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Metal-Mediated Reduction of Alkanenitriles to Imido Ligands. Formation of the Imido Complexes $Re(NCH_2R)X_3(dppbe)$ (R = Me, Et, *i*-Pr; X = Cl, Br) from the Reactions of the Octahalodirhenate(III) Anions with 1,2-Bis(diphenylphosphino)benzene in Nitrile Solvents (RCN)

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The reactions of $(n\text{-}Bu_4N)_2Re_2X_8$ (X = Cl, Br) with the bidentate phosphine ligand 1,2-bis(diphenylphosphino)benzene (dppbe) in hot methanol afford the mononuclear rhenium(III) complexes *trans*-$[ReCl_2(dppbe)_2]Cl\cdot 4H_2O$ and *trans*-$[ReBr_2(dppbe)_2]Br$. When similar reactions are carried out in hot nitrile solvents RCN (R = Me, Et for X = Cl; R = Me, Et, *i*-Pr for X = Br) that contain a few drops of concentrated HX, the mononuclear (alkylimido)rhenium(V) complexes $Re(NCH_2R)X_3(dppbe)$ are usually formed. The only exception is the reaction between $(n\text{-}Bu_4N)_2Re_2Cl_8$ and dppbe in acetonitrile, which affords *trans*-$ReCl_2(dppbe)_2$. The structure of this complex was established by X-ray crystallography. It crystallizes in the monoclinic space group $P2_1/n$ with $a = 10.856$ (1) Å, $b = 12.664$ (1) Å, $c = 18.169$ (2) Å, $\beta = 91.09$ (1)°, $V = 2497.6$ (7) Å^3, and $Z = 2$. The structure was refined to $R = 0.029$ ($R_w = 0.035$) for 2450 data with $I > 3.0\sigma(I)$. The formation of the (alkylimido)rhenium(V) complex $Re(NCH_2Et)Cl_3(dppbe)$ also occurs upon reacting the preformed dirhenium(II) complex α-$Re_2Cl_4(dppbe)_2$ with propionitrile and concentrated HCl. This result suggests that the latter complex, which is prepared by reacting $Re_2Cl_4(P\text{-}n\text{-}Pr_3)_4$ with dppbe in benzene or toluene, is a likely intermediate in the conversion of $(n\text{-}Bu_4N)_2Re_2Cl_8$ to $Re(NCH_2Et)Cl_3(dppbe)$. It is likely that α-$Re_2Cl_4(dppbe)_2$ undergoes intramolecular disproportionation followed by cleavage of the Re–Re bond to give mononuclear Re(I) and Re(III) species and that the former species provides the four electrons necessary for the reduction of the nitrile ligand. The characterization of the alkylimido complexes has included measurement of their ^1H and $^{31}P\{^1H\}$ NMR spectra and their electrochemical properties (using the cyclic voltammetric technique). X-ray crystallographic studies on $Re(NCH_2Et)X_3(dppbe)$ (X = Cl, Br) have shown that the complexes contain similar pseudooctahedral structures with an axial *n*-propylimido ligand trans to a Re–X bond and a chelating dppbe ligand and a pair of cis Re–X bonds occupying the equatorial plane. Crystal data for $Re(NCH_2Et)Cl_3(dppbe)$ at 20 ± 1 °C are as follows: monoclinic space group $P2_1/m$, $a = 10.877$ (3) Å, $b = 16.881$ (2) Å, $c = 11.199$ (4) Å, $\beta = 115.24$ (1)°, $V = 1860$ (2) Å^3, and $Z = 2$. The structure was refined to $R = 0.032$ ($R_w = 0.043$) for 2300 data with $I > 3.0\sigma(I)$. Crystal data for $Re(NCH_2Et)Br_3(dppbe)$ at 22 ± 1 °C are as follows: monoclinic space group $P2_1/c$, $a = 16.677$ (2) Å, $b = 10.852$ (2) Å, $c = 18.382$ (4) Å, $\beta = 95.81$ (1)°, $V = 3310$ (2) Å^3, and $Z = 4$. The structure was refined to $R = 0.055$ ($R_w = 0.079$) for 3135 data with $I > 3.0\sigma(I)$. The linearity of the Re–N–C unit (175.4 (5) and 178.7 (8)° for X = Cl and Br, respectively) and the shortness of the Re–N bond (1.699 (5) and 1.719 (8) Å for X = Cl and Br, respectively) are consistent with a description of the (alkylimido)rhenium unit as $Re\equiv N\text{—}CH_2R$. For both complexes, refinement of the alkyl chain was complicated by a disorder of this $CH_2CH_2CH_3$ fragment about the trans axial X–Re–N–C unit.

Introduction

As part of our studies dealing with the synthetic and structural chemistry of the α- and β-isomers of the type $M_2X_4(LL)_2$ (M = Mo, Re; X = Cl, Br; LL = bidentate phosphine ligand), in which the ligands LL either chelate the individual metal atoms (α-isomers) or bridge the dimetal unit (β-isomers),[1,2] we have examined the reactivities of salts of the $[Mo_2X_8]^{4-}$ anions (X = Cl, Br) with the ligand 1,2-bis(diphenylphosphino)benzene (abbreviated dppbe).[3] Whereas mild reaction conditions (room temperature, methanol as solvent) afford α-$Mo_2X_4(dppbe)_2$, more forcing reaction conditions (refluxing 1-propanol) give mononuclear *trans*-$MoX_2(dppbe)_2$ in good yield.[3] An examination of the reactions between $(n\text{-}Bu_4N)_2Re_2X_8$ (X = Cl, Br) and dppbe in alcohol and nitrile solvents has likewise revealed a propensity for metal–metal bond cleavage to occur. Although the species *trans*-$[ReX_2(dppbe)_2]^+$ are formed when alcohol solvents are used, we find that when these reactions are carried out in organic nitriles (RCN), the alkylimido species $Re(NCH_2R)X_3(dppbe)$ are major products. These latter species are formed by novel redox reactions. The details of this chemistry are now reported, including the structure determinations of *trans*-$ReCl_2(dppbe)_2$ and $Re(N\text{-}n\text{-}Pr)X_3(dppbe)$ (X = Cl, Br). A few of these results have been the subject of a preliminary report.[4]

Experimental Section

Starting Materials. The following compounds were prepared by standard procedures: $(n\text{-}Bu_4N)_2Re_2X_8$ (X = Cl or Br)[5,6] and $Re_2Cl_4(P\text{-}n\text{-}Pr_3)_4$.[7] The ligand 1,2-bis(diphenylphosphino)benzene was purchased from Strem Chemical Co. and used as received. The organic nitriles and all other solvents were purchased from commercial sources and thoroughly deoxygenated prior to use.

Reaction Procedures. All reactions were performed under a nitrogen atmosphere by using standard vacuum-line techniques.

A. Synthesis of α-$Re_2Cl_4(dppbe)_2$. A mixture of $Re_2Cl_4(P\text{-}n\text{-}Pr_3)_4$ (0.20 g, 0.17 mmol), dppbe (0.30 g, 0.67 mmol), and benzene (10 mL) was refluxed for 24 h. The resulting reaction mixture was allowed to cool to room temperature. The green solid was filtered off, washed with benzene, hexanes, and diethyl ether, and dried; yield 0.08 g (33%). Anal. Calcd for $C_{64.5}H_{52.5}Cl_4P_4Re_2$ (i.e. $Re_2Cl_4(dppbe)_2\cdot 0.75C_6H_6$): C, 52.85; H, 3.61; Cl, 9.67. Found: C, 52.79; H, 4.01; Cl, 9.65.

As an alternative procedure, toluene was used as the reaction solvent in place of benzene and the reaction time was increased to 2 days. The green solid was filtered off, washed with toluene and ethanol, and dried; yield 53%. Anal. Calcd for $C_{63.5}H_{52}Cl_4P_4Re_2$ (i.e., $Re_2Cl_4(dppbe)_2\cdot 0.5C_7H_8$): C, 52.48; H, 3.61. Found: C, 52.64; H, 3.90. The presence of half a molecule of toluene of crystallization was confirmed by ^1H NMR spectroscopy (in CD_2Cl_2).

