Ethanol Oxidation by Imidorhenium(V) Complexes: Formation of Amidorhenium(III) Complexes

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The reaction of $Re(NC_6H_4R)Cl_3(PPh_3)_2$ (R = H, 4-Cl, 4-OMe) with 1,2-bis(diphenylphosphino)ethane (dppe) is investigated in refluxing ethanol. The reaction produces two major products, $Re(NC_6H_4R)Cl(dppe)_2^{2+}$ (R = H, **1-H**; R = Cl, **1-Cl**; R = OMe, **1-OMe**) and the rhenium(III) species $Re(NHC_6H_4R)Cl(dppe)_2^{+}$ (R = H, **2-H**; R = Cl, **2-Cl**). Complexes **1-H** (orthorhombic, *Pcab*, $a = 22.3075(10)$ Å, $b = 23.1271(10)$ Å, $c = 23.3584(10)$ Å, $Z = 8$), **1-Cl** (triclinic, $P\bar{1}$, $a = 11.9403(6)$ Å, $b = 14.6673(8)$ Å, $c = 17.2664(9)$ Å, $\alpha = 92.019(1)°$, $\beta = 97.379(1)°$, $\gamma = 90.134(1)°$, $Z = 2$), and **1-OMe** (triclinic, *P*1, $a = 11.340(3)$ Å, $b = 13.134(4)$ Å, $c = 13.3796(25)$ Å, $\alpha = 102.370(20)°$, $\beta = 107.688(17)°$, $\gamma = 114.408(20)°$, $Z = 1$) are crystallographically characterized and show an average Re−N bond length (1.71 Å) typical of imidorhenium(V) complexes. There is a small systematic decrease in the Re−N bond length on going from Cl to H to OMe. Complex **2-Cl** (monoclinic, *Cc*, $a = 24.2381(11)$ Å, $b = 13.4504(6)$ Å, $c = 17.466(8)$ Å, $\beta = 97.06900(0)°$, $Z = 4$) is also crystallographically characterized and shows a Re−N bond length (1.98 Å) suggestive of amidorhenium(III). The rhenium(III) complexes exhibit unusual proton NMR spectra where all of the resonances are found at expected locations except those for the amido protons, which are at 37.8 ppm for **2-Cl** and 37.3 ppm for **1-H**. The phosphorus resonances are also unremarkable, but the ^{13}C spectrum of **2-Cl** shows a significantly shifted resonance at 177.3 ppm, which is assigned to the ipso carbon of the phenylamido ligand. The extraordinary shifts of the amido hydrogen and ipso carbon are attributed to second-order magnetism that is strongly focused along the axially compressed amido axis. The reducing equivalents for the formation of the Re(III) product are provided by oxidation of the ethanol solvent, which produces acetal and acetaldehyde in amounts as much as 30 equiv based on the quantity of rhenium starting material. Equal amounts of hydrogen gas are produced, suggesting that the catalyzed reaction is the dehydrogenation of ethanol to produce acetaldehyde and hydrogen gas. Metal hydrides are detected in the reaction solution, suggesting a mechanism involving β-elimination of ethanol at the metal center. Formation of the amidorhenium(III) product possibly arises from migration of a metal hydride in the imidorhenium(V) complex.

The oxidation of small molecules by transition metal complexes with multiply bonded heteroatom ligands is an attractive concept for realizing useful transformations.[1−5] Ligand pairs such as oxo/hydroxo, nitrido/amido, and phenylimido/phenylamido are related by a proton and electron and could, in principle, be interconverted by the addition of a hydrogen atom from an organic substrate coupled with a change in oxidation state of the metal:[6]

$$\mathrm{M{=}O} + \mathrm{H}^{\bullet} \rightleftharpoons \mathrm{M{-}OH} \tag{1}$$

$$\mathrm{M{=}N} + \mathrm{H}^{\bullet} \rightleftharpoons \mathrm{M{=}NH} \tag{2}$$

$$\mathrm{M{=}NPh} + \mathrm{H}^{\bullet} \rightleftharpoons \mathrm{M{-}N(H)Ph} \tag{3}$$

The attractiveness of such schemes is that, following the addition of the hydrogen atom, the reduced form of the metal complex could be returned to the oxidized form by common oxidants, such as dioxygen, to complete a catalytic cycle.[7] The strong multiple bonds between the metal and heteroatom should ensure that the ligand remains coordinated to produce a robust catalyst; however, the electronic stabilization via axial compression and low d-electron count can potentially lower the reactivity of the oxidant. Alternatively, more common pathways for activation of C−H bonds involve formation of metal hydrides following either oxidative addition of the C−H bond or β-elimination to form a coordinated π-bond.[8−10] Recycling with dioxygen can also be envisioned in these cases, although, in aqueous media, protonation of metal hydrides to form hydrogen is a more common route to catalyst regeneration.[9]

We report here an imidorhenium(V) system that appears initially to abstract hydrogen atoms according to eq 3. Reaction of $Re(NC_6H_4R)Cl_3(PPh_3)_2$ (R = H, 4-Cl, 4-OMe) with 1,2-bis(diphenyl)phosphino)ethane (dppe) in ethanol produces multiple equivalents of acetaldehyde and the rhenium(V) complex $Re(NC_6H_4R)Cl(dppe)_2^{2+}$ where R = H (**1-H**), 4-Cl (**1-Cl**), or

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(1) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988. Mayer, J. M. In *Advances in Transition Metal Coordination Chemistry*; Che, C.-M., Ed.; JAI Press: Greenwich, CT, 1996; Vol. 1, pp 105−158.

(2) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401.

(3) Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*, 239.

(4) Liu, W.; Thorp, H. H. In *Advances in Transition Metal Coordination Chemistry*; Che, C.-M., Ed.; JAI Press: Greenwich, CT, 1996; Vol. 1, p 187.

(5) Mayer, J. M. *Acc. Chem. Res.* **1998**, *31*, 441.

(6) Meyer, T. J. *J. Electrochem. Soc.* **1984**, *131*, 221C.

(7) Winkler, J. R.; Gray, H. B. *Inorg. Chem.* **1985**, *24*, 346.

