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Structural Determination and Acidolysis Reactions of *Ortho*-Metalated Rhenium Tetrahydride Compounds Prepared from Reactions of $ReH_7(PPh_3)_2$ with Benzylic Imines

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Reactions between $ReH_7(PPh_3)_2$ and a series of benzylic imines, PhCHNR (R = Me, Ph, or Bn), produce the compounds $ReH_4[\eta^2\text{-}(1,2\text{-}C_6H_4)CHNR](PPh_3)_2$. One such compound, $ReH_4[\eta^2\text{-}(1,2\text{-}C_6H_4)CHNPh](PPh_3)_2$, was characterized by X-ray diffraction analysis. The compound $ReH_4[\eta^2\text{-}(1,2\text{-}C_6H_4)CHNPh](PPh_3)_2$ crystallizes in the $P\bar{1}$ space group with the following unit cell dimensions: $a = 12.422(3)$ Å, $b = 12.696(3)$ Å, $c = 13.604(5)$ Å, $\alpha = 93.26(2)°$, $\beta = 90.66(2)°$, $\gamma = 107.03(2)°$, $V = 2047.2$ Å^3, and $Z = 2$. The structure was refined to $R(F_o) = 0.029$ ($R_w(F_o) = 0.034$) for 5352 data with $I > 3.0\sigma(I)$. The structure determination indicates that *ortho*-metalation of the imine reactant occurs during the reaction of $ReH_7(PPh_3)_2$ with PhCHNPh. The observation of four ν(Re−H) absorptions in the infrared spectrum of each $ReH_4[\eta^2\text{-}(1,2\text{-}C_6H_4)CHNR](PPh_3)_2$ compound indicates that the rhenium-bound hydrogen atoms, in these compounds, are better regarded as classical hydride ligands rather than as elongated dihydrogen ligands. Acidolysis reactions of the compounds $ReH_4[\eta^2\text{-}(1,2\text{-}C_6H_4)CHNR](PPh_3)_2$, with $HBF_4 \cdot Et_2O$ in acetonitrile, result in loss of the *ortho*-metalated imine ligands from the rhenium coordination spheres and in reduction of the imine functional groups to secondary ammonium cations. One hydride ligand is transferred to the imine carbon atom, during the course of each acidolysis reaction.

Introduction

There has been considerable interest in the reactions of $ReH_7(PPh_3)_2$ with nitrogen donor molecules.[1−6] The reactions of $ReH_7(PPh_3)_2$ with simple imines ($R_2C{=}NR$), however, have been unexplored. Meanwhile, reactions between simple imines and other transition metal complexes have drawn much attention.[7−11] Such reactions have produced complexes which include N-bound imine ligands, bidentate *ortho*-metalated ligands, iminoacyl ligands, bridging amide ligands, and ligands which result from coupling of the imine functional group with other unsaturated functional groups. Given the propensity of imines to form interesting ligands and, with a single exception, the lack of reports for reactions between imines and transition metal polyhydride complexes, we chose to investigate the reactions of some benzylic imines with the rhenium polyhydride complex $ReH_7(PPh_3)_2$.[7]

The first purpose of our investigation was to determine whether reactions between $ReH_7(PPh_3)_2$ and benzylic imines would form stable products that include the imine functional group and, if so, to determine the manner in which the imine-containing molecule binds to rhenium. If we could prepare a rhenium hydride compound with a bound imine functional group, our goal would be to determine whether rhenium-bound hydride ligands could effect the reduction of the imine functional group. This paper describes the results of our investigations.

Experimental Section

Starting Materials. The complexes $ReH_7(PPh_3)_2$, $Re_2H_8(PPh_3)_4$ and $[ReH(NCMe)_4(PPh_3)_2](BF_4)_2$ were prepared by standard literature

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methods.[5,6,12] All other reagents and solvents were obtained from commercial sources. All reactions were performed under an atmosphere of nitrogen.

A. Thermal Reactions of $ReH_7(PPh_3)_2$. (i) $ReH_4[\eta^2$-(1,2-C_6H_4)-CHNMe]$(PPh_3)_2$. A slurry containing 0.182 g of $ReH_7(PPh_3)_2$ (0.254 mmol) and 0.90 mL of benzylidenemethylamine (7.8 mmol) was heated, at 70 °C, for 5 min. A 50 mL portion of methanol was added to the dark green solution. Mustard yellow microcrystals precipitated from the solution and were collected by suction filtration. The precipitate was washed three times with 25 mL portions of methanol and then dried under vacuum; yield 0.180 g (85%). Anal. Calcd for $C_{44}H_{42}NP_2Re$: C, 63.45; H, 5.08; N, 1.68. Found: C, 63.27; H, 5.07; N, 1.66.