B. Reactions of $(n\text{-}Bu_4N)_2Re_2X_8$ (X = Cl, Br) with 1,2-Bis(diphenylphosphino)benzene in Alcohol Solvents. (i) *trans*-$[ReCl_2(dppbe)_2]Cl\cdot 4H_2O$. A mixture of $(n\text{-}Bu_4N)_2Re_2Cl_8$ (0.10 g, 0.09 mmol), dppbe (0.17 g, 0.38 mmol), and methanol (10 mL) was refluxed for 3 days. The resulting reaction mixture was cooled to room temperature, and the yellow filtrate was evaporated to dryness. The yellow residue was recrystallized from dichloromethane/diethyl ether to afford yellow crystals of *trans*-$[ReCl_2(dppbe)_2]Cl\cdot 4H_2O$, yield 0.08 g (38%). Anal. Calcd for $C_{60}H_{56}Cl_3O_4P_4Re$: C, 57.31; H, 4.49. Found: C, 57.35; H, 4.02. The hydrate is formed because of the presence of adventitious water in the solvent. The IR spectrum (Nujol mull) of this product showed ν(OH) at 3310 and 3665 cm^{-1}. Similar procedures with ethanol or 1-propanol as reaction solvents (reaction times of 3 days and 1 h, respectively) gave an identical product in yields of 29% and 24%, respectively.

(ii) *trans*-$[ReBr_2(dppbe)_2]Br$. A mixture of $(n\text{-}Bu_4N)_2Re_2Br_8$ (0.20 g, 0.13 mmol), dppbe (0.24 g, 0.54 mmol), methanol (10 mL), and 10 drops of aqueous HBr (48%) was refluxed for 4 days. The resulting

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reaction mixture was cooled to room temperature and filtered. The filtrate was evaporated to dryness and the residue recrystallized from CH_2Cl_2/diethyl ether. The orange product that resulted was filtered off, washed with H_2O, hexanes, and diethyl ether, and dried; yield 0.07 g (40%). Anal. Calcd for $C_{60}H_{48}Br_3P_4Re$: C, 54.62; H, 3.67. Found: C, 54.13; H, 3.76.

The use of methanol (in the absence of 48% HBr) or ethanol as reaction solvents gave the same product in isolated yields of 28% and 48%, respectively.

C. Reactions of $(n\text{-}Bu_4N)_2Re_2X_8$ (X = Cl, Br) with 1,2-Bis(diphenylphosphino)benzene in Nitrile Solvents. (i) *trans*-$ReCl_2$(dppbe)$_2$. A mixture of $(n\text{-}Bu_4N)_2Re_2Cl_8$ (0.06 g, 0.05 mmol), dppbe (0.10 g, 0.22 mmol), and acetonitrile (10 mL) was refluxed in the presence of a pine boiling stick for 12 h. The resulting reaction mixture was cooled to room temperature. A red-orange crystalline product was filtered off, washed with acetonitrile, hexanes, and diethyl ether, and dried; yield 0.05 g (51%). Anal. Calcd for $C_{60}H_{48}Cl_2P_4Re$: C, 62.66; H, 4.40. Found: C, 62.60; H, 4.40.

Even when this reaction was carried out in the presence of a small amount of concentrated aqueous HCl, the rhenium(V)–imido complex $Re(NCH_2CH_3)Cl_3$(dppbe) was not formed. This reaction course contrasts with that of the analogous bromide (see procedure C(iii)).

The complex *trans*-$ReCl_2$(dppbe)$_2$ was found to react with CCl_4 to form yellow *trans*-[$ReCl_2$(dppbe)$_2$]Cl. A mixture of these red-orange crystals (0.05 g, 0.04 mmol), CCl_4 (10 mL), and dichloromethane (5 mL) was refluxed for 2 days and then allowed to cool to room temperature. The yellow solution was reduced in volume, and diethyl ether was added to precipitate a yellow product. This was filtered off, washed with hexanes and diethyl ether, and dried; yield 0.05 g (97%). The product was identified as [$ReCl_2$(dppbe)$_2$]Cl on the basis of its electrochemical properties and IR spectrum.

(ii) $Re(NCH_2CH_2CH_3)Cl_3$(dppbe)·CH_2Cl_2. A mixture of $(n\text{-}Bu_4N)_2Re_2Cl_8$ (0.100 g, 0.088 mmol), dppbe (0.137 g, 0.308 mmol), and aqueous HCl (2 drops, 12 N) was refluxed in propionitrile (10 mL) for 20 h. The reaction mixture was cooled to room temperature and filtered. The filtrate was evaporated to dryness, and the residue was extracted with dichloromethane (25 mL). The resulting solution was layered with diethyl ether (40 mL) and stored in the freezer. After 1 week purple crystals had formed. The crystals were filtered off, washed with diethyl ether (10 mL), and dried in vacuo; yield 0.008 g (11%). Anal. Calcd for $C_{34}H_{33}Cl_5NP_2Re$: C, 46.35; H, 3.77. Found: 46.73; H, 3.96. ^1H NMR spectral measurements (in $CDCl_3$) confirmed the presence of 1 equiv of dichloromethane. Further identification of this complex was based on a single-crystal X-ray structure analysis on a batch of crystals grown from chloroform (vide infra).

When concentrated aqueous HCl was not added to the reaction mixture, the product was orange crystalline *trans*-$ReCl_2$(dppbe)$_2$, yield 50% (see procedure C(i)).

(iii) $Re(NCH_2CH_3)Br_3$(dppbe)·0.5$CHCl_3$. A mixture of $(n\text{-}Bu_4N)_2Re_2Br_8$ (0.103 g, 0.069 mmol), dppbe (0.122 g, 0.273 mmol), and 2 drops of aqueous HBr (48%) in acetonitrile (10 mL) was refluxed for 20 h. After the reaction mixture was allowed to cool to room temperature, a dark green solid was collected by filtration. This green solid was then dissolved in chloroform (25 mL) and layered with ethanol (90 mL), and the solution was placed in the freezer for 5 days. The purple crystals that formed were filtered off, washed with ethanol (ca. 10 mL), and dried in vacuo; yield 0.021 g (17%). Anal. Calcd for $C_{32.5}H_{30.5}Br_3Cl_{1.5}NP_2Re$: C, 40.03; H, 3.05. Found: C, 40.48; H, 3.12.

(iv) $Re(NCH_2CH_2CH_3)Br_3$(dppbe). This complex was prepared from the reaction between $(n\text{-}Bu_4N)_2Re_2Br_8$, dppbe, and propionitrile (acidified with 48% HBr), with the use of a procedure analogous to that in section C(ii); yield 34%. The identity of this product was established by X-ray crystallography (vide infra).

(v) $Re(NCH_2CH(CH_3)_2)Br_3$(dppbe). This complex was prepared with the use of a procedure analogous to that in section C(iii); yield 37%. Anal. Calcd for $C_{34}H_{33}Br_3NP_2Re$: C, 43.28; H, 3.53. Found: C, 42.74; H, 3.72.

D. Reactions of α-Re_2Cl_4(dppbe)$_2$. (i) Propionitrile. A mixture of α-Re_2Cl_4(dppbe)$_2$ (0.037 g, 0.026 mmol) and 2 drops of aqueous HCl (12 N) was refluxed in propionitrile (8 mL) for 24 h. The mixture was cooled to room temperature and filtered. The filtrate was evaporated to dryness and the residue extracted into dichloromethane (20 mL). The purple complex $Re(NCH_2CH_2CH_3)Cl_3$(dppbe) was precipitated by the addition of ethanol (40 mL). The complex was recrystallized from dichloromethane/ethanol; yield 0.0125 g (30%). The spectroscopic and electrochemical properties of this complex were identical with the properties of the sample prepared in procedure C(ii).

(ii) 1,2-Bis(diphenylphosphino)benzene. A mixture of α-Re_2Cl_4(dppbe)$_2$ (0.098 g, 0.069 mmol), 1 equiv of dppbe (0.0305 g, 0.068 mmol), and 2 drops of aqueous HCl (12 N) in propionitrile (10 mL) was refluxed for 18 h. The mixture was cooled to room temperature. An orange powder was collected by filtration, washed with diethyl ether, and dried in vacuo. The orange compound was identified as *trans*-$ReCl_2$(dppbe)$_2$ on the basis of its electrochemical properties; yield 0.058 g (36%).