(8) Bryndza, H. E.; Calabrese, J. C.; Marsi, M.; Roe, D. C.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 4805.

(9) Holtcamp, M. W.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1997**, *119*, 848. Arndtsen, B. A.; Bergman, R. G. *Science* **1995**, *270*, 1970.

(10) Conry, R. R.; Mayer, J. M. *Organometallics* **1991**, *10*, 3160.

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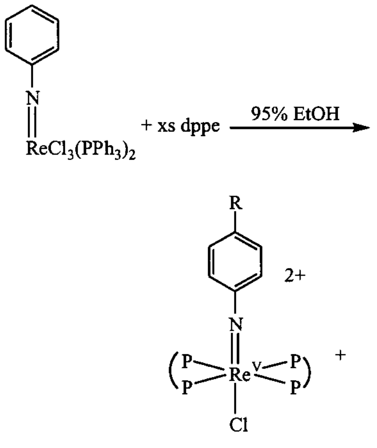
4-OMe (**1-OMe**). The reaction also produces a similar amount of the rhenium(III) complex $Re(NHC_6H_4R)Cl(dppe)_2^+$ where R = H (**2-H**) or Cl (**2-Cl**):



(4)

1 **2**

The amido complex **2** exhibits an unusual ^1H NMR spectrum with a strong paramagnetic shift of the amido proton to 38.5 ppm and little effect on any of the other resonances. Although it is tempting to assign the catalytic reaction as addition of a hydrogen atom (or hydride) from ethanol to the imido group (as in eq 3), closer scrutiny reveals the presence of small amounts of rhenium hydride complexes, implying a mechanism where addition of the hydrogen atom occurs at the metal. Subsequent migration of the hydride ligand to the nitrogen heteroatom to form the amidorhenium(III) complex possibly halts the catalytic cycle.

Experimental Section

Materials. Chemicals, unless noted otherwise, were of reagent grade and were used as received from commercial sources. $ReOCl_3(PPh_3)_2$[11] and 1-acetyl-2-(*p*-chlorophenyl)hydrazine[12] were prepared according to published procedures. All syntheses were performed using air-sensitive techniques under nitrogen or argon. Ethanol was deaerated by a 30 min nitrogen purge. NMR spectra were obtained using Bruker WM 250 MHz, Varian Gemini 300 MHz, and Bruker Avance 400 MHz spectrometers. Elemental analyses were performed by Atlantic Microlab.

Metal Complexes. *mer*-$Re(4\text{-}NC_6H_4R)Cl_3(PPh_3)_2$ (R = H, Cl),[13] *fac*-$Re(4\text{-}NC_6H_4Cl)Cl_3(dppe)$,[13] and $[Re(4\text{-}NC_6H_4R)Cl(dppe)_2](PF_6)_2$ (R = H, Cl, OCH_3)[14] were prepared by following reported procedures. These metal complexes all gave satisfactory elemental analyses.

$[ReCl_2(dppe)_2](PF_6)_2$, $[Re(4\text{-}NHC_6H_4Cl)Cl(dppe)_2]PF_6$, and $[Re(4\text{-}NC_6H_4Cl)Cl(dppe)_2](PF_6)_2$. A 200 mL ethanol solution of $Re(4\text{-}NC_6H_4Cl)Cl_3(PPh_3)_2$ (0.180 g, 0.191 mmol) was refluxed with 8 equiv of dppe for 48 h under an atmosphere of nitrogen. The reaction mixture was filtered to remove any precipitated $[ReO_2(dppe)_2]Cl_2$ and unreacted dppe, and the dark orange filtrate was rotary-evaporated to dryness. The resulting residue was dissolved in CH_2Cl_2, and the solution was loaded onto a neutral deactivated alumina column. After the column was washed with CH_2Cl_2 to remove excess dppe, 20:1 CH_3CN/ethanol was used to elute $[Re(4\text{-}NHC_6H_4Cl)Cl(dppe)_2]Cl$ ((**2-Cl**)Cl) as the first major band. This yellow band was evaporated, dissolved in a minimum amount of ethanol, and precipitated as the PF_6^- salt upon addition of excess NH_4PF_6. X-ray-quality orange crystals were obtained by layering pentane over a CH_2Cl_2 solution. Yield: 0.073 mmol, 38%. Anal. Calcd for $ReC_{58}H_{53}NCl_2P_5F_6\cdot 1.25CH_2Cl_2$: C, 51.00; H, 4.01; N, 1.00; Cl, 11.43. Found: C, 50.50; H, 3.99; N, 1.07; Cl, 11.41. ^1H NMR (CH_2Cl_2, ppm): 37.8 (s, b, 1H, NH), 7.65−6.8 (m, 40H, Ph), 6.29, 4.72 (d of d, 4H, $-NC_6H_4-$), 3.0 (m, 8H, $-CH_2CH_2-$). $^{13}C\{^1H\}$ NMR (CH_2Cl_2, ppm): 177.3 (s), 145.2 (s), 138.6 (t, b), 137.0 (t), 133.9 (s), 133.2 (s), 132.8 (s), 131.6 (s), 130.0 (s), 129.7 (s), 128.6 (s), 122.9 (s), 28.8 (m, $-CH_2CH_2-$). ^{13}C NMR (CH_2Cl_2, ppm): 177.3 (b, s), 145.2 (t), 138.6 (m, b), 137.0 (t, b), 133.9 (d of t), 133.2 (d), 132.8 (d), 131.6 (d), 130.0 (d of t), 129.7 (d), 128.6 (d), 122.9 (d of d), 28.8 (t of m, $-CH_2CH_2-$). ^{31}P NMR (CH_2Cl_2, ppm): −34.5 (s, dppe), −145.0 (septet, PF_6^-). UV−vis (CH_3CN, nm (ϵ): 224 (84 000), 264 (22 000), 368 (8 600), 446 (11 000).