(ii) $ReH_4[\eta^2$-(1,2-C_6H_4)CHNPh]$(PPh_3)_2$. This compound was prepared by reacting 0.164 g of $ReH_7(PPh_3)_2$ (0.228 mmol) with 1.046 g of benzylideneaniline (5.78 mmol), at 82 °C, for 15 min. The product was isolated in a manner similar to that of A(i); yield 0.162 g (79%). Anal. Calcd for $C_{49}H_{44}NP_2Re$: C, 65.76; H, 4.95; N, 1.56. Found: C, 65.69; H, 4.93; N, 1.69. ^1H NMR spectroscopic examination of a reaction mixture, following complete thermolysis, showed no evidence for reduction of imine to amine.

(iii) $ReH_4[\eta^2$-(1,2-C_6H_4)CHNBn]$(PPh_3)_2$. This compound was prepared by reacting 0.123 g of $ReH_7(PPh_3)_2$ (0.171 mmol) with 1.0 mL of benzylidenebenzylamine (5.3 mmol), at 82 °C, for 15 min. The product was isolated in a manner similar to that of A(i); yield 0.108 g (69%). Anal. Calcd for $C_{50}H_{46}NP_2Re$: C, 66.06; H, 5.10; N, 1.54. Found: C, 66.07; H, 5.13; N, 1.65.

B. Acidolysis Reactions of the Compounds $ReH_4[\eta^2$-(1,2-C_6H_4)-CHNR]$(PPh_3)_2$. (i) $ReH_4[\eta^2$-(1,2-C_6H_4)CHNMe]$(PPh_3)_2$ with Tetrafluoroboric Acid−Diethyl Ether Complex. A slurry of 0.1034 g of $ReH_4[\eta^2$-(1,2-C_6H_4)CHNMe]$(PPh_3)_2$ (0.124 mmol), suspended in 1.0 mL of acetonitrile, was treated with 64 μL of tetrafluoroboric acid−diethyl ether complex (0.37 mmol). After 15 min, precipitation was induced by the addition of 50 mL of diethyl ether. The precipitate was collected by suction filtration. The crude precipitate was washed three times with 30 mL portions of diethyl ether and then washed three times with 30 mL portions of water. The resultant pure precipitate of $[ReH(NCMe)_4(PPh_3)_2](BF_4)_2$ (0.0657 g, 0.0626 mmol, 50% yield) was dried under vacuum. We were unable to isolate the product $[Bn(Me)NH_2]BF_4$ from reaction mixtures. Identification of $[Bn(Me)NH_2]BF_4$ was based upon a benzylic resonance in the ^1H NMR spectra of reaction mixtures ($\delta = 3.69$ ppm, $J_{HH} = 6.0$ Hz). The benzylic ^1H NMR resonance increased in intensity, but was otherwise unchanged, when acidolysis reaction mixtures were spiked with equal moles of Bn(Me)NH and additional $HBF_4 \cdot Et_2O$.

(ii) $ReH_4[\eta^2$-(1,2-C_6H_4)CHNPh]$(PPh_3)_2$ with Tetrafluoroboric Acid−Diethyl Ether Complex. A slurry of 0.0994 g of $ReH_4[\eta^2$-(1,2-C_6H_4)CHNPh]$(PPh_3)_2$ (0.110 mmol), suspended in 1.0 mL of acetonitrile, was treated with 57 μL of tetrafluoroboric acid−diethyl ether complex (0.33 mmol). After 30 min, precipitation was induced by the addition of 50 mL of diethyl ether. The precipitate was collected by suction filtration. The crude precipitate was washed three times with 30 mL portions of diethyl ether and dried. The crude dry precipitate was washed with water to remove $[Bn(Ph)NH_2]BF_4$. The resultant pure product, $[ReH(NCMe)_4(PPh_3)_2](BF_4)_2$ (0.0681 g, 0.0649 mmol, 59% yield), was dried under vacuum. The salt $[Bn(Ph)NH_2]BF_4$ (0.0082 g, 0.0303 mmol, 28% yield) was recovered from the filtrate by slow evaporation of the water washings. The salt $[Bn(Ph)NH_2]BF_4$ was also observed, in situ, as in method B(i) ($\delta = 4.56$ ppm, $J_{HH} = 6.2$ Hz).