Table I. Crystallographic Data for *trans*-$ReCl_2$(dppbe)$_2$ (**1**), $Re(NC_3H_7)Cl_3$(dppbe)·$CHCl_3$ (**2**), and $Re(NC_3H_7)Br_3$(dppbe) (**3**)

	1	**2**	**3**
chem formula	$ReCl_2P_4C_{60}H_{48}$	$ReCl_6P_2NC_{34}H_{32}$	$ReBr_3P_2NC_{33}H_{31}$
a, Å	10.856 (1)	10.877 (3)	16.677 (2)
b, Å	12.664 (1)	16.881 (2)	10.852 (2)
c, Å	18.169 (2)	11.199 (4)	18.382 (4)
β, deg	91.09 (1)	115.24 (1)	95.8 (1)
V, Å^3	2497.6 (7)	1860 (2)	3310 (2)
Z	2	2	4
fw	1150.05	915.51	929.50
space group	$P2_1/n$ (No. 14)	$P2_1/m$ (No. 11)	$P2_1/c$ (No. 14)
T, °C	20 ± 1	20 ± 1	22 ± 1
λ, Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
ρ_{calcd}, g cm^{-3}	1.529	1.635	1.833
μ(Mo Kα), cm^{-1}	27.38	38.55	74.26
transm coeff	1.000–0.567	1.000–0.646	1.000–0.763
R^a	0.029	0.032	0.055
$R_w{}^b$	0.035	0.043	0.079

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

The purple complex $Re(NCH_2CH_2CH_3)Cl_3$(dppbe) was isolated from the reaction filtrate as in procedure D(i); yield 0.032 g (29%).

E. Reduction of *trans*-[$ReCl_2$(dppbe)$_2$]Cl·4H_2O to *trans*-$ReCl_2$(dppbe)$_2$. A small quantity of *trans*-[$ReCl_2$(dppbe)$_2$]Cl·4H_2O (0.07 g, 0.06 mmol) was heated in acetonitrile (10 mL) for 2 days in the presence of a pine boiling stick. Orange crystals of *trans*-$ReCl_2$(dppbe)$_2$ formed on the stick and the sides of the reaction vessel. The resulting reaction mixture was filtered while hot, and the orange crystals were washed with acetonitrile, dichloromethane, and diethyl ether and then dried; yield 0.02 g (31%). This product was identified as *trans*-$ReCl_2$(dppbe)$_2$ on the basis of its electrochemical properties.

The yellow filtrate was evaporated to dryness and the residue recrystallized from dichloromethane. The yellow crystals, which were identified as unreacted *trans*-[$ReCl_2$(dppbe)$_2$]Cl·4H_2O, were filtered off, washed with diethyl ether, and dried; yield 0.04 g (57%).

Preparation of Single Crystals of *trans*-$ReCl_2$(dppbe)$_2$ (1), $Re(NC_3H_7)Cl_3$(dppbe) (2), and $Re(NC_3H_7)Br_3$(dppbe) (3). Crystals of complex **1** were harvested directly from the preparative reaction mixture (procedure C(i)). In the case of **2**, suitable crystals were obtained by the slow evaporation of a chloroform solution of this complex. The bromide analogue **3** was obtained as single crystals by the slow diffusion of a CH_2Cl_2 solution of this complex into ethanol. After several days, purple crystals of **3** had deposited on the walls of the glass vessel.

X-ray Crystallographic Procedures. The structures of **1**–**3** were determined by the application of standard procedures. The basic crystallographic data for these three structures are listed in Table I. The cell parameters are based on 25 reflections with $19.3 < \theta < 21.2°$ for **1**, $21.0 < \theta < 23.0°$ for **2**, $17.0 < \theta < 22.1°$ for **3**. Three standard reflections were measured every 5000 s of beam exposure during data collection and displayed no systematic variations in intensity. Calculations were performed on a MicroVAX computer using the Enraf-Nonius structure determination package.

The structures were solved by the use of the Patterson heavy-atom method, which revealed the positions of the Re atoms. The remaining atoms were located in succeeding difference Fourier syntheses. Lorentz and polarization corrections were applied to the data. In all instances an empirical absorption correction was applied,[8] the linear absorption coefficients being 27.38 (for **1**), 38.55 (for **2**), and 74.26 cm^{-1} (for **3**). No corrections were made for extinction. The structures were refined by full-matrix least-squares techniques where the function minimized was $\sum w(|F_o|-|F_c|)^2$, where *w* is a weighting factor defined as $w = 1/\sigma^2(F_o)$. For all three structures, positions for hydrogen atoms of the phenyl rings were calculated by assuming idealized geometry and a C–H bond distance of 0.95 Å. Hydrogens were also included for the *n*-propyl group of the disordered imido ligand of **2** but not for its bromide analogue **3** (vide infra). In the case of **1** and **3**, we assigned arbitrary values for

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Table II. Positional Parameters and Equivalent Isotropic Displacement Parameters ($Å^2$) for the Non-Phenyl Atoms of **1** and Their Estimated Standard Deviations[a]

atom	*x*	*y*	*z*	*B*
Re	0	0	0	2.101 (6)
Cl	0.2003 (1)	0.0154 (1)	0.05915 (8)	3.49 (3)
P(1)	0.1100 (1)	0.0642 (1)	−0.10635 (8)	2.44 (3)
P(2)	−0.0169 (1)	0.1872 (1)	0.01850 (8)	2.57 (3)
C(1)	0.1624 (5)	0.2004 (5)	−0.0870 (3)	2.6 (1)
C(2)	0.1120 (5)	0.2533 (5)	−0.0272 (3)	2.8 (1)
C(3)	0.1560 (6)	0.3532 (5)	−0.0094 (4)	3.6 (2)
C(4)	0.2449 (7)	0.4015 (5)	−0.0513 (4)	3.9 (2)
C(5)	0.2890 (6)	0.3515 (5)	−0.1125 (4)	3.8 (2)
C(6)	0.2487 (6)	0.2510 (5)	−0.1303 (3)	3.2 (1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$. Data for the phenyl atoms are available as supplementary material.

B(H), i.e. the isotropic equivalent thermal parameter for the hydrogen atoms, of 5 and 6 $Å^2$, respectively, whereas for **2** we assumed that B(H) was equal to $1.3[B_{eqv}(C)]$ at the time of the inclusion of this parameter in the refinement procedure. While these hydrogen atoms were used in the calculation of F_c, they were not included in the least-squares refinement. For **1** and **2**, all atoms except hydrogen were refined anisotropically. The same was true for **3**, with the exception of carbon atoms C(3), C(4), C(5), and C(6) of the disordered *n*-propylimido ligand (vide infra). Corrections for anomalous scattering were applied to all atoms refined anisotropically.[9]

The structure refinements were routine with two exceptions. During the course of the structure analysis of **2** and **3**, it became apparent that the CH_2CH_3 fragment of the *n*-propylimido ligand was disordered. In both structures, this ligand is contained within a pocket that is formed by two of the phenyl rings of dppbe. For **2**, a model was developed in which this fragment was disordered about the plane that contains the Cl(2)–Re–N(1)–C(1) unit and bisects the bonds C(11)–C(11) and C(13)–C(13) of the C_6H_4 ring of the dppbe ligand. Since the space group for **2** is $P2_1/m$, this requires that the disorder be about the crystallographically imposed mirror plane. Half of the disorder is shown in Figure 2; an equivalent C(1)–C(2)–C(3) chain, related to the first by the mirror plane, represents the other half. Consequently, atoms C(1) and C(2) represent sites of half-occupancy. The full disorder is shown in a figure available as supplementary material. In the case of **3**, a similar model for the disorder was developed, although in this case there is no crystallographically imposed mirror plane. Half of the disorder is shown in Figure 3; the alkyl chain C(2)–C(3)–C(4) represents the other half. The rather large thermal parameters associated with C(3), C(4), C(5), and C(6) reveal some inadequacies in this model. Nonetheless, this is a satisfactory solution overall, one that is fully substantiated by the spectroscopic properties of this complex.

During the course of the structure refinement of **2**, a region of electron density at a nonbonding distance to the rhenium complex was assumed to be lattice chloroform. It was modeled on this assumption with entirely satisfactory results. This solvent molecule is situated on a special position, which exhibits mirror symmetry, and was refined with full occupancy.

The highest peaks in the final difference Fourier maps for **1**–**3** were 1.15, 2.01, and 0.89 e $Å^{-3}$, respectively.