The second major band was peach-colored and eluted with 10:1 CH_3CN/ethanol as $[Re(4\text{-}NC_6H_4Cl)Cl(dppe)_2]Cl_2$ ((**1-Cl**)Cl_2). Workup was identical to that for (**2-Cl**)Cl, giving a brown product. X-ray-quality brown crystals were obtained by layering pentane over a CH_2Cl_2 solution. Yield: 0.099 mmol, 52%. Anal. Calcd for $ReC_{58}H_{52}Cl_2F_{12}NP_6$: C, 48.58; H, 3.66; N, 0.98; Cl, 4.94. Found: C, 48.33; H, 3.64; N, 1.12; Cl, 4.90. ^1H NMR (CH_2Cl_2, ppm): 7.6−6.95 (m, 40H, Ph), 6.80, 5.62 (d of d, 4H, $-NC_6H_4-$), 3.32 (t, b, $-CH_2CH_2-$). $^{13}C\{^1H\}$ NMR (CH_2Cl_2, ppm): 147.7 (s), 141.2 (s), 133.8 (s), 133.3 (s), 133.0 (s), 130.6 (s), 130.0 (s), 129.7 (s), 127.2 (m), 29.1 (septet, $-CH_2CH_2-$). ^{13}C NMR (CH_2Cl_2, ppm): 147.7 (t), 141.2 (t), 133.8 (d), 133.3 (d), 133.0 (d), 130.6 (d), 130.0 (d of d), 129.7 (d), 127.2 (m, b), 29.1 (t of m, $-CH_2CH_2-$). ^{31}P NMR (CH_2Cl_2, ppm): 9.0 (s, dppe), −145.0 (septet, PF_6^-). UV−vis (CH_3CN, nm (ϵ): 224 (81 000), 254 (60 000), 362 (18 000), 476 (3 000), 562 (230).

Two minor bands were also recovered from the column. The first minor band contained $[ReCl_2(dppe)_2]Cl_2$ ((**3**)Cl), which was isolated by evaporation and precipitated as the PF_6^- salt from ethanol. X-ray-quality brown crystals of $[ReCl_2(dppe)_2](PF_6)_2$ were obtained by layering pentane over a CH_2Cl_2 solution. Yield: 0.008 mmol, 4%. ^1H NMR (CH_2Cl_2, ppm): 16.3 (d, 16H, ortho), 9.60 (s, 8H, methylene), 9.12 (t, 8H, para) and 8.10 (t, 16H, meta). The second minor band to elute was $ReH_4(dppe)_2$ (white), which was characterized by proton NMR. Both of these bands eluted before the major products.

$[Re(NHC_6H_5)Cl(dppe)_2]PF_6$ and $[Re(NC_6H_5)Cl(dppe)_2](PF_6)_2$. A 200 mL ethanol solution of $Re(NC_6H_5)Cl_3(PPh_3)_2$ (0.173 g, 0.191 mmol) was refluxed with 8 equiv of dppe for 48 h under an atmosphere of nitrogen. The solution was filtered to remove any precipitated $[ReO_2(dppe)_2]Cl$ and unreacted dppe, and the dark orange filtrate was rotary-evaporated to dryness. The resulting residue was dissolved in CH_2Cl_2, and the solution was loaded onto a neutral deactivated alumina column. After the column was washed with CH_2Cl_2 to remove excess dppe, 20:1 CH_3CN/ethanol was used to elute $[Re(NHC_6H_5)Cl(dppe)_2]Cl$ ((**2-H**)Cl) as a yellow band. This layer was evaporated, redissolved in a minimum amount of ethanol, and reprecipitated as the PF_6^- salt by addition of excess NH_4PF_6. The tan product was collected and washed with ethanol, hexanes, and diethyl ether. Yield: 0.010 mmol, 5%. ^1H NMR (CD_3CN, ppm): 37.3 (s, b, 1H, NH), 7.4−6.9 (m, 40H, Ph), 6.30 (m, b, 3H, $-NC_6H_5$), 5.15 (m, b, 2H, $-NC_6H_5$), 3.1 (m, b, 8H, $-CH_2CH_2-$).

A last orange band eluted with 10:1 CH_3CN/ethanol as $[Re(NC_6H_5)Cl(dppe)_2]Cl_2$ ((**1-H**)Cl_2). Workup of this band was identical to that of $[Re(NHC_6H_5)Cl(dppe)_2]Cl$, giving a brown product. X-ray-quality brown crystals were obtained by layering pentane over a CH_2Cl_2 solution of the brown product. Yield: 0.092 mmol, 48%. Anal. Calcd for $ReC_{58}H_{53}ClF_{12}NP_6\cdot CH_3CN$: C, 49.99; H, 3.92; N, 1.94; Cl, 2.43. Found: C, 49.75; H, 4.02; N, 1.79; Cl, 2.41. ^1H NMR (CH_2Cl_2, ppm): 7.61 (t, 1H, NC_6H_5 para), 7.55−6.9 (m, 40H, Ph), 6.82 (t, 2H, NC_6H_5 meta), 5.72 (d, 2H, NC_6H_5 ortho), 3.3 (t, b, 8H, $-CH_2CH_2-$).

$[Re(4\text{-}NC_6H_4OCH_3)Cl(dppe)_2](PF_6)_2$ ((1-OMe)$(PF_6)_2$). The complex was prepared according to the procedure for $[Re(NC_6H_5)Cl(dppe)_2]PF_6$ using $Re(4\text{-}NC_6H_4OCH_3)Cl_3(PPh_3)_2$ as the starting material to give the brown product. X-ray-quality crystals were obtained by layering pentane over a CH_2Cl_2 solution of the brown product. Yield: 57%. ^1H NMR (CH_2Cl_2, ppm): 7.60−6.98 (m, 40H, Ph), 6.25 (d, 2H, $-NC_6H_4-$), 5.64 (d, 2H, $-NC_6H_4-$), 3.24 (t, b, $-CH_2CH_2-$), 1.42 (s, 3H, OCH_3).

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[11] Chatt, J.; Rowe, G. A. *J. Chem Soc.* **1962**, 4019. Parshall, G. W. *Inorg. Synth.* **1977**, *17*, 110.