(iii) $ReH_4[\eta^2$-(1,2-C_6H_4)CHNPh]$(PPh_3)_2$ with Deuteriochloric Acid. The compound $ReH_4[\eta^2$-(1,2-C_6H_4)CHNPh]$(PPh_3)_2$ (0.032 g, 0.036 mmol) was combined, in CD_3CN (0.4 mL), with 37% $DCl_{(D_2O)}$ (0.3 mL, 3.6 mmol). The reaction was monitored by ^1H NMR spectroscopy (vide infra). No attempt was made to isolate products from the reaction mixture.

(iv) $ReH_4[\eta^2$-(1,2-C_6H_4)CHNBn]$(PPh_3)_2$ with Tetrafluoroboric Acid−Diethyl Ether Complex. A slurry of 0.100 g of $ReH_4[\eta^2$-(1,2-C_6H_4)CHNBn]$(PPh_3)_2$ (0.110 mmol) was treated with 57 μL of tetrafluoroboric acid−diethyl ether complex (0.33 mmol). The products were isolated in the same manner as in method B(ii): $[ReH(NCMe)_4(PPh_3)_2](BF_4)_2$ (0.079 g, 0.075 mmol, 69% recovery) and $(Bn_2NH_2)BF_4$ (0.011 g, 0.039 mmol, 35% recovery). The salt $(Bn_2NH_2)BF_4$ was also observed, in situ, as in method B(i) ($\delta = 4.22$ ppm, $J_{HH} = 5.7$ Hz).

(v) Quantitative Determination of the Gas Evolved from the Reaction of $ReH_4[\eta^2$-(1,2-C_6H_4)CHNBn]$(PPh_3)_2$ with Tetrafluoroboric Acid−Diethyl Ether Complex. A 50 mL round-bottomed flask, equipped with a sidearm, was charged with 0.2675 g (0.2943 mmol) of $ReH_4[\eta^2$-(1,2-C_6H_4)CHNBn]$(PPh_3)_2$ and 5.0 mL of acetonitrile. A second, similar, round-bottomed flask was charged with 5.0 mL of acetonitrile. No rhenium compound was added to the second apparatus. The sidearms of both flasks were connected to water-filled burets equipped with leveling bulbs. Pressures were equalized between the laboratory, and the round-bottomed flasks and initial volumes were recorded. Via syringe, 1.0 mL of tetrafluoroboric acid−diethyl ether complex was added to each reaction vessel. The flasks were stirred occasionally, by hand, over the course of the next 24 h. After 24 h, internal pressures were again equalized with the laboratory pressure and the volumes of water displaced were recorded. A total of 11.49 mL of water was displaced by the vapor pressures of the reagents and products, in the rhenium-containing reaction vessel. A total of 3.52 mL of water was displaced by the vapor pressures of the reagents present in the control reaction vessel. Using the ideal gas law, a measured pressure of 745 Torr, a measured temperature of 297 K, and a volume of gas evolved of 7.97 mL, it was determined that 0.321 mmol of gas was evolved from the acidolysis reaction of $ReH_4[\eta^2$-(1,2-C_6H_4)CHNBn]$(PPh_3)_2$. The ratio of moles of gas evolved per moles of $ReH_4[\eta^2$-(1,2-C_6H_4)CHNBn]$(PPh_3)_2$ reacted was 1.09.

C. X-ray Structure Determination. An orange single crystal was obtained by dissolving a sample of $ReH_4[\eta^2$-(1,2-C_6H_4)CHNPh]$(PPh_3)_2$ in 0.5 mL of benzene and layering 0.5 mL of methanol over this solution. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement using the setting angles of 25 reflections in the range $17 < \theta < 21°$. The space group was determined to be $P\bar{1}$ (No. 2). Data were collected, at 295 K, using the ω scan technique. Lorentz and polarization corrections were applied to the data. The structure was solved by the direct method SIR92 and by Fourier techniques.[13] Except as noted in the table of positional parameters, hydrogen atoms were located and added to the structure factor calculations but not refined. The final cycle of refinement converged with unweighted and weighted agreement factors of $R_1 = \sum|F_o - F_c|/\sum F_o = 0.029$ and $R_2 = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2} = 0.034$. The highest peak in the final difference Fourier had a height of 0.75 e/Å^3 with an estimated error based on δF of 0.10.[14] Refinement was done using Mo1EN.[15]

Results

(a) Reactions of $ReH_7(PPh_3)_2$ with Benzylic Imines. Thermal reactions between $ReH_7(PPh_3)_2$ and the benzylic imines PhCHNR (R = Me, Ph, or Bn) lead to the products $ReH_4[\eta^2$-(1,2-C_6H_4)CHNR]$(PPh_3)_2$ (eq 1). The structure of one such

$$ReH_7(PPh_3)_2 + C_6H_5CHNR \rightarrow ReH_4[\eta^2\text{-}(1,2\text{-}C_6H_4)CHNR](PPh_3)_2 + 2H_2 \quad (1)$$

product, $ReH_4[\eta^2$-(1,2-C_6H_4)CHNPh]$(PPh_3)_2$, was determined by single-crystal X-ray diffraction analysis (Figure 1). Details and results of the X-ray diffraction analysis of $ReH_4[\eta^2$-(1,2-C_6H_4)CHNPh]$(PPh_3)_2$ are given in Table 1 and the Supporting Information. The intramolecular bond distances and angles for the structure are given in Table 2.