Positional parameters and their errors for the non-phenyl atoms of **1**–**3** are listed in Tables II–IV. Important intramolecular bond distances and angles for **1** are given in Table V, while those for **2** and **3** are compared in Table VI. Tables giving full details of the crystal data and data collection parameters (Tables S1–S3), the non-hydrogen positional parameters (Tables S4–S6), the positional parameters for the hydrogen atoms (Tables S7–S9), the anisotropic thermal parameters (Tables S10–S12), and complete bond distances (Tables S13–S15) and bond angles (Tables S16–S18) are available as supplementary material, as well as figures that show the full atomic numbering schemes for **1** and **3** (Figures S1 and S2) and the disorder of the *n*-propylimido ligand in **2** (Figure S3).

Table III. Positional Parameters and Equivalent Isotropic Displacement Parameters ($Å^2$) for the Non-Phenyl Atoms of **2** and Their Estimated Standard Deviations[a]

atom	*x*	*y*	*z*	*B*
Re	0.92822 (2)	$^3/_4$	0.67465 (3)	2.532 (6)
Cl(1)	1.1068 (1)	0.65228 (9)	0.7351 (1)	3.86 (3)
Cl(2)	0.9606 (2)	$^3/_4$	0.9006 (2)	4.03 (5)
P(1)	0.7542 (1)	0.65478 (9)	0.6503 (1)	2.76 (3)
N(1)	0.8759 (6)	$^3/_4$	0.5084 (5)	2.7 (1)
C(1)	0.818 (1)	$^3/_4$	0.360 (1)	7.1 (3)
C(2)	0.942 (3)	0.772 (2)	0.310 (2)	12.2 (9)
C(3)	1.037 (2)	0.833 (1)	0.346 (2)	8.1 (6)
C(11)	0.6054 (5)	0.7090 (4)	0.6417 (5)	3.2 (1)
C(12)	0.4909 (5)	0.6676 (4)	0.6360 (6)	4.2 (1)
C(13)	0.3790 (5)	0.7087 (5)	0.6308 (6)	4.9 (2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$. Data for the phenyl atoms are available as supplementary material.

Table IV. Positional Parameters and Equivalent Isotropic Displacement Parameters ($Å^2$) for the Non-Phenyl Atoms of **3** and Their Estimated Standard Deviations[a]

atom	*x*	*y*	*z*	*B*
Re	0.74977 (4)	0.08505 (6)	0.29876 (3)	2.69 (1)
Br(1)	0.6450 (1)	−0.0851 (2)	0.3039 (1)	5.49 (5)
Br(2)	0.8525 (2)	−0.0761 (2)	0.2732 (2)	7.73 (7)
Br(3)	0.7837 (1)	0.0520 (2)	0.4365 (1)	5.25 (5)
P(1)	0.8663 (2)	0.2123 (4)	0.2871 (2)	2.58 (8)
P(2)	0.7387 (2)	0.0949 (4)	0.1669 (2)	2.77 (8)
N(1)	0.6857 (7)	0.208 (1)	0.3056 (6)	3.0 (3)
C(2)	0.634 (1)	0.310 (2)	0.311 (1)	6.4 (5)
C(3)	0.577 (3)	0.274 (5)	0.386 (3)	9 (1)*
C(4)	0.519 (5)	0.185 (7)	0.359 (4)	14 (2)*
C(5)	0.544 (4)	0.267 (6)	0.337 (4)	12 (2)*
C(6)	0.517 (4)	0.324 (6)	0.398 (4)	13 (2)*
C(11)	0.8923 (9)	0.194 (1)	0.1939 (8)	2.6 (3)
C(12)	0.8356 (9)	0.143 (1)	0.1407 (7)	2.6 (3)
C(13)	0.854 (1)	0.137 (2)	0.0690 (9)	3.8 (4)
C(14)	0.932 (1)	0.176 (2)	0.0513 (9)	4.5 (4)
C(15)	0.986 (1)	0.221 (2)	0.1015 (9)	4.1 (4)
C(16)	0.968 (1)	0.230 (1)	0.1747 (8)	3.5 (4)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$. The values marked with an asterisk are for an isotropically refined atom. Data for the phenyl atoms are available as supplementary material.

Table V. Important Bond Distances (Å) and Bond Angles (deg) for **1**[a]

	Distances		
Re–Cl	2.415 (2)	P(2)–C(221)	1.844 (7)
Re–P(1)	2.431 (2)	C(1)–C(2)	1.398 (9)
Re–P(2)	2.402 (2)	C(1)–C(6)	1.391 (9)
P(1)–C(1)	1.848 (6)	C(2)–C(3)	1.388 (9)
P(1)–C(111)	1.833 (6)	C(3)–C(4)	1.38 (1)
P(1)–C(121)	1.850 (6)	C(4)–C(5)	1.37 (1)
P(2)–C(2)	1.842 (7)	C(5)–C(6)	1.38 (1)
P(2)–C(211)	1.836 (7)		
	Angles		
Cl–Re–Cl	180.0	P(1)–Re–P(1)	180.0
Cl–Re–P(1)	82.81 (6)	P(1)–Re–P(2)	79.70 (6)
Cl–Re–P(1)	97.19 (6)	P(1)–Re–P(2)	100.30 (6)
Cl–Re–P(2)	85.88 (6)	P(2)–Re–P(2)	180.0
Cl–Re–P(2)	94.12 (6)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Physical Measurements. Infrared spectra (4000–150 cm^{-1}) were recorded as Nujol mulls with a Perkin-Elmer 1800 Fourier transform spectrometer. Electronic absorption spectra were recorded on IBM Instruments 9420 UV-visible (900–200-nm) and Hewlett-Packard H-P8451A (820–190-nm) spectrophotometers. Electrochemical experiments were carried out by using a Bioanalytical Systems Inc. Model CV-1A instrument on dichloromethane solutions that contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. A platinum-bead working electrode and platinum-wire auxiliary electrode were used. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to the Ag/AgCl electrode at room temperature and are

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(9) (a) Cromer, D. T. *International Tables for X-ray Crystallography*: Kynoch: Birmingham, England, 1974; Vol IV, Table 2.3.1. (b) For the scattering factors used in the structure solution, see: Cromer, D. T.; Waber, J. T. *Ibid.*; Table 2.2B.

Table VI. Comparison of Selected Bond Distances (Å) and Bond Angles (deg) for **2** and **3**[a]

Distances

2		**3**	
Re-Cl(1)	2.415 (1)	Re-Br(1)	2.551 (1)
		Re-Br(3)	2.563 (1)
Re-Cl(2)	2.402 (2)	Re-Br(2)	2.525 (2)
Re-P(1)	2.409 (1)	Re-P(1)	2.411 (3)
		Re-P(2)	2.415 (3)
Re-N(1)	1.699 (5)	Re-N(1)	1.719 (8)
P(1)-C(11)	1.826 (4)	P(1)-C(11)	1.819 (9)
		P(2)-C(12)	1.809 (9)
N(1)-C(1)	1.51 (1)	N(1)-C(2)	1.41 (1)
C(1)-C(2)	1.70 (2)	C(2)-C(5)	1.69 (5)
C(2)-C(3)	1.39 (3)	C(5)-C(6)	1.40 (6)
C(11)-C(11)	1.38 (1)	C(11)-C(12)	1.40 (1)
C(11)-C(12)	1.407 (7)	C(11)-C(16)	1.40 (1)
		C(12)-C(13)	1.39 (1)
C(12)-C(13)	1.381 (7)	C(13)-C(14)	1.44 (1)
C(13)-C(13)	1.39 (1)	C(14)-C(15)	1.31 (2)
		C(15)-C(16)	1.41 (1)