[12] Hearn, M. J.; Magee, D. J.; Alhart, R.; Gleva, M.; Goldstein, S.; Levy, F.; Muenzen, C.; Neuringer, I.; Racin, M.; Rosenberg, J.; Silva, H.; Williams, P. *J. Chem. Eng. Data* **1985**, *30*, 129.

[13] Chatt, J.; Dilworth, J. R.; Leigh, G. J. *J. Chem. Soc. A* **1970**, 2239.

[14] Bakir, M.; Paulson, S.; Goodson, P.; Sullivan, B. P. *Inorg. Chem.* **1992**, *31*, 1127.

Table 1. Crystallographic Data

	(**1-OMe**)$(PF_6)_2$	(**1-Cl**)$(PF_6)_2$	(**1-H**)$(PF_6)_2 \cdot CH_2Cl_2$	(**2-Cl**)PF_6	(**3**)$(PF_6)_2$
formula	$C_{61}H_{58}N_2OF_{12}ClP_6Re$	$C_{58}H_{52}NF_{12}Cl_2P_6Re$	$C_{58}H_{53}NF_{12}ClP_6Re \cdot CH_2Cl_2$	$C_{59}H_{54}NF_6Cl_4P_5Re$	$C_{52}H_{48}F_{12}Cl_2P_6Re$
temp, °C	25	25	25	25	25
MW	1470.61	1433.98	1484.47	1378.98	1343.87
cryst system	triclinic	triclinic	orthorhombic	monoclinic	monoclinic
space group	*P*1	$P\bar{1}$	*Pcab*	*Cc*	$P2_1/c$
a, Å	11.340(3)	11.9403(6)	22.3075(10)	24.2381(11)	11.1953(6)
b, Å	13.134(4)	14.6673(8)	23.1272(10)	13.4504(6)	13.3364(7)
c, Å	13.3796(25)	17.2664(9)	23.3584(10)	17.466(8)	16.9539(9)
α, deg	102.370(20)	92.019(1)			
β, deg	107.688(17)	97.379(1)		97.06900(0)	96.763(1)
γ, deg	114.408(20)	90.134(1)			
V, $Å^3$	1590.7(6)	2996.9(3)	12050.8(9)	5651(3)	2513.69(23)
Z	1	2	8	4	2
D_{calcd}, Mg/m^3	1.535	1.589	1.636	1.621	1.776
F(000)	735.74	1429.30	5926.42	2761.42	1335.25
μ(Mo Kα), mm^{-1}	2.20	2.35	2.39	2.54	2.80
no. of rflns collected	5615	17489	66372	30904	35318
no. of unique reflns	5615	10316	10663	9448	7312
R^a	0.039	0.043	0.057	0.048	0.040
$R_w{}^b$	0.056	0.050	0.044	0.066	0.065
GOF	2.13	2.09	2.77	4.19	2.64

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

Crystallography. Single crystals of $[Re(4\text{-}NC_6H_4OCH_3)Cl(dppe)_2](PF_6)_2$ ((**1-OMe**)$(PF_6)_2$), $[Re(4\text{-}NC_6H_4Cl)Cl(dppe)_2](PF_6)_2$ ((**1-Cl**)$(PF_6)_2$), $[Re(NC_6H_5)Cl(dppe)_2](PF_6)_2$ ((**1-H**)$(PF_6)_2$), $[Re(4\text{-}NHC_6H_4Cl)Cl(dppe)_2]PF_6$ ((**2-Cl**)PF_6), and $[ReCl_2(dppe)_2](PF_6)_2$ ((**3**)$(PF_6)_2$) were grown by layering pentane over CH_2Cl_2 solutions. Intensity data were collected on a Siemens CCD SMART or Rigaku AFC/65 diffractometer with Mo Kα radiation (λ = 0.710 73 Å) and a graphite monochromator using the ω-scan mode. Adsorption corrections were made using SADABS for CCD data and ψ-scans for Rigaku data. The structures were solved by direct methods, and missing non-hydrogen atoms were located in subsequent difference Fourier maps. Structure refinement on F_o was achieved by full-matrix least-squares techniques. During the final least-squares cycles, hydrogen atoms were included in calculated positions and allowed to ride on the atoms to which they were bonded. All computations were performed using the NRCVAX suite of programs. Crystallographic data are given in Table 1.

Catalytic Reactions. Procedures here are identical to the synthetic procedures given above for the amido complexes but with the following additional precautions because acetaldehyde evaporates at 20.8 °C. Each reaction mixture was refluxed under a chilled condenser (−20 °C) and minimal argon flow. After the refluxing period, the reaction solution was allowed to cool and, with the apparatus still intact, the solution flask was immersed in a −20 °C bath. After 20 min, the condenser was emptied of the coolant to allow maximum accumulation of acetaldehyde in a chilled flask. The reaction vessel was then removed from the rest of the apparatus, immediately capped, and stored in a freezer. As needed, a small portion of the chilled reaction solution was quickly filtered and sealed.

For a GC run, the filtered and sealed solution was allowed to warm to room temperature before injection. Organic products were chromatographed at 35 °C on a 4280A Hewlett-Packard gas chromatograph equipped with an HP-FFAP column and mass spectrometer. Hydrogen gas was detected at 30 °C on a 5890A Hewlett-Packard gas chromatograph equipped with a thermal conductivity detector and a 5 Å molecular sieve column using argon carrier gas. Quantitative analysis of an individual GC component was performed by a calibration of standards employing a Hewlett-Packard ChemStation electronic integrator.

Results and Discussion

Synthesis and Structures. The complexes $Re(4\text{-}NC_6H_4R)Cl_3(PPh_3)_2$ were synthesized for R = H, Cl, and OCH_3 according to published procedures;[13,15] we found the phenylhydrazine procedure[13] to provide pure product most consistently. The $Re(4\text{-}NC_6H_4R)Cl_3(PPh_3)_2$ complexes were converted to the corresponding $Re(4\text{-}NC_6H_4R)Cl(dppe)_2{}^{2+}$ salts according to a literature procedure developed[14,16] for the unsubstituted complex. In this protocol, $Re(4\text{-}NC_6H_4R)Cl_3(PPh_3)_2$ is refluxed in ethanol for 20−48 h with an excess of dppe under an inert atmosphere. The imido complex was readily purified by chromatography on alumina in acetonitrile/ethanol. Metathesis to the PF_6^- salts produced analytically pure solids that were air- and moisture-stable for months.