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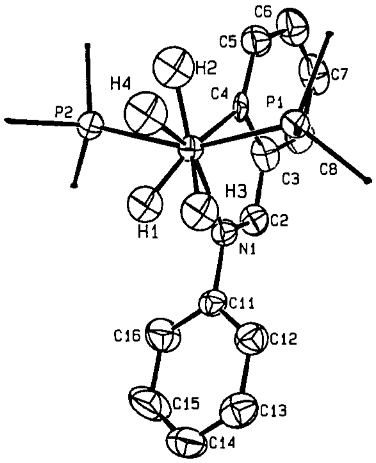

Figure 1. ORTEP representation of the structure of $ReH_4[\eta^2\text{-}(1,2\text{-}C_6H_4)CHNPh](PPh_3)_2$. The thermal ellipsoids are drawn at the 50% probability level, and the *ipso* carbon atoms of the PPh_3 phenyl rings are represented as circles of arbitrary radius.

Table 1. Crystallographic and Data Collection Parameters for $ReH_4[\eta^2\text{-}(1,2\text{-}C_6H_4)CHNPh](PPh_3)_2$

formula	$ReP_2NC_{49}H_{44}$
fw	895.05
space group	$P\bar{1}$ (No. 2)
a, Å	12.422(3)
b, Å	12.696(3)
c, Å	13.604(5)
α, deg	93.26(2)
β, deg	90.66(2)
γ, deg	107.03(2)
V, Å^3	2047(2)
Z	2
ρ_{calcd}, g/cm^3	1.455
temp, K	295
λ, Å	0.710 73
transm coeff	0.654, 0.935
$R(F_o)^a$	0.029
$R_w(F_o)^b$	0.034

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

X-ray diffraction analysis of $ReH_4[\eta^2\text{-}(1,2\text{-}C_6H_4)CHNPh](PPh_3)_2$ indicates that the imine reactant binds to rhenium through two atoms (N(1) and C(4)) and that a five-membered metallocyclic ring, which is fused with an *ortho*-metalated six-membered ring, forms during the reactions of $ReH_7(PPh_3)_2$ with benzylic imines. Except for rhenium, bond angles about the atoms that form the fused rings are all within the range of 114.5−130.2°. The largest deviations from the 120° angles expected for sp^2-hybridized atoms occur at C4.

Single-crystal X-ray diffraction analysis of $ReH_4[\eta^2\text{-}(1,2\text{-}C_6H_4)CHNPh](PPh_3)_2$ also established the presence of four hydrogen atoms bound to rhenium. The rhenium-bound hydrogen−hydrogen contact distances range from 2.91 to 1.33 Å. The shortest distance, 1.33 Å, occurs for H(1) and H(3). The 1.33 Å distance between H1 and H3 is similar to the 1.357 Å hydrogen−hydrogen contact distance reported for a neutron diffraction study of $ReH_7[P(C_6H_4CH_3\text{-}4)_3]_2$.[16]

Table 2. Selected Bond Distances (Å) and Bond Angles (deg)