Angles

2		**3**	
Cl(1)-Re-Cl(2)	88.01 (4)	Br(1)-Re-Br(2)	89.20 (5)
Cl(1)-Re-Cl(1)	86.18 (6)	Br(1)-Re-Br(3)	86.88 (4)
Cl(1)-Re-P(1)	170.75 (4)	Br(1)-Re-P(1)	168.32 (7)
Cl(1)-Re-P(1)	94.32 (4)	Br(1)-Re-P(2)	94.93 (7)
Cl(1)-Re-N(1)	99.3 (1)	Br(1)-Re-N(1)	97.1 (3)
		Br(2)-Re-Br(3)	90.06 (5)
Cl(2)-Re-P(1)	82.78 (4)	Br(2)-Re-P(1)	79.15 (7)
		Br(2)-Re-P(2)	80.10 (7)
Cl(2)-Re-N(1)	170.0 (2)	Br(2)-Re-N(1)	171.2 (2)
		Br(3)-Re-P(1)	93.97 (7)
		Br(3)-Re-P(2)	169.96 (7)
		Br(3)-Re-N(1)	96.5 (3)
P(1)-Re-P(1)	83.72 (5)	P(1)-Re-P(2)	82.28 (8)
P(1)-Re-N(1)	89.8 (1)	P(1)-Re-N(1)	94.4 (3)
		P(2)-Re-N(1)	93.1 (3)
Re-N(1)-C(1)	175.4 (5)	Re-N(1)-C(2)	178.7 (8)
N(1)-C(1)-C(2)	110 (1)	N(1)-C(2)-C(5)	111 (2)
C(1)-C(2)-C(3)	132 (2)	C(2)-C(5)-C(6)	118 (4)

[a] Data have been arranged so as to compare related distances and angles between the two structures. For the disordered *n*-propylimido ligands, parameters are given for half of the disorder. Numbers in parentheses are estimated standard deviations in the least significant figures.

uncorrected for junction potentials. Under our experimental conditions, $E_{1/2}$ = +0.47 V vs Ag/AgCl for the ferrocenium/ferrocene couple, which was used as an internal standard. Conductivity measurements were performed with the use of an Industrial Instruments Inc. Model RC-16B2 conductivity bridge. ^{1}H NMR spectra were recorded on Varian XL-200 and Varian Gemini-200 spectrometers. Resonances were referenced internally to the residual protons in the incompletely deuteriated solvent. ^{31}P{^{1}H} NMR spectra were recorded on a Varian XL-200 spectrometer operated at 80.98 MHz with an internal deuterium lock and aqueous 85% H_3PO_4 as an external standard.

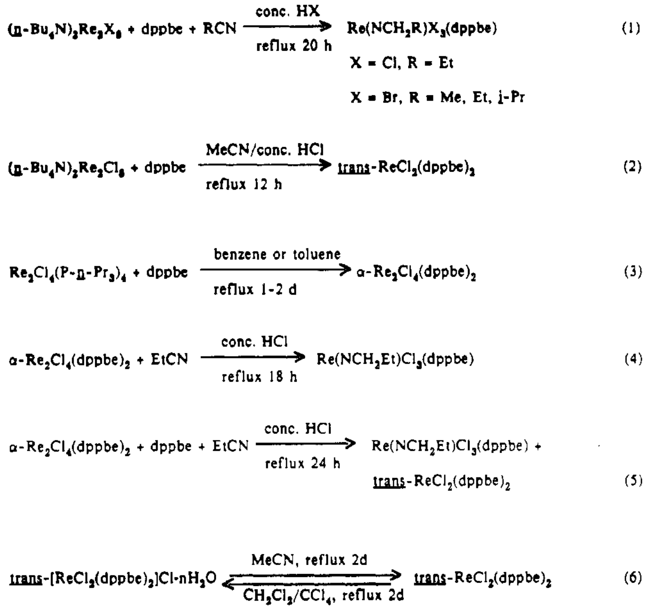
Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University Microanalytical Laboratory.

Results

The reactions of $(n\text{-}Bu_4N)_2Re_2X_8$ (X = Cl, Br) with the bidentate phosphine ligand 1,2-bis(diphenylphosphino)benzene, 1,2-$C_6H_4(PPh_2)_2$ (abbreviated dppbe), in hot methanol afford the mononuclear rhenium(III) complexes *trans*-$[ReCl_2(dppbe)_2]Cl{\cdot}4H_2O$ and *trans*-$[ReBr_2(dppbe)_2]Br$. The electrochemical and spectroscopic properties of these complexes resemble those of their recently prepared analogues *trans*-$[ReCl_2(dppee)_2]Cl{\cdot}4H_2O$ and *trans*-$[ReBr_2(dppee)_2]Br{\cdot}H_2O$ (dppee = *cis*-$Ph_2PCH{=}CHPPh_2$).[10] The cyclic voltammograms (CV's) of solutions of these complexes in 0.1 M TBAH/CH_2Cl_2 show processes that are assigned to the Re(IV)/Re(III), Re(III)/Re(II), and Re(II)/Re(I) couples. In the case of *trans*-$[ReCl_2(dppbe)_2]Cl{\cdot}4H_2O$, these are as follows (scan rate 200 mV s^{-1}): $E_{1/2}$(ox) = +1.51 V, $E_{1/2}$(red) = −0.32 V, and $E_{1/2}$(red) = −1.48 V vs Ag/AgCl. The corresponding processes for *trans*-$[ReBr_2(dppbe)_2]Br$ are as follows: $E_{1/2}$(ox) = +1.48 V, $E_{1/2}$(red) = −0.24 V, and $E_{p,c}$ = −1.42 V vs Ag/AgCl. The oxidation of the outer-sphere halide ions (chloride or bromide) was also observed in the cyclic voltammograms at $E_{p,a}$ = +1.15 V (X = Cl) and at $E_{p,a} \simeq$ +0.8 and +1.0 V (X = Br). A conductivity measurement on an acetonitrile solution of $[ReBr_2(dppbe)_2]Br$ (4.8 × 10^{-4} M) showed that it behaved as a 1:1 electrolyte (Λ_M = 123 Ω^{-1} cm^2 mol^{-1}). The electronic absorption spectra of these complexes (recorded in dichloromethane) are similar to those reported for other complexes of the type *trans*-$[ReX_2(L\text{-}L)_2]X$ (X = Cl, Br; L-L = dppee,[10] $Ph_2PCH_2CH_2PPh_2$ (dppe),[11] $Me_2PCH_2CH_2PMe_2$ (dmpe),[12] $Ph_2PNHPPh_2$ (dppa).[13] For example, the λ_{max} value for *trans*-$[ReCl_2(dppbe)_2]Cl{\cdot}4H_2O$ is at 432 nm (ϵ = 4800), with a shoulder at 475 nm, while for *trans*-$[ReCl_2(dppee)_2]Cl{\cdot}4H_2O$,[10] λ_{max} occurs at 424 nm (ϵ = 2800) with a shoulder at 455 nm. The corresponding spectral data for *trans*-$[ReBr_2(dppbe)_2]Br$ are λ_{max} = 444 nm (ϵ = 4100) and 486 nm (ϵ = 2900).

When the reactions between $(n\text{-}Bu_4N)_2Re_2X_8$ and dppbe are carried out in hot nitrile solvents RCN (R = Me, Et, *i*-Pr), to which has been added a few drops of the appropriate concentrated aqueous hydrohalic acid, the principal products are the mononuclear rhenium(V)-imido complexes $Re(NCH_2R)X_3(dppbe)$. The one exception is in the case of the reaction between $(n\text{-}Bu_4N)_2Re_2Cl_8$ and dppbe in acetonitrile, from which *trans*-$ReCl_2(dppbe)_2$ was the only identifiable product. These and related transformations are shown in Scheme I (eqs 1–6).

Scheme I



$$(\underline{n}\text{-}Bu_4N)_2Re_2X_8 + dppbe + RCN \xrightarrow[\text{reflux 20 h}]{\text{conc. HX}} Re(NCH_2R)X_3(dppbe) \qquad (1)$$

X = Cl, R = Et

X = Br, R = Me, Et, i-Pr

$$(\underline{n}\text{-}Bu_4N)_2Re_2Cl_8 + dppbe \xrightarrow[\text{reflux 12 h}]{\text{MeCN/conc. HCl}} \underline{trans}\text{-}ReCl_2(dppbe)_2 \qquad (2)$$

$$Re_2Cl_4(P\text{-}\underline{n}\text{-}Pr_3)_4 + dppbe \xrightarrow[\text{reflux 1-2 d}]{\text{benzene or toluene}} \alpha\text{-}Re_2Cl_4(dppbe)_2 \qquad (3)$$

$$\alpha\text{-}Re_2Cl_4(dppbe)_2 + EtCN \xrightarrow[\text{reflux 18 h}]{\text{conc. HCl}} Re(NCH_2Et)Cl_3(dppbe) \qquad (4)$$

$$\alpha\text{-}Re_2Cl_4(dppbe)_2 + dppbe + EtCN \xrightarrow[\text{reflux 24 h}]{\text{conc. HCl}} Re(NCH_2Et)Cl_3(dppbe) + \underline{trans}\text{-}ReCl_2(dppbe)_2 \qquad (5)$$

$$\underline{trans}\text{-}[ReCl_2(dppbe)_2]Cl{\cdot}nH_2O \underset{\text{CH}_2\text{Cl}_2\text{/CCl}_4\text{, reflux 2d}}{\overset{\text{MeCN, reflux 2d}}{\rightleftarrows}} \underline{trans}\text{-}ReCl_2(dppbe)_2 \qquad (6)$$