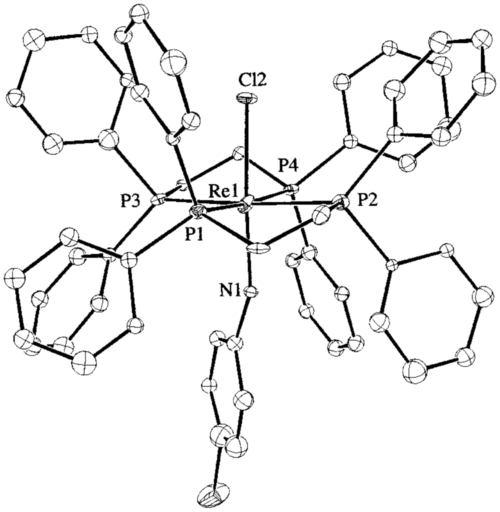

Figure 1. ORTEP drawing (50% probability level for the thermal ellipsoids) of the cation from the X-ray structure of $[Re(4\text{-}NC_6H_4Cl)Cl(dppe)_2](PF_6)_2$ ((**1-Cl**)$(PF_6)_2$). Hydrogen atoms have been omitted.

The PF_6^- complexes of **1-H**, **1-Cl**, and **1-OMe** were characterized by X-ray crystallography (Table 1). The representative structure of the **1-Cl** complex is shown in Figure 1, and the significant bond lengths and angles are given for all three complexes in Table 2. For (**1-H**)$(PF_6)_2$, the bond distances and angles observed were identical to those observed by Bakir et al.[14] The geometry deviates from octahedral symmetry because of axial compression, and the bulky dppe ligands are

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(15) Forsellini, E.; Casellato, U.; Graziani, R.; Carletti, M. C.; Magon, L. *Acta Crystallogr., Sect. C* **1984**, *C40*, 1795. La Monica, G.; Cenini, S. *Inorg. Chim. Acta* **1978**, *29*, 183.

(16) Bakir, M.; McKenzie, J. A. M.; Sullivan, B. P. *Inorg. Chim. Acta* **1997**, *254*, 9.

Table 2. Selective Crystallographic Lengths (Å) and Angles (deg) for $[Re(4\text{-}NC_6H_4R)Cl(dppe)_2](PF_6)_2$ (**1**) and $[Re(NHC_6H_4Cl)(dppe)_2]PF_6$ (**2**)

	1-Cl	**1-H**	**1-OMe**	**2-Cl**
Re−N	1.729(4)	1.721(4)	1.687(9)	1.978(5)
Re−Cl	2.3694(14)	2.3811(14)	2.3878(25)	2.3726(21)
Re−P	2.52, 2.52, 2.53, 2.54	2.49, 2.51, 2.53, 2.54	2.50, 2.51, 2.52, 2.53	2.43, 2.47, 2.47, 2.48
Re−N−PhR	179.0	173.3	175.7	147.0
Cl−Re−N	179.0	175.0	178.1	176.3
Cl−Re−P	84.5, 85.6, 86.4, 88.1	81.5, 82.6, 87.2, 87.7	81.3, 83.4, 83.8, 87.0	84.2, 87.6, 89.2, 91.9

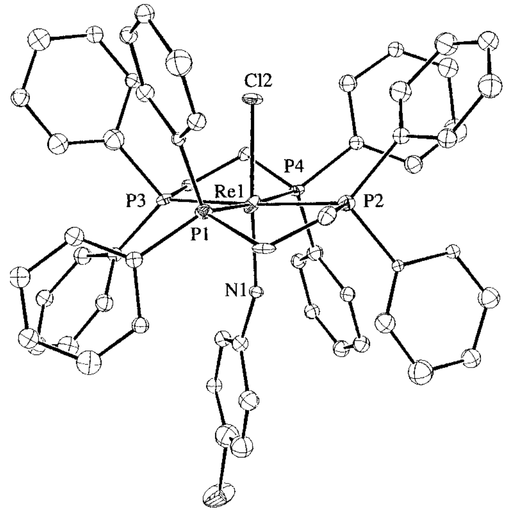

Figure 2. ORTEP drawing (50% probability level for the thermal ellipsoids) of the cation from the X-ray structure of $[Re(4\text{-}NHC_6H_4\text{-}Cl)Cl(dppe)_2]PF_6$ ((**2-Cl**)PF_6). Hydrogen atoms have been omitted.

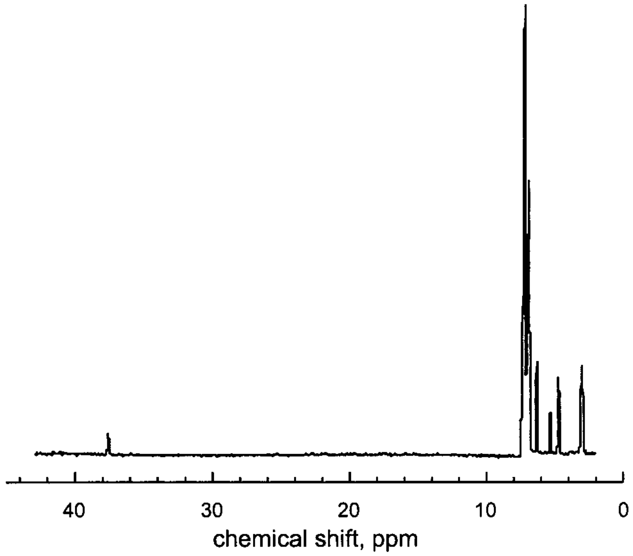

Figure 3. Proton NMR spectrum of $[Re(4\text{-}NHC_6H_4Cl)Cl(dppe)_2]PF_6$ ((**2-Cl**)PF_6) in CD_2Cl_2.

bent away from the imido ligand.[17] The rhenium−phenylimido angle is nearly linear (179° for R = Cl), indicating significant electronic donation from nitrogen to rhenium, resulting in formation of a multiple bond. The similar rhenium imido complexes $[ReNPh(OEt)(bpy)_2](PF_6)_2$[16] and $[ReNPh(OH)(dppb)_2]Cl_2{\cdot}2H_2O$[14] exhibit longer Re−N distances of 1.740(6) and 1.757(10) Å, respectively, due to a greater trans effect of the alkoxo and hydroxo ligands compared to the chloro ligand (dppb = 1,2-bis(diphenyldiphosphino)benzene). The Re−N bond length showed only a modest shortening as the electron-donating ability of R decreased.