	Distances		
Re−P(1)	2.3876(14)	N(1)−C(11)	1.445(6)
Re−P(2)	2.3791(14)	C(2)−C(3)	1.422(7)
Re−N(1)	2.142(3)	C(3)−C(4)	1.419(6)
Re−C(4)	2.159(4)	C(3)−C(8)	1.414(7)
Re−H(1)	1.44(5)	C(4)−C(5)	1.417(7)
Re−H(2)	1.61(5)	C(5)−C(6)	1.382(7)
Re−H(3)	1.67(6)	C(6)−C(7)	1.367(7)
Re−H(4)	1.77(5)	C(7)−C(8)	1.375(8)
N(1)−C(2)	1.293(6)		
	Angles		
P(1)−Re−P(2)	157.35(4)	C(4)−Re−H(4)	135.4(19)
P(1)−Re−N(1)	99.45(11)	H(1)−Re−H(2)	124(3)
P(1)−Re−C(4)	85.94(13)	H(1)−Re−H(3)	50(3)
P(1)−Re−H(1)	122(2)	H(1)−Re−H(4)	77(2)
P(1)−Re−H(2)	86(2)	H(2)−Re−H(3)	128(2)
P(1)−Re−H(3)	72.0(19)	H(2)−Re−H(4)	56(3)
P(1)−Re−H(40	85(2)	H(3)−Re−H(4)	75(3)
P(2)−Re−N(1)	99.36(12)	Re−N(1)−C(2)	119.5(3)
P(2)−Re−C(4)	87.14(13)	Re−N(1)−C(11)	123.8(2)
P(2)−Re−H(1)	75(2)	C(2)−N(1)−C(11)	116.6(4)
P(2)−Re−H(2)	72(2)	N(1)−C(2)−C(3)	116.6(4)
P(2)−Re−H(3)	124.4(9)	C(2)−C(3)−C(4)	114.5(4)
P(2)−Re−H(4)	85(2)	C(2)−C(3)−C(8)	122.7(4)
N(1)−Re−C(4)	74.20(15)	C(4)−C(3)−C(8)	122.6(5)
N(1)−Re−H(1)	75.9(17)	Re−C(4)−C(3)	115.1(3)
N(1)−Re−H(2)	152.6(19)	Re−C(4)−C(5)	130.2(3)
N(1)−Re−H(3)	78.3(15)	C(3)−C(4)−C(5)	114.5(4)
N(1)−Re−H(4)	150.4(19)	C(4)−C(5)−C(6)	122.3(4)
C(4)−Re−H(1)	142.1(18)	C(5)−C(6)−C(7)	121.6(5)
C(4)−Re−H(2)	79.3(19)	C(6)−C(7)−C(8)	119.5(5)
C(4)−Re−H(3)	141.1(17)	C(3)−C(8)−C(7)	119.5(4)

Infrared spectra of the $ReH_4[\eta^2\text{-}(1,2\text{-}C_6H_4)CHNPh](PPh_3)_2$ compound provides for unambiguous characterization of the H(1)−Re−H(3) unit as a pair of hydride ligands. Four ν(Re−H) absorptions were observed in both the solid state and solution infrared spectra of $ReH_4[\eta^2\text{-}(1,2\text{-}C_6H_4)CHNPh](PPh_3)_2$ (KBr pellet, 2066 (vw), 2000 (m), 1956 (m), and 1898 cm^{-1} (w); CH_2Cl_2 solution, 2062 (vw), 1985 (m), 1963 (sh), and 1916 cm^{-1} (w)). Four ν(Re−H) absorptions were also observed in the KBr pellet infrared spectra of the other two $ReH_4[\eta^2\text{-}(1,2\text{-}C_6H_4)CHNR](PPh_3)_2$ compounds (R = Me, 2047 (vw), 1981 (m), 1962 (w), and 1925 cm^{-1} (w); R = Bn, 2049 (vw), 1968 (m), 1941 (m), and 1900 cm^{-1} (w)). The above pattern of four ν(Re−H) absorptions also occurs for the closely related, and structurally characterized, tetrahydride complex $ReH_4(hq)(PPh_3)_2$ (hq = the anion of 2-hydroxyquinoline).[2] Given the four Re−H stretching absorptions in the infrared spectrum of each $ReH_4[\eta^2\text{-}(1,2\text{-}C_6H_4)CHNR](PPh_3)_2$ compound, we conclude that all four rhenium-bound hydrogen atoms, on each compound, should be regarded as classical hydride ligands.

Along with the ν(Re−H) absorptions discussed above, the infrared spectrum of each $ReH_4[\eta^2\text{-}(1,2\text{-}C_6H_4)CHNR](PPh_3)_2$ compound exhibits a ν(C=N) absorption (R = Me, 1530 cm^{-1} (w); R = Ph, 1553 cm^{-1} (m); R = Bn, 1528 cm^{-1} (w)). The ligand C=N stretching absorptions occur at significantly lower energies than the free imine C=N stretching absorptions. For example, the ν(C=N) absorption in PhCHNMe occurs at 1651 cm^{-1}. We believe that the decrease in C=N stretching energy is due to interaction between the Re(V) nonbonded electron pair and the π system of the essentially planar, *ortho*-metalated ligand (vide infra).

