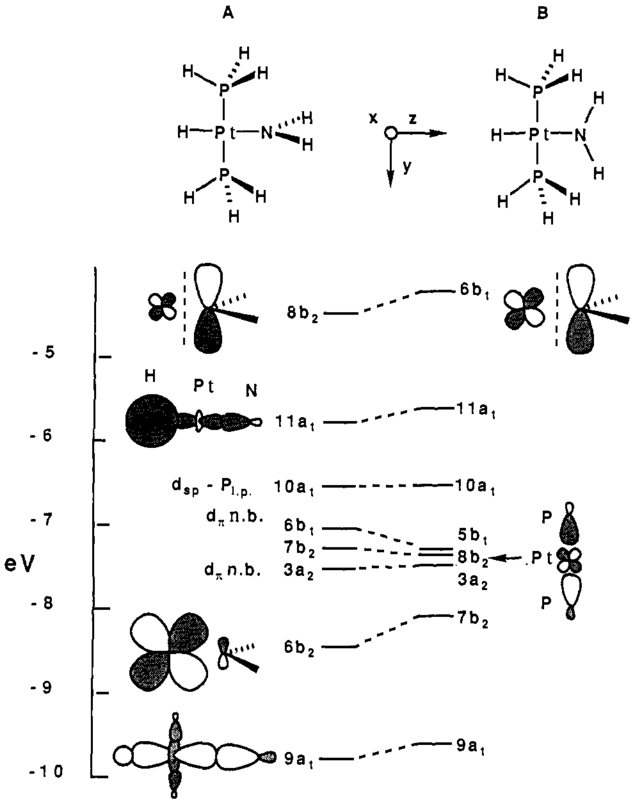

Figure 7. Results of SCF-Xα-DV calculations for C_{2v} $PtH(NH_2)(PH_3)_2$ for two orientations of the planar NH_2 group shown.

intermediate hydridoalkyl complex of exceptional stability forms, which requires heating at 70 °C for 12 h to induce reductive elimination of the organic product. The reaction of II with acrylonitrile reaches completion within 30 min at room temperature and yields the organic product ($PhOCH_2CH_2CN$) and the platinum(0) olefin complex. The intermediate hydridoalkyl complex of the ether is unstable, as would normally be expected for hydridoalkyl complexes of platinum(II) with small tertiary phosphines, and is not observed.

The question of why the amide hydridoalkyl addition products are stable while the alkoxide ones are not may result from nitrogen donation to the metal. For a C-bound aryl ether intermediate, a similar donation from oxygen should be much weaker (i.e. amines are good ligands for Pt(II), while ethers are not). For example, the phenyl isocyanate insertion product shows platinum coupling ($^4J_{Pt-H}$ = 10 Hz) to the distant N-H proton; a coupling that would be negligible without nitrogen coordination to the metal (compare this to the $^2J_{Pt-H}$ coupling of 22 Hz for I). This same 10-Hz coupling to the amine proton is seen in both the methyl acrylate and acrylonitrile insertion products; however, in those cases there is ambiguity as to whether coupling from the neighboring CH_2 group is causing the observed splitting. The presence of a 10-Hz coupling in all three complexes could imply that the amine group interacts with platinum in each case. This interaction could hinder isomerization to the cis structure necessary for reductive elimination. A similar effect occurs in palladium chemistry, where nucleophilic attack of amine on coordinated olefin yields an intermediate 4-coordinate alkyl complex where the pendant amine (on the alkyl) swings back and coordinates to the metal.[59]

Theoretical Studies. Two C_{2v} geometries were explored in SCF-DV-Xα calculations of *trans*-$PtH(NH_2)(PH_3)_2$. One contained the planar NH_2 group perpendicular to the square plane about Pt (i.e. similar to the experimental geometry of NHPh and NPh_2 complexes), and in the other the NH_2 group was coplanar with the square plane about Pt. These will be designated isomer A and B, respectively. Results of these calculations are summarized in Figure 7, which shows the energy level scheme for the uppermost occupied orbitals. These orbitals can be attributed to the four d orbitals expected for square-planar Pt(II), which are $10a_1$, $3a_2$, $6b_2$, and $9a_1$, for isomer A. Three other high-lying orbitals $7b_2$, $11a_1$, and $8b_2$ for A can be attributed to a phosphorus lone-pair orbital, $7b_2$, the P-H σ orbital, $11a_1$, and the π lone pair on the NH_2^- group, $8b_2$.