From the reaction that produced **1-Cl** was isolated an additional yellow product exhibiting NMR resonances that were shifted from but similar to those of the starting material. This product was crystallized as a PF_6^- salt, and the X-ray crystal data (Table 2) and structure (Figure 2) showed a single counteranion and a bent nitrogen ligand with a Re−N−C angle of 150°. The Re−N distance of 1.98 Å was considerably longer than that in **1-Cl**. Although a hydrogen atom bound to the aromatic nitrogen was not located in the X-ray structure, the new complex is assigned as an amidorhenium(III) species, $Re(4\text{-}NHC_6H_4R)Cl(dppe)_2^+$ (**2-Cl**). As discussed below, the NMR spectrum of **2-Cl** exhibits numerous sharp resonances that exclude the possibility of a paramagnetic Re(IV) product. The average Re−P bond length was 2.47 Å, which is an expected value for Re(III)−P.[18] A similar reaction of $Re(NPh)Cl_3(PPh_3)_2$ with dppe produced the unsubstituted amido complex $Re(NHPh)Cl(dppe)_2^+$ (**2-H**), which was not crystallized but was characterized by NMR.

Reaction of **2-Cl** with I_2 cleanly produced **1-Cl** as determined by NMR spectroscopy. Similarly, oxidation of **2-H** produced **1-H**. However, reaction of **1-H** and **1-Cl** with reductants (cobaltocene or Zn/Hg amalgam) produced no reaction, and hydride donors ($NaBH_4$ or $(CH_3CH_2)_3BH$) caused only liberation of the amido ligand as the free aniline derivative.

NMR Properties. The room-temperature ^1H NMR spectrum of **2-Cl** was unusual (Figure 3). Sharp resonances corresponding to the phosphine ligand protons and the phenyl protons on the amido ligand occurred at expected values (slightly shifted compared to those of the imido derivative), but initial attempts to locate and assign the amido NH proton were unsuccessful. In contrast, the ^1H NMR spectra for the analogous amidorhenium complexes $Re(NHPh)(H)_2(P(CH_3)_3)_3$,[19] $[Re(NHPh)I(P(CH_3)_3)_4]I$,[20] and $ReCpNO(NHPh)(PPh_3)$[21] show relatively sharp peaks for NH protons at 2.85, 3.64, and 3.69 ppm, respectively. Eventually, a somewhat broadened singlet was located in the spectrum of **2-Cl** at 37.8 ppm that integrated properly for the single NH proton over a wide concentration range (Figure 3). Lowering the acquisition temperature to −40 °C shifted this peak to 37.3 ppm, a shift that was smaller than and was in a direction opposite to that expected for contact or pseudocontact paramagnetism.[22] For the **2-H** analogue, a similar NH resonance at 37.3 ppm was located and behaved similarly

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[17] Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197. Bright, D.; Ibers, J. A. *Inorg. Chem.* **1968**, *7*, 1099. Bright, D.; Ibers, J. A. *Inorg. Chem.* **1969**, *8*, 703. Bright, D.; Ibers, J. A. *Inorg. Chem.* **1969**, *8*, 709.

[18] Aslanov, L.; Mason, R.; Wheeler, A. G.; Whimp, P. O. *J. Chem Soc., Chem. Commun.* **1970**, 30.

[19] Chiu, K. W.; Wong, W.-K.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *Polyhedron* **1982**, *1*, 37.

[20] Chiu, K. W.; Howard, C. G.; Rzepa, H. S.; Sheppard, R. N.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *Polyhedron* **1982**, *1*, 441.

[21] Dewey, M. A.; Knight, D. A.; Arif, A.; Gladysz, J. A. *Chem. Ber.* **1992**, *125*, 815.

[22] (a) Randall, E. W.; Shaw D. *J. Chem. Soc. A* **1969**, 2867. (b) Chatt, J.; Leigh, G. J.; Mingos, D. M. P.; Randall, E. W.; Shaw, D. *J. Chem. Soc., Chem. Commun.* **1968**, 419. (c) Chatt, J.; Leigh, G. J.; Mingos, D. M. P. *J. Chem. Soc. A* **1969**, 1674. (d) Gunz, H. P.; Leigh, G. J. *J. Chem. Soc. A* **1971**, 2229. (e) Chatt, J.; Leigh, J.; Mingos, D. M. P.; Paske, R. J. *J. Chem. Soc. A* **1968**, 2636.

with respect to concentration and temperature. Addition of D_2O to the solution caused the resonance to diminish, indicating exchange with solvent deuterons.

Large, temperature-independent shifts are known to occur in the spectra of pseudooctahedral d^4 rhenium complexes as well as those of other low-spin d^4 metals and are attributable to second-order paramagnetism.[22] Although these complexes are diamagnetic in the ground state, large spin−orbit coupling parameters (2500 cm^{-1} for Re)[22] allow for anisotropy in the ligand fields via second-order paramagnetism. Proton resonances that are sharp but shifted dramatically downfield are observed for other Re(III) complexes;[22] however, the specific directionality observed for **2-H** and **2-Cl** is unusual. In the other Re(III) complexes exhibiting shifted resonances, the paramagnetism influences many protons in all directions,[22] whereas the only shifted resonances for **2-H** and **2-Cl** are those due to the NH protons. Thus, the second-order paramagnetism is strongly focused along the axially compressed *z* axis. The small decrease in NMR shift with decreasing temperature is observed because, at lower temperatures, fewer vibrational levels are occupied, energy separation increases, and mixing of the paramagnetic level decreases.[22]

A paramagnetic Re(III) nucleus shortens the relaxation time of bonded phosphorus nuclei, and second-order paramagnetic complexes traditionally exhibit undetectable, heavily shifted, or broadened phosphorus peaks.[23] For example, $ReCl_3(P(CH_3)_2Ph)_3$[22a] exhibits broad ^{31}P NMR peaks at 3420 and 4212 ppm and *mer*-$ReCl_3(PCH_3Ph_2)_3$ exhibits[24] significantly broadened phosphorus resonances. In contrast, the ^{31}P NMR spectrum of **2-Cl** shows a single sharp phosphorus peak at −34.5 ppm (44.4 Hz) that resembles the resonance for the corresponding **1-Cl**, which occurs at 9.0 ppm (10.0 Hz). Apparently, the second-order paramagnetism does not affect the ligands in the *xy* plane that are not on the compressed amido axis.