The $\{^1H\}^{31}P$ and ^1H NMR spectral properties of the $ReH_4[\eta^2\text{-}(1,2\text{-}C_6H_4)CHNR](PPh_3)_2$ compounds were also measured $\{^1H\}^{31}P$ NMR of $ReH_4[\eta^2\text{-}(1,2\text{-}C_6H_4)CHNR](PPh_3)_2$ (C_6D_6): R = Me, δ = 34.07 (s); R = Ph, δ = 32.95 (s); R = Bn, δ = 33.82 (s). ^1H NMR of $ReH_4[\eta^2\text{-}(1,2\text{-}C_6H_4)CHNR](PPh_3)_2$ (C_6D_6): R = Me, δ = 6.4−7.7 (m) (34H), δ = 6.36 (t) (1H), J_{HP} = 7.4 Hz, δ = 3.05 (s) (3H), δ = −4.45 (s) (4H); R = Ph, δ = 5.9−7.9 (m) (39H), δ = 6.36 (t) (1H), J_{HP} = 7.6 Hz, δ = −3.98 (s) (4H); R = Bn, δ = 6.2−8.0 (m) (39H), δ = 6.37 (m) (1H), δ = 4.66 (s) (2H), δ = −4.20 (t) (4H), J_{HP} = 18.4 Hz. A single hydride resonance is observed in the room-

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temperature ^{1}H NMR spectrum of each compound. The hydride resonance of only one of the reported compounds, $ReH_4[\eta^2\text{-}(1,2\text{-}C_6H_4)CHNBn](PPh_3)_2$, displays resolved coupling to rhenium-bound ^{31}P nuclei, at room temperature. We attribute the lack of resolved coupling, for the hydride resonances of the R = Me or Ph compounds, to the commonly observed slow fluxionality of rhenium hydride ligands, at room temperature, on the NMR time scale.[4,17,18]

The overall structure of $ReH_4[\eta^2\text{-}(1,2\text{-}C_6H_4)CHNPh](PPh_3)_2$ is best described as a distorted dodecahedron about the central rhenium atom. The central rhenium atom, the rhenium-bound nitrogen and carbon atoms of the *ortho*-metalated imine ligand (N(1) and C(4)), and the hydride ligands H(2) and H(4) are all essentially coplanar. The remaining four atoms bound to rhenium (P(1), P(2), H(1), and H(3)) are also nearly coplanar. The rhenium center, however, is displaced from the P(1), P(2), H(1), and H(3) plane, in the direction of the N(1) and C(4) atoms. The sum of the bond angles about rhenium, for the P(1), P(2), H(1), and H(3) plane, is 354°. The structure of $ReH_4[\eta^2\text{-}(1,2\text{-}C_6H_4)CHNPh](PPh_3)_2$, as determined by X-ray diffraction analysis, is very similar to the structure of the compound $ReH_4(hq)(PPh_3)_2$.[2]

(b) Acidolysis Reactions of the Compounds $ReH_4[\eta^2\text{-}(1,2\text{-}C_6H_4)CHNR](PPh_3)_2$. We began our investigation of the bound imine functional group by treating the $ReH_4[\eta^2\text{-}(1,2\text{-}C_6H_4)CHNR](PPh_3)_2$ compounds with tetrafluoroboric acid−diethyl ether complex ($HBF_4\cdot Et_2O$), in acetonitrile. The rhenium-containing product from the acidolysis of each $ReH_4[\eta^2\text{-}(1,2\text{-}C_6H_4)CHNR](PPh_3)_2$ compound was found to be $[ReH(NCMe)_4(PPh_3)_2](BF_4)_2$.[5] The effervescence of a gaseous product was also found during the acidolysis reaction of each $ReH_4[\eta^2\text{-}(1,2\text{-}C_6H_4)CHNR](PPh_3)_2$ compound. The gas produced from an acidolysis reaction of $ReH_4[\eta^2\text{-}(1,2\text{-}C_6H_4)CHNBn](PPh_3)_2$ was quantitatively determined to be 1 equiv of gas for each 1 equiv of $ReH_4[\eta^2\text{-}(1,2\text{-}C_6H_4)CHNBn](PPh_3)_2$ reacted. Given the stoichiometries of reactants and products, in these acidolysis reactions, we are certain that the gas evolved, during the acidolysis reactions described above, was hydrogen (*vide infra*).