The electrochemical and spectroscopic properties of $Re(NCH_2R)X_3(dppbe)$ are given in Table VII. The identities of $Re(NCH_2Et)Cl_3(dppbe)$ and $Re(NCH_2Et)Br_3(dppbe)$ were further established by X-ray crystallography; the details of these structure solutions are presented in the Experimental Section and the results considered further in the next section. The identification of *trans*-$ReCl_2(dppbe)_2$ was also based upon a single-crystal X-ray structure determination. Its electrochemical properties resemble those of *trans*-$[ReCl_2(dppbe)_2]Cl{\cdot}4H_2O$ (vide supra), with the

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Table VII. Electrochemical and Spectral Properties of $Re(NCH_2R)X_3(dppbe)$

	CV half-wave potentials,[a] V			IR ν(Re–X),[b] cm^{-1}	electronic abs λ,[c] nm	^{1}H NMR,[d] δ			$^{31}P\{^1H\}$ NMR,[e] δ
complex	$E_{1/2}$(ox.)	$E_{p,c}$	$E_{p,c}$			CH_α	CH_β	CH_γ	
$Re(NCH_2Et)Cl_3(dppbe)$	+1.22 (90)	−1.30	−1.61	315 (s), 284 (s), 263 (m)	550 (100), 350 (2000)[g]	−0.34 (t of t)	+1.31 (m)	+0.70 (t)	+23.9 (s)
$Re(NCH_2Me)Br_3(dppbe)$	+1.21 (90)	−1.16	−1.49		580 (70), 362 (1300)[g]	−0.44 (q of t)	+0.91 (t)		+19.7 (s)
$Re(NCH_2Et)Br_3(dppbe)$	+1.22 (110)	−1.26	−1.60	220 (s), 200 (s), 169 (m)	565 (60), 360 (2300)[g]	−0.80 (t of t)	+1.41 (m)	+0.71 (t)	+18.9 (s)
$Re(NCH_2\text{-}i\text{-}Pr)Br_3(dppbe)$	+1.21[f] (130)	−1.10	−1.36		580 (130), 365 (2400)[g]	−1.25 (d of t)	+1.91 (m)	+0.64 (t)	+17.7 (s)

[a] Measured on 0.1 M $TBAH/CH_2Cl_2$ solutions and referenced to the Ag/AgCl electrode, with a scan rate (v) of 200 mV s^{-1} at a Pt-bead electrode. Numbers in parentheses are the $E_{p,a} - E_{p,c}$ values (mV). [b] Nujol mull. [c] Recorded on dichloromethane solutions; molar extinction coefficients (M^{-1} cm^{-1}) given in parentheses. [d] Recorded in CD_2Cl_2. Resonances are for the alkyl group of the imido ligand. The symbols α, β, and γ refer to the proximity of the carbon atom of the alkyl chain to the nitrogen atom. Abbreviations are as follows: m = multiplet, t = triplet, d of t = doublet of triplets, t of t = triplet of triplets, q of t = quartet of triplets. [e] Recorded in CD_2Cl_2. Abbreviations: s = singlet. [f] Approximate value since $i_{p,a} > i_{p,c}$. [g] Approximate value for ϵ since this absorption is a shoulder on a rising absorption.

exception of the couple at $E_{1/2} = -0.32$ V, which now corresponds to an oxidation of the bulk complex. The complex α-$Re_2Cl_4(dppbe)_2$ (eq 3, Scheme I), has properties that are characteristic of the Re_2^{4+} core and the presence of chelating dppbe ligands.[13,14] The CV of this complex in 0.1 M $TBAH/CH_2Cl_2$ revealed the presence of a reversible one-electron oxidation at $E_{1/2} = +0.29$ V, an irreversible oxidation at $E_{p,a} = +1.14$ V, and an irreversible reduction at $E_{p,c} = -1.41$ V vs Ag/AgCl. The low-frequency IR spectrum (Nujol mull) of this complex displays ν(Re–Cl) modes at 312 s and 285 m cm^{-1}. These bands are similar to those reported for other dirhenium complexes that contain the *cis*-$ReCl_2$(L-L) unit, i.e. α-$Re_2Cl_4(L\text{-}L)_2$.[14-16] It exhibits a low-energy absorption band at ≃860 nm in its electronic absorption spectrum (Nujol mull). This band is similar to those reported for other complexes of the type α-$Re_2Cl_4(L\text{-}L)_2$ (L-L = dppe,[15] dppee,[14] dmpe,[14] or $Ph_2P(CH_2)_3PPh_2$ (dppp)[16]) and is distinctly different from the spectra exhibited by isomers of the type β-$Re_2Cl_4(L\text{-}L)_2$ (L-L = dppe[17] or dppee[14]), which contain intramolecular bridging phosphine ligands. The $^{31}P\{^1H\}$ NMR spectrum of this complex (recorded in CD_2Cl_2) shows a singlet at δ +28.2; this chemical shift is characteristic of chelating five-membered rings.[14]

Discussion

While the $(n\text{-}Bu_4N)_2Re_2X_8$ (X = Cl, Br) salts react with dppbe in methanol in the expected fashion,[10] to give the nonredox cleavage products *trans*-$[ReX_2(dppbe)_2]X\cdot nH_2O$, the formation of the mononuclear imido complexes $Re(NCH_2R)X_3(dppbe)$ when refluxing nitrile solvents (RCN) are used was unexpected. The latter reaction course is of particular interest for several reasons. First, it constitutes a novel route to transition-metal imido species, one whose potential has not previously been realized,[18] although there are instances where trinuclear iron[19] and ruthenium[20] carbonyl clusters have been used to stabilize intermediates in the hydrogenation of nitriles in the presence of weak acids. Second, this method is applicable to alkylimido species of the type $M(NCH_2R)$, which, in the case of rhenium, are very scarce[18,21] and limited to the case of R = H[22-25] and, in a very few instances, R = Me or Et.[24] There are also a few examples of *tert*-butylimido complexes of rhenium known,[26] although in these instances the α-carbon atom contains no hydrogens. Third, these reactions represent a novel use of multiply bonded dimetal complexes to bring about the multielectron reduction of organic substrates. Note that the examples described in this report constitute an interesting alternative to the *reductive coupling* of organic nitriles; such a reaction course can ensue when the dimetal unit remains intact and can serve as a template for the coupling to take place upon the coordination of two or more nitrile ligands.[27]

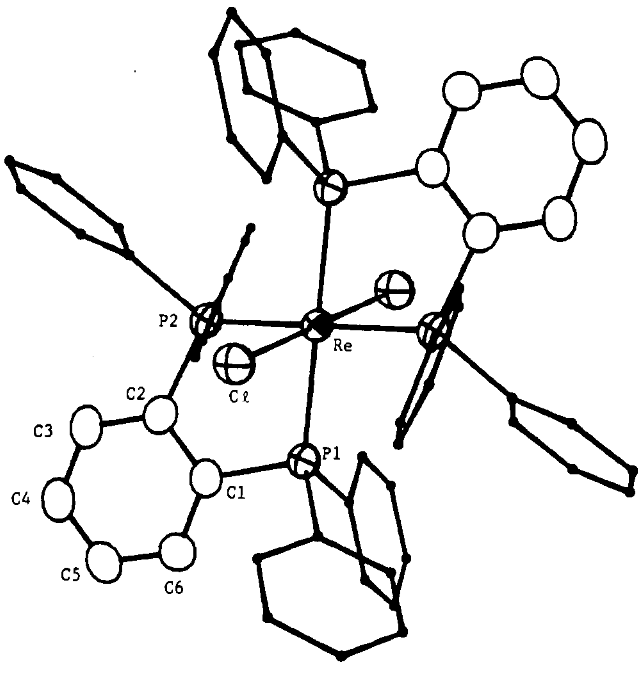

Figure 1. ORTEP representation of the structure of *trans*-$ReCl_2(dppbe)_2$. The thermal ellipsoids are drawn at the 50% probability level except for the carbon atoms of the phenyl rings, which are circles of arbitrary radius.