Carbon and proton-gated carbon NMR spectra were obtained for **1-Cl** and **2-Cl** because we suspected that the resonance for the ipso carbon in **2-Cl** should also be highly shifted downfield. Indeed, the ^{13}C spectrum of **1-Cl** showed no unusual resonances and the spectrum of **2-Cl** exhibited a shifted peak at 177.3 ppm for the ipso phenylamido carbon, which is well outside of the normal range for sp^2 carbons.[25] The ^{13}C resonances for the other phenylimido carbons and phosphine carbons in **2-Cl** were unremarkable. Only two Re(III) complexes, $ReCl_3(PEt_2Ph)_3$ and $ReCl_3(P^nPr_2Ph)_3$, have previously been characterized by ^{13}C NMR.[26] Both exhibit numerous significantly shifted and broadened carbon resonances, and the ipso carbons of the phosphine ligands are undetectable.

Catalytic C−H Activation. Chatt and Shaw previously noted the possibility of hydride and carbonyl formation when a transition metal halide complex with tertiary phosphine ligands is in contact with an alcoholic medium, especially if the conditions are vigorous.[27] Solutions obtained after refluxing the imidorhenium(V) starting material with dppe were analyzed by GC-MS, and catalytic amounts of acetaldehyde and acetal were detected and verified by coelution with authentic samples. The acetal presumably forms via reaction of produced acetaldehyde with the ethanol solvent. Quantification of acetaldehyde and acetal indicated 30 mol equiv of oxidation products, i.e., (mol of acetal + mol of acetaldehyde)/mol of rhenium, for the **1-Cl** reaction and 16 equiv for the **1-H** reaction. Hydrogen gas was also detected in the head gas of the reaction mixture by GC and identified by coelution with an authentic sample. Periodic samplings from a sealed reaction system showed increasing hydrogen gas in the same quantity as acetal + acetaldehyde. These observations suggest that the rhenium system catalyzes the equilibrium

Table 3. Combined Moles of Acetaldehyde and Acetal Per Mole of Rhenium Starting Material under Various Reaction Conditions

conditions[a]	turnovers
$Re(4\text{-}NC_6H_4Cl)Cl_3(PPh_3)_2$ + 8dppe	29
$Re(4\text{-}NC_6H_4Cl)Cl_3(PPh_3)_2$ + 8dppe + excess H_2	16
$Re(4\text{-}NC_6H_4Cl)Cl_3(PPh_3)_2$ + dppe	<1
$Re(4\text{-}NC_6H_4Cl)Cl_3(dppe)$	0
$Re(4\text{-}NC_6H_4Cl)Cl_3(dppe)$ + 8dppe	21
$Re(4\text{-}NC_6H_4Cl)Cl_3(PPh_3)_2$ + 8dmpe	0

[a] Typical procedures are given in the Experimental Section. Unless otherwise noted, conditions were 0.191 mmol of Re and 200 mL of 95% ethanol, refluxed for 48 h under argon.

$$CH_3CH_2OH \rightleftharpoons CH_3CHO + H_2 \qquad (5)$$

In fact, addition of excess H_2 to the reaction solution lowered the quantity of acetal + acetaldehyde (Table 3), as expected. As written, eq 5 is thermodynamically uphill; however, the removal of H_2 in the refluxing medium likely drives the reaction.

The transformation of ethanol to acetaldehyde and hydrogen provided a likely source of the amido proton in **1-Cl** and **1-H**. Use of CH_3CD_2OH solvent produced CH_3CDO and $(CH_3CD_2O)_2(CH_3)CD$ but gave no deuterated amido nitrogen that could be detected by ^2D NMR. However, the methylene protons of ethanol cannot be discounted as a source because the catalysis requires water that exchanges with the amido deuteron.

The substrate oxidation was specific to ethanol and the presence of water. Reaction in 95% 2-propanol did not produce acetone, even when combined with ethanol for better solubility. Performing the reaction in dried absolute ethanol also gave no experimentally significant quantities of the oxidation products. Using 80% or 99% ethanol reduced the yield of acetaldehyde in both cases, probably because of changes in the water-dependent equilibrium of acetaldehyde−acetal exchange in ethanol. Detectable formation of acetic acid did not occur in any case.

A number of experiments were performed to determine the nature of the catalyst (Table 3). Small amounts of two additional rhenium-containing products were detected in the reaction. The $ReH_4(dppe)_2^+$ complex was detected by its characteristic NMR quintet at −5.4 ppm.[28] The $ReCl_2(dppe)_2^{2+}$ complex (**3**) was also isolated and characterized by X-ray crystallography; the structure was similar to that of an analogous complex of a related phosphine.[29] The yield of each of these products was less than 5% based on the total rhenium. Each of the detected metal-containing products (**1-Cl**, **2-Cl**, $ReH_4(dppe)_2^+$, or **3**) was refluxed with dppe in ethanol and produced no acetaldehyde or acetal. Addition of only 1 equiv of dppe to $Re(4\text{-}NC_6H_4Cl)Cl_3(PPh_3)_2$ did not lead to acetaldehyde formation. The complex bearing a single diphosphine ligand, $Re(4\text{-}NC_6H_4Cl)Cl_3(dppe)$,[13] was prepared and refluxed in ethanol without added dppe, which