The remaining products from the acidolysis reactions of the $ReH_4[\eta^2\text{-}(1,2\text{-}C_6H_4)CHNR](PPh_3)_2$ compounds, in acetonitrile, were the secondary ammonium salts $[Bn(R)NH_2]BF_4$. (The R group for the product of each reaction corresponds to the R group present in the corresponding *ortho*-metalated starting materials.) The cations were identified in situ by ^{1}H NMR spectroscopy. Two of the salts were isolated as solids (*vide supra*). The complete stoichiometry of the acidolysis reactions described above is given in eq 2.

$$ReH_4[\eta^2\text{-}(1,2\text{-}C_6H_4)CHNR](PPh_3)_2 + 3H^+ + 4MeCN \rightarrow [ReH(NCMe)_4(PPh_3)_2]^{2+} + [PhCH_2(R)NH_2]^+ + H_2 \quad (2)$$

We were interested in determining what role the rhenium-bound hydrides play in the reduction of *ortho*-metalated imine ligands into secondary ammonium ions. Consequently, we changed the acidic reactant from $HBF_4\cdot Et_2O$ to $DCl_{(D_2O)}$. The only compound studied with the $DCl_{(D_2O)}$ reagent was $ReH_4[\eta^2\text{-}(1,2\text{-}C_6H_4)CHNPh](PPh_3)_2$. The reaction mixture was studied *in situ* by ^{1}H NMR spectroscopy. The chemical shift and coupling constant of one ^{1}H NMR resonance observed, upon completion of the reaction ($\delta = -4.65$ ppm, $J_{PH} = 66$ Hz, in the solvent CD_3CN), indicates that this resonance is due to the $[ReH(NCCD_3)_4(PPh_3)_2]^{2+}$ ion.

We note that the secondary ammonium ion $[PhCH_2(Ph)ND_2]^+$ was also observed upon completion of the $DCl(D_2O)$ acidolysis reaction. The identification of $[PhCH_2(Ph)ND_2]^+$ is based upon a resonance at 4.56 ppm, in the ^{1}H NMR spectrum of the reaction mixture. The 4.56 ppm resonance corresponds to the benzylic proton resonance of $[PhCH_2(Ph)NH_2]^+$ (*vide supra*). The benzylic proton resonance, in the $DCl_{(D_2O)}$ reaction mixture, occurs as a singlet. No geminal coupling to deuterium is observed, nor is any vicinal coupling to protons bound to nitrogen observed. We believe that the lack of geminal coupling to deuterium indicates one hydride ligand is transferred to the imine carbon atom during the reaction course, making the benzyl methylene group a CH_2 group rather than a CHD group. Integration of this methylene ^{1}H NMR resonance versus the resonances of the aromatic protons also corresponds to the presence of a CH_2 methylene group rather than a CHD methylene group. The observed lack of vicinal coupling to protons bound to nitrogen, under our experimental conditions, indicates that both atoms added to the imine nitrogen, upon acidolysis, arise from $DCl_{(D_2O)}$ rather than from hydride ligands. The complete $DCl_{(D_2O)}$ acidolysis reaction stoichiometry is given in eq 3.

$$ReH_4[\eta^2\text{-}(1,2\text{-}C_6H_4)CHNPh](PPh_3)_2 + 3D^+ + 4MeCN \rightarrow [ReH(NCMe)_4(PPh_3)_2]^{2+} + [(C_6H_5)CH_2(Ph)ND_2]^+ + HD \quad (3)$$

Discussion

(a) Reactions of $ReH_7(PPh_3)_2$ with Benzylic Imines. *Ortho*-metalation of benzylic imines, during their reactions with $ReH_7(PPh_3)_2$, was not completely unexpected. *Ortho*-metalation of benzylic imines has been reported with other transition metal complexes.[8,9] Furthermore, $ReH_7(PPh_3)_2$ is known to activate aryl C−H bonds. One of the first reported properties of either $ReH_7(PPh_3)_2$ or $ReD_7(PPh_3)_2$ was the ability of $ReD_7(PPh_3)_2$ to exchange deuteride ligands for hydride ligands, with benzene (C_6H_6) serving as the source of hydride.[6] Subsequent reports have further demonstrated the propensity of $ReH_7(PPh_3)_2$ or putative ReH_5P_2 species (P = tertiary phosphine) to activate aryl C−H bonds.[17,19] Thus, while we were not seeking to generate an *ortho*-metalated ligand, it is not surprising that such a ligand would form in the above reactions.

Despite several reports of aryl C−H bond activations by $ReH_7(PPh_3)_2$ and other rhenium polyhydride compounds, the $ReH_4[\eta^2\text{-}(1,2\text{-}C_6H_4)CHNR](PPh_3)_2$ complexes reported herein represent, to the best of our knowledge, the first examples of stable complexes which contain four or more hydride ligands and a σ bond between rhenium and an aryl carbon center. We believe that the primary factor which contributes to the stability of the σ bonds between aryl carbon atoms and rhenium, in the presence of four hydride ligands, is the chelate effect. We note that the compounds reported herein and the compound $ReH_4(\eta^3\text{-}2\text{-isopropylallyl})(dppe)$ (dppe = 1,2-bis(diphenylphosphino)-