Of the reactions we studied that were carried out in nitrile solvents, only one failed to give an imido complex. This was the reaction between $(n\text{-}Bu_4N)_2Re_2Cl_8$ and dppbe in acidified acetonitrile, which afforded *trans*-$ReCl_2(dppbe)_2$ as the main product. This difference may reflect the greater difficulty of reducing a metal chloride relative to its analogous bromide,[28] coupled with the lower reaction temperature in refluxing acetonitrile compared to the other nitriles that were used. The characterization of this product included an X-ray structure determination (Figure 1 and Table V), which established its very close structural relationship

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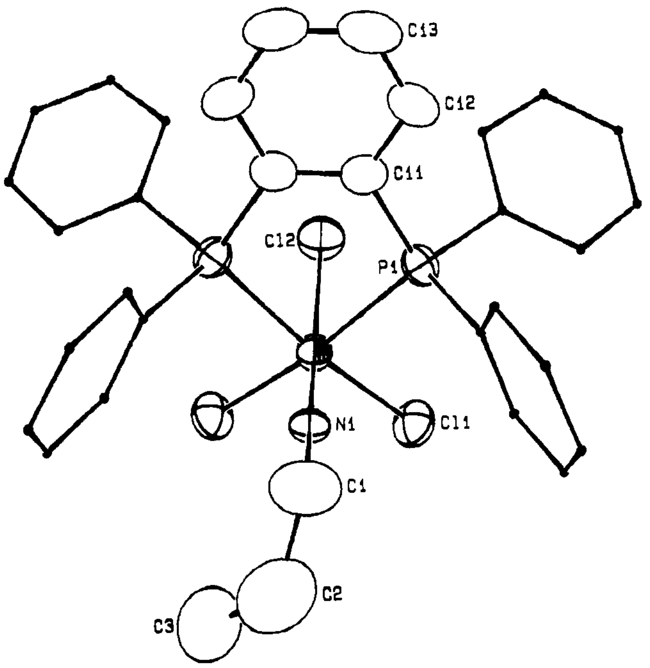

Figure 2. ORTEP representation of the structure of $Re(NCH_2Et)Cl_3(dppbe)$. The thermal ellipsoids are drawn at the 50% probability level except for the carbon atoms of the phenyl rings, which are circles of arbitrary radius. This view represents half of the disorder associated with the CH_2CH_3 fragment of the *n*-propylimido ligand.

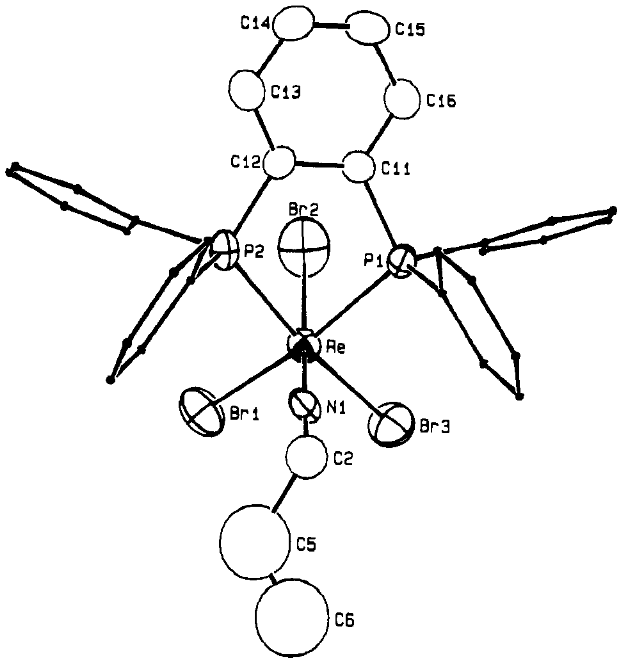

Figure 3. ORTEP representation of the structure of $Re(NCH_2Et)Br_3(dppbe)$. The thermal ellipsoids are drawn at the 50% probability level except for the carbon atoms of the phenyl rings, which are circles of arbitrary radius. This represents half of the disorder associated with the CH_2CH_3 fragment of the *n*-propylimido ligand. Atoms C(5) and C(6) have counterparts C(3) and C(4) in the other half of the disorder.

to *trans*-$ReCl_2(dppee)_2$ (dppee = $Ph_2PCH{=}CHPPh_2$).[10] The Re–Cl distance for *trans*-$ReCl_2(dppbe)_2$ of 2.415 (2) Å is essentially the same as that of its dppee analogue. There is a modest disparity in the Re–P distances of *trans*-$ReCl_2(dppbe)_2$ (2.431 (2) and 2.402 (2) Å), whereas for *trans*-$ReCl_2(dppee)_2$ the Re–P distances are identical (2.405 (2) and 2.404 (2) Å). In both structures the Cl–Re–Cl and *trans* P–Re–P angles are required by symmetry to be 180°. This structure determination is noteworthy in that it is only the second one on a mononuclear complex of the type $ReX_2(phosphine)_4$ (X = halide).

The X-ray crystal structure determinations of $Re(NCH_2Et)X_3(dppbe)$ (X = Cl, Br) are the first to be carried out on (alkylimido)rhenium(V) species other than methylimido derivatives.[22,23] ORTEP representations of these structures are shown in Figures 2 and 3, while a comparison of the important structural parameters is given in Table V. Both structure solutions were complicated by a disorder involving the *n*-propylimido ligands, although in each instance the disorder was satisfactorily modeled (see Experimental Section) and the structural conclusions were confirmed by ^1H NMR spectroscopy (Table VII). Of particular note are the short Re–N and N–C distances (1.699 (5) and 1.51 (1) Å, respectively, for X = Cl, and 1.719 (8) and 1.41 (1) Å, respectively, for X = Br) and the associated Re–N–C angle that approaches linearity (175.4 (5)° for X = Cl and 178.7 (8)° for X = Br). These data are clearly in accord with an alkylimido moiety and an interaction best represented as $Re{\equiv}N{-}CH_2R$.[18,22,23] The differences in Re–N and C–N distances between the two structures may reflect some small differences in $Re(d_\pi) \leftarrow N(p_\pi)$ bonding, which may be slightly greater in the case of the chloride complex where the more polar Re–Cl bonds (compared to Re–Br) should increase the positive charge at the metal center and therefore enhance the extent of multiple bonding. However, the Re–N bonds are not statistically different (within 3σ), and while the C–N bonds are clearly different, part of this may be an artifact of our modeling of the disorder associated with the *n*-propyl groups.

An interesting feature of the ^1H NMR spectra of the alkylimido complexes is the upfield shift of the α-CH_2 protons (Table VII), out of the range usually encountered for "normal" alkyl resonances. We attribute these unusual chemical shifts to the interactions of the α-protons with the phenyl rings of the dppbe ligands. The dppbe ligand is relatively rigid, and as can be seen in the structures of $Re(NCH_2Et)X_3(dppbe)$ (Figures 2 and 3), two of its phenyl rings create a pocket around the alkylimido group. If we model the interactions using the solid-state structures of $Re(NCH_2Et)X_3(dppbe)$, we find that the α-hydrogens are very close to the perpendicular of these phenyl rings.[29] The anisotropy associated with the phenyl rings can then be calculated[30] to lead to an upfield shift for these proton resonances of approximately 2.3 ppm. Our experimental observations accord with this expectation.