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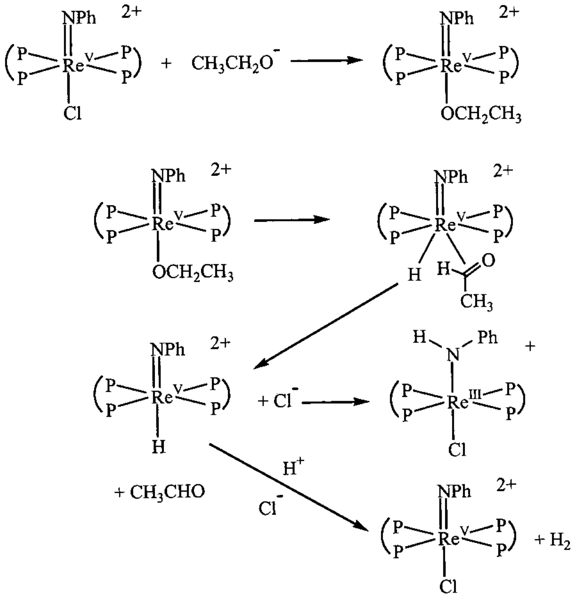
(23) Randall, E. W.; Shaw, D. *Mol. Phys.* **1965**, *10*, 41.
(24) Cotton, F. A.; Luck, R. L. *Inorg. Chem.* **1989**, *28*, 2181.
(25) Drago, R. S. *Physical Methods in Chemistry*; Harcourt Brace Jovanovich: Orlando, Fl, 1992; Chapter 7.
(26) Mitsopoulou, C. A.; Mahieu, N.; Motevalli, M.; Randall, E. W. *J. Chem. Soc., Dalton Trans.* **1996**, 4563.
(27) Chatt, J.; Shaw, B. L. *Chem. Ind.* **1961**, 290. Chatt, J.; Shaw, B. L.; Field, A. E. *J. Chem. Soc.* **1964**, 3466.
(28) Freni, M.; Demichelis, R.; Giusto D. *J. Inorg. Nucl. Chem.* **1967**, *29*, 1433.
(29) Cotton, F. A.; DeCanio, E. C.; Kibala, P. A.; Vidyasagar, K. *Inorg. Chim. Acta* **1991**, *184*, 221.

produced no oxidation products; addition of excess dppe initiated catalysis to produce 21 turnovers. Therefore, formation of the catalyst appears to require both diphosphine ligands. Replacement of dppe with the less bulky 1,2-bis(dimethylphosphino)-ethane (dmpe) produced no reaction.

The detection of rhenium hydrides, the failure of **1** to react with hydride donors to form **2**, and the inertness of **2** toward ethanol oxidation suggest that the oxidation of ethanol occurs through a metal hydride intermediate rather than by direct addition of a hydride ion or a hydrogen atom to the imido nitrogen. A logical reaction course would be coordination of ethoxide, which then undergoes β-elimination to produce coordinated acetaldehyde and hydride (eqs 6 and 7). A similar β-elimination from coordinated methoxide to form formaldehyde is known in platinum chemistry.[8] Following loss of acetaldehyde, migration of hydride to the imido ligand produces the amido complex, which is not catalytically active (eq 8).



(6)

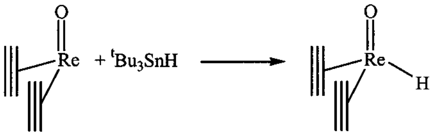
(7)

(8)

Alternatively, the metal hydride complex can be protonated to produce dihydrogen and the starting imido complex, restarting the catalytic cycle.[9] Reaction of **2-Cl** or **2-H** with acids did not produce hydrogen gas. Performing the reaction in the presence of added aniline did not increase the amount of oxidation product, so the nitrogen ligand likely remains coordinated throughout the catalytic process.

The collective evidence supports a mechanism of ethanol oxidation by **1** that does not involve formal reduction of the metal. This observation counters the intuitive notion that a Re(V) complex like **1** is likely to be an oxidant. In fact, the π-donation from the imido ligand and the associated electronic stabilization resulting from the doubly occupied d_{xy} orbital creates a very stable oxidation state.[7,30] Other axially compressed complexes of Re(V) are similarly inert.[31] Although this feature has prohibited the development of strong oxidants based on Re(V),[32] the stabilization permits the catalysis observed here by allowing for reactions that do not change the oxidation state, such as eq 7 and the subsequent protonation of the metal hydride. In fact, the reduction to Re(III) likely halts the catalytic cycle, so in this case, action of Re(V) as an oxidant is deleterious to catalytic activity. These studies suggest that, instead of providing a robust oxidant, a multiply bonded, high-valent metal center can provide a robust site for C−H bond activation at the metal, as observed for generally lower-valent complexes.[8−10]

An interesting parallel exists between these findings and the observations of Conry and Mayer on the reaction of low-valent Re−oxo complexes with hydrogen atom donors.[10] In Mayer's study, Re(II)−O complexes were observed to abstract hydrogen atoms to from metal hydrides:



In this reaction, the hydrogen atom donation also occurs at the metal rather than at the oxo ligand, although such a reaction for low-valent Re(II) is perhaps more readily understood than the reaction here for Re(V). Nonetheless, electrochemical and photochemical studies have shown that many Re(V) complexes are better reductants than oxidants,[30−32] which, as has been noted elsewhere, is an indicator that observed hydrogen atom transfer reactivity is likely to occur at the metal.[5]

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Supporting Information Available: X-ray crystallographic files, in CIF format, for the hexafluorophosphate salts of **1-Cl**, **1-H**, **1-OMe**, **2-Cl**, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(30) Brewer, J. C.; Thorp, H. H.; Slagle, K. M.; Brudvig, G. W.; Gray, H. B. *J. Am. Chem. Soc.* **1991**, *113*, 3171.

(31) Brewer, J. C.; Gray, H. B. *Inorg. Chem.* **1989**, *28*, 3334.

(32) Thorp, H. H.; Van Houten, J.; Gray, H. B. *Inorg. Chem.* **1989**, *28*, 889.