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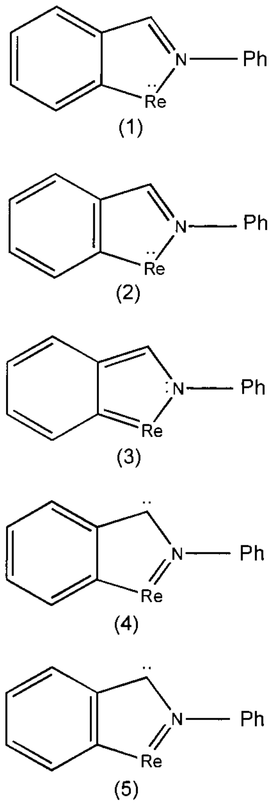

Figure 2. Valence bond resonance structures, excepting Dewar-type structures, for the *ortho*-metalated ligand found within the complex $ReH_4[\eta^2\text{-}(1,2\text{-}C_6H_4)CHNPh](PPh_3)_2$.

ethane), which contains a σ bond between a rhenium tetrahydride center and an allylic carbon atom, all include the σ-bound carbon atom as part of a chelating ligand.[18] It appears that benzylic imines are the first substrates, for C−H bond activation at a rhenium polyhydride center, which contain a donor atom with the ability to occupy a second rhenium coordination site.

Another factor that appears to contribute to the stability of the Re−C bonds, in the compounds $ReH_4[\eta^2\text{-}(1,2\text{-}C_6H_4)CHNR](PPh_3)_2$, involves donation of the formally Re(V) nonbonded electron pair into the π system of the *ortho*-metalated ligand. For simplicity, the electronic structure of the *ortho*-metalated ligands can be described, in valence bond terms, by the resonance structures found in Figure 2. Structures 1 and 2 likely contribute greatly to the overall stability of the *ortho*-metalated ligands. Structure 3 also appears to contribute to the stability of the *ortho*-metalated ligands, at least in part, because the rhenium orbital that contains the nonbonded electron pair will overlap better with the larger C $2p_z$ atomic orbital than with the smaller N $2p_z$ atomic orbital. A Re−C π bonding contribution, as depicted in structure 3, would also account for the observed decrease in C−N stretching energy, upon coordination (vide supra). The contribution of structure 3, to the electronic structure of the *ortho*-metalated ligand system, also seems to be supported by a comparison of the 2.159 Å Re−C distance in $ReH_4[\eta^2\text{-}(1,2\text{-}C_6H_4)CHNPh](PPh_3)_2$ with the 2.214 Å Re−C distance found in the compound $ReH_4(\eta^3\text{-}2\text{-isopropylallyl})(dppe)$.[18]

(b) Acidolysis Reactions of the Compounds $ReH_4[\eta^2\text{-}(1,2\text{-}C_6H_4)CHNR](PPh_3)_2$. Our purpose, in reacting benzylic imines with $ReH_7(PPh_3)_2$, was to prepare rhenium polyhydride compounds for a subsequent investigation into the reactions of hydride ligands with imine functional groups. The results of our investigation demonstrate that an imine functional group can be reduced to a secondary ammonium functional group through the action of a rhenium-bound hydride ligand and 2 equiv of acid. The reduction described herein, however, is quite different from the catalytic reduction of imines that occur at certain platinum metal complexes.[7] Catalytic reduction of an imine functional group requires the transfer of 2 equiv of hydrogen atoms from the metal center to the imine ligand and requires π coordination of the imine ligand. The reduction described in this report involves the transfer of only one hydride ligand from rhenium to the imine functional group, and the imine that is reduced binds, at least initially, to rhenium through nitrogen rather than through the imine π cloud.

Conclusion

The unsaturated imine functional group, bound to a rhenium polyhydride center, appears to be substantially more reactive than the unsaturated nitrile or isocyanide functional groups which we have studied previously.[5,20] We have found that reduction of an imine functional group occurs upon acidolysis of imine-stabilized rhenium polyhydride compounds. During acidolysis reactions, a hydride ligand is transferred from rhenium to the imine carbon center. Thus, the imine functional group is the first heteroatom-containing unsaturated functional group demonstrated to react with the hydride ligands of rhenium polyhydride compounds. Alkenes, alkynes, and aromatic rings have previously been shown to react with the hydride ligands of rhenium polyhydride compounds.[1,17−19,21]

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Supporting Information Available: Listings of the full details of the crystal data and data collection parameters, positional parameters, thermal parameters, complete bond distances and bond angles, torsion angles, and multiplicities for $ReH_4[\eta^2\text{-}(1,2\text{-}C_6H_4)CHNPh](PPh_3)_2$ (15 pages). Ordering information is given on any current masthead page.

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