The $8b_2$ orbital is 86% N pπ and 9% Pt dπ with antibonding character. The bonding counterpart is $6b_2$; however, the extent of mixing is small. No significant mixing of Pt 6p orbital character (a potential π acceptor orbital on Pt) was found, and the Pt-N π bond order is zero. In the all-planar isomer B, the $6b_1$ orbital correlates with $8b_2$ in A. This orbital becomes destabilized and acquires more antibonding character (83% N pπ and 14% Pt dπ) because the corresponding bonding counterpart ($5b_1$) lies closer in energy. This is evident in the energy level scheme where $6b_1$ rises in energy relative to $8b_2$ and $5b_1$ decreases in B relative to the corresponding orbital, $6b_1$, in A. Consistent with the observed nucleophilic reactivity of *trans*-$PtH(NHPh)(PEt_3)_2$, the nitrogen lone-pair orbital is predicted to be the highest occupied orbital in the complex. The calculations further suggest an enhanced reactivity for the planar isomer B from both electronic effects (raising in energy of $6b_1$) and the greater accessibility of the lone-pair orbital to electrophiles. Thus, although isomer A may be more stable because of electronic and steric factors, B may be the reactive species.

The second highest occupied orbital, $11a_1$, is dominated by σ bonding between H^- (52%), a p_z–d_{z^2} hybrid orbital on platinum (14%), and the σ lone-pair orbital on NH_2^- (24%). It changes little in character in isomer B. Below this $10a_1$ is predominantly a dsp hybrid 77% localized on Pt and changes insignificantly between A and B. The $6b_1$ orbital is nonbonding (95% Pt d) in A but correlates to $5b_1$ in B to mix in 9% N pπ character. As noted above it is the bonding counterpart to $6b_1$ in isomer B. The $7b_2$ ($8b_2$ in B) orbital is the antisymmetric combination of phosphorus lone-pair orbitals, which cannot overlap well with the symmetric d orbitals. The $3a_2$ dπ orbital interacts only slightly with π-acceptor orbitals on the PH_3 ligand and can be regarded as nonbonding in both A and B. In A the $6b_2$ orbital (67% d, 5% N π, 28% PH_3) exhibits more covalent character than $7b_2$ in B (75% d, 17% PH_3), which explains its greater stability; however, the extent of mixing with the NH_2^- π orbital is about half that as occurred in $5b_1$ for B. Finally the Pt-N σ-bonding orbital, with some Pt-H and Pt-P σ character admixed, is assigned to the energetically most stable orbital, $9a_1$ shown (35% d, 38% N σ lone pair, 13% P lone pair, 5% H).

Conclusion

The chemistry of *trans*-$PtH(NHPh)(PEt_3)_2$ combines the possibilities of insertion into the Pt-N or Pt-H bonds, reductive elimination of aniline combined with the chemistry of $Pt(PEt_3)_2$, oxidative addition directly to I to form Pt(IV), dissociation of the anilido anion trans to hydride, and electrophilic attack at the coordinated anilido group. Considering potential reactivities it is helpful to recall a recent report[2] that determined homolytic bond strengths for Pt-X bonds decrease in the order C $\sim$ H > O > N; these authors also noted that heterolytic cleavage of the Pt-X bond should be easier for oxygen than nitrogen according to the pK_a's of the conjugate acids. While the homolytic bond strengths may place oxygen higher than nitrogen, there is no doubt that anilide binds more tightly to Pt(II) than phenoxide in the context of metathesis reactions. In comparing some equilibria, one can rationalize the reactivity either from a bond heterolysis or homolysis viewpoint. Thus, addition of 1 equiv of phenol to I quantitatively produces II, in agreement with the overriding 10^{20} pK_a difference between phenol and aniline.[57] Alternatively, the values of 86.5 ± 2 kcal/mol for the O-H bond enthalpy in phenol and 88.0 ± 2 kcal/mol for the N-H bond enthalpy in aniline,[60] along

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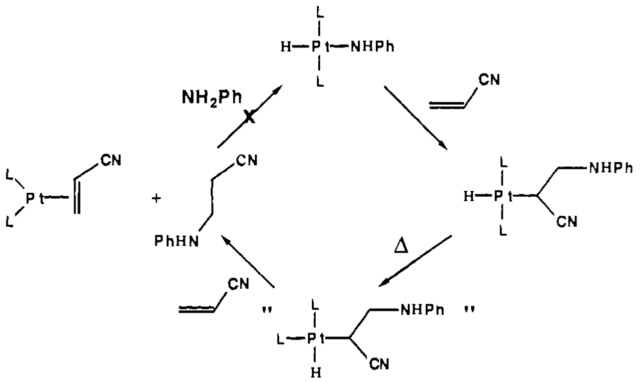
(59) Hegedus, L. S.; Åkermark, B.; Zetterberg, K.; Olsson, L. F. *J. Am. Chem. Soc.* **1984**, *106*, 7122.

(60) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

Scheme III



with a stronger Pt–O vs Pt–N bond (in a homolytic sense) would lead to the same conclusion. The incomplete reaction between I and H_2O follows from its lower acidity relative to phenol,[48] as well as from the greater O–H bond strength (119 ± 1 kcal/mol) of water.[52]

When comparing differences in the reactivity of I and II toward insertion of unsaturated substrates, one expects the weak base phenoxide to be a much better leaving group than anilide, and complex II generally shows increased reactivity compared to I. Isotopic labeling experiments for I suggest that free anilide was not involved as an intermediate, but the Pt-NHPh group acted as the nucleophile. The theoretical calculations for I predict that repulsion between filled $d\pi$ orbitals on Pt and the $p\pi$ lone-pair orbital on the amide ligand destabilizes the amide lone-pair orbital. This will enhance the nucleophilicity at nitrogen in the Pt-NHR moiety. A similar effect should operate in analogous alkoxide or aryloxide complexes. The nucleophilic character of a phenoxide ligand bound to a late-transition metal has been confirmed by recent reports of hydrogen bonding between the oxygen atom of metal-bound phenoxide and free phenol.[61] When the insertion of acrylonitrile is used as an example, the rate-determining step is probably intramolecular transfer of anion (phenoxide or anilide) to the coordinated olefin. For phenoxide, the weak heterolytic bond to platinum would facilitate transfer, while the reverse would be true for the more tightly bond anilide. This is opposite to the reactivity expected for the addition of the free nucleophile to acrylonitrile since, in the absence of platinum, the weaker base (phenoxide) should undergo nucleophilic attack on acrylonitrile slower than the more basic anilide ion. This reversal of reactivity implies direct metal-assisted transfer of the nucleophile to olefin through coordination of both substrates to the metal center as depicted in Scheme II. If one only uses homolytic bond strengths as a guide,[2] the stronger Pt–O bond might be expected (incorrectly) to be less reactive than the Pt–N bond toward insertion. Quantitative measurements for the rates of insertion as a function of substrate polarity are needed to determine the homolytic vs heterolytic character of insertion reactions with metal alkoxides and amides.

The insertion, reductive elimination sequence observed for acrylonitrile (Scheme III) falls one step short of a catalytic cycle for amination of an olefin. Qualitative observations of the equilibria for hydrogenation of anilide and the stability of the dihydride product suggest a thermodynamic limitation on the N–H oxidative addition step. This identifies a key problem to be solved in future research if a catalytic cycle based on the chemistry of Scheme III is to be realized.

One surprising aspect of the reactivity of I and II is the lack of chemistry from the Pt–H moiety. Its primary role appears to be a directing group to facilitate insertion–electrophilic attack at the trans position. A secondary role for hydride may be the electronic stabilization of a trans geometry, which slows the thermodynamically favorable reductive elimination of aniline in the case of I. Addition of ligands, which are not susceptible to insertion (e.g. unsubstituted olefins, CO, or PR_3 ligands), promotes N–H reductive elimination in I. Several substituted furans induced reductive elimination of aniline from I concomitant with C–H oxidative addition. This conflicts with what one might expect based on pK_a values for the N–H (30.7)[57] vs C–H (35.6)[56] groups. Here the stronger homolytic Pt–C vs Pt–N bond[2] helps explain the trend.

The Pt–X bonds of 2.125 (5) Å, 2.098 (9) Å, and 2.198 (13) Å in I (X = NHPh), II (X = OPh), and III [X = CH(CN)(CH$_2$NHPh)], respectively, parallel the trend in covalent radii C > N > O. This accounts for a 0.02–0.03 Å difference between each member of the series[62] but does not explain the larger difference (~0.08 Å) between the Pt–C and Pt–N bonds. Since the Pt–O and Pt–N π interactions can only be repulsive, the extra shortening in these latter compounds probably results from the difference in hybridization (sp^3 for C in III vs sp^2 for N and O in I and II). Dewar has proposed[63] the equation $r_{C-C} = 1.692-0.0051$ (mean % s character) Å to correlate carbon–carbon single-bond lengths with hybridization. Thus, a change from sp^3 to sp^2 hybridization should result in an additional shortening of ~0.04 Å and the effect may be greater in metal complexes.

Acknowledgment. This material was based on work supported by the National Science Foundation (Grant CHE-85-04088). We thank Johnson Matthey for a generous loan of platinum metal and M. D. Fryzuk and C. D. Montgomery for a preprint of ref 1a. We also thank Glenn A. Miller for invaluable assistance with the crystal structures.

Supplementary Material Available: Tables of anisotropic temperature factors, bond distances and angles, and hydrogen coordinates (15 pages); listings of structure factors (41 pages). Ordering information is given on any current masthead page.

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