An important question that now arises concerns the mechanism of these nitrile reductions. Formally, a four-electron reduction and concomitant protonation occur. Interestingly, in our earlier preliminary report,[4] we had not recognized the importance of adding acid to the reaction mixture since we had found that the thermal reaction of $(n\text{-}Bu_4N)_2Re_2Br_8$ with dppbe in propionitrile afforded $Re(NCH_2Et)Br_3(dppbe)$ without acid being added. At the time, this was the only reaction of this type that we investigated which gave a mononuclear imido complex. We now believe that the samples of $(n\text{-}Bu_4N)_2Re_2Br_8$ we originally used contained small amounts of acid in the crystals, probably present as $(n\text{-}Bu_4N)_2Re_2Br_8{\cdot}x(H_3O)Br$. In a related context, we note that the ^1H NMR spectra of the original samples of $Re(NCH_2Et)Br_3(dppbe)$ that we obtained[4] showed *two* sets of resonances for the α-protons of the *n*-propylimido group. These resonances were centered at δ –0.80 and δ –0.56, and each was a triplet of triplets.[4] We originally thought that this was evidence for deprotonation of the imido group,[31] but we now know that while the former resonance is due to authentic $Re(NCH_2Et)Br_3(dppbe)$, the latter is probably due to a mixed-halide derivative such as $Re(NCH_2Et)Br_2Cl(dppbe)$. The separate sets of β- and γ-protons

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(29) A representative calculation for $Re(NCH_2Et)Br_3(dppbe)$ is as follows. Fractional coordinates for the calculated positions of the two hydrogens on C(2) for half of the disorder are as follows: H(1), 0.5993, 0.3199, 0.2671; H(2), 0.6645, 0.3832, 0.3207. From these data, H(1) is calculated to be 4.20 Å from the center of one phenyl ring at an angle of 16.6° from the perpendicular and 2.92 Å (at an angle of 25.9°) from the second phenyl ring. The corresponding parameters for H(2) are 2.95 Å (at 23.0°) and 4.03 Å (at 15.9°). Similar results are obtained for the other half of the disorder.

(30) Johnson, C. E., Jr.; Bovey, F. A. *J. Chem. Phys.* **1958**, *29*, 1012.

(31) The deprotonation of (alkylimido)rhenium(V) species to give $Re{-}N{=}CHR$ (R = H, Me, Et) has been reported by Chatt and co-workers.[24]

for the *n*-propylimido groups of these two species are coincident in the ^1H NMR spectra. The mixed-halide complex was formed because of the presence of a chloride contaminant in the samples of $(n\text{-}Bu_4N)_2Re_2Br_8$. The latter complex is formed by the reaction of $(n\text{-}Bu_4N)_2Re_2Cl_8$ with concentrated HBr (48%) in boiling methanol;[11] apparently, the bromide-for-chloride substitution had not proceeded to completion in the preparation of these samples, a reaction course that is not without precedent.[32] These conclusions are supported by the following experiments. If a 10:1 mixture of concentrated HBr/concentrated HCl is substituted for the concentrated HBr in the preparation of $Re(NCH_2Et)Br_3(dppbe)$ from $(n\text{-}Bu_4N)_2Re_2Br_8$ (see procedure C(iv) in the Experimental Section), then a mixture of $Re(NCH_2Et)Br_3(dppbe)$ and $Re(NCH_2Et)Br_2Cl(dppbe)$ is formed, the former complex predominating. If, on the other hand, a 1:10 mixture of concentrated HBr/concentrated HCl is used, the mixed-halide species predominates (by ^1H NMR spectroscopy). The formation of these complexes can also be followed by $^{31}P\{^1H\}$NMR spectroscopy; the tribromide complex shows a singlet at δ +18.9, while the mixed-halide is characterized by a singlet at δ +22.8. It is possible that it is the halide ligand trans to the imido group that is the most kinetically labile[23,33] and therefore the one most readily substituted in these halide-exchange reactions, although we note that from the structure determinations there is no evidence for such a structural trans effect. On the contrary, the Re–X bond trans to the imido ligand is slightly shorter than the related cis Re–X bonds (Table VI).

The presence of acid in the form of the aqueous hydrohalic acid is important since, with $HBF_4{\cdot}Et_2O$, $HBF_4(aq)$, or H_2O in place of HX, no (alkylimido)rhenium species were formed unless halide ion (in the form of $n\text{-}Bu_4NX$) was also added. Thus, acid plus halide ion are necessary ingredients for the occurrence of these nitrile to imido ligand conversions.

In view of the propensity of the quadruply bonded Re_2^{6+} core to be reduced by phosphines to give complexes of the general type $Re_2X_4(PR_3)_4$ (X = halide; PR_3 = a monodentate or half a bidentate phosphine),[1,2] we anticipated that such a reaction step would also occur during the course of the reactions involving the dppbe ligand (eq 1, Scheme I). Accordingly, we set out to prepare a complex of the type $Re_2X_4(dppbe)_2$ in order to ascertain whether it might be a reasonable intermediate on the way to $Re(NCH_2R)X_3(dppbe)$. For this purpose $\alpha\text{-}Re_2Cl_4(dppbe)_2$ was prepared (eq 3, Scheme I); it was found to react with propionitrile in the presence of concentrated HCl (eq 4, Scheme I) in the same fashion as did a mixture of $(n\text{-}Bu_4N)_2Re_2Cl_8$ and dppbe (eq 1, Scheme I). Accordingly, we believe that it is reasonable to suggest that the latter reaction proceeds via $\alpha\text{-}Re_2Cl_4(dppbe)_2$ or some closely related species. Since the conversions of $\alpha\text{-}Re_2Cl_4(dppbe)_2$ and the $(n\text{-}Bu_4N)_2Re_2X_8$/dppbe mixtures to $Re(NCH_2R)X_3(dppbe)$ proceed in yields of less than 50%, these reactions very likely involve a disproportionation step such as $Re^{II}Re^{II} \rightarrow Re^{I} + Re^{III}$ to give a coordinatively unsaturated Re(I) center that is complexed by nitrile ligands. This center can then serve as the source of the four electrons necessary to reduce the nitrile ligand. Although we have not been able to isolate a mononuclear Re(III) complex from these nitrile reaction mixtures, when the reaction between $\alpha\text{-}Re_2Cl_4(dppbe)_2$ and propionitrile/concentrated HCl is carried out in the presence of 1 equiv of dppbe (eq 5, Scheme I), *trans*-$ReCl_2(dppbe)_2$ is isolated in addition to $Re(NCH_2Et)Cl_3(dppbe)$. We believe that this result is in accord with the initial generation of Re(III), since we have shown that the authentic rhenium(III) complex *trans*-$[ReCl_2(dppbe)_2]Cl{\cdot}4H_2O$ is reduced to *trans*-$ReCl_2(dppbe)_2$ in hot acetonitrile (eq 6, Scheme I).

Although the conversion of coordinated nitriles to amines by hydrogen, or proton and hydride additions,[19,20,34–36] and the reverse, namely, the oxidation of coordinated amines to give nitriles,[37] are important metal-mediated reactions, very few systems display the combination of characteristics that we have encountered in our studies dealing with the conversion of nitriles to alkylimides. Specifically, we refer to the metal being the source of the reducing equivalents, without the need to generate an intermediate metal–hydride complex, and a source of protons being necessary only to protonate the reduced nitrile fragment. There is an interesting report by Wilkinson and co-workers[38] concerning the conversion of $[CrCl(NCMe)(dmpe)_2]BPh_4$ into *trans*-$[Cr(NCH_2Me)Cl(dmpe)_2]SO_3CF_3$ (dmpe = $Me_2PCH_2CH_2PMe_2$) upon the treatment of the former complex with $Ba(SO_3CF_3)_2$ in methanol. While their product is "isoelectronic" with $Re(NCH_2Me)X_3(dppbe)$, the mechanisms of these reactions are presumably different. We also note that Pombeiro et al.[39] have found that the treatment of the Re(I) complex *trans*-$ReCl(NCC_6H_4OMe\text{-}4)(dppe)_2$ (dppe = $Ph_2PCH_2CH_2PPh_2$) with HBF_4 affords $[ReCl(N{=}CHC_6H_4OMe\text{-}4)(dppe)_2]BF_4$, a complex which contains a methyleneamido ligand. This is formally a two-electron redox reaction with concomitant protonation of the reduced nitrile and represents an intermediate stage in the reduction of a nitrile to an alkylimido species by Re(I). The reason this reaction terminates at the Re(III) stage rather than proceeding further (through another two-electron step), as we have observed in our system, is probably a consequence of the poorer reducing capability of $[ReCl(N{=}CHR)(dppe)_2]^+$ compared to a species such as $[ReX(N{=}CHR)(NCR)_2(dppbe)]^+$. The results of Pombeiro et al.[39] support our contention that a key step in the reduction of nitriles by multiply bonded dirhenium species is probably disproportionation of the Re_2^{4+} core to generate a reactive mononuclear Re(I) site that is a potent four-electron reductant.

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Supplementary Material Available: For the structures of *trans*-$ReCl_2(dppbe)_2$, $Re(NC_3H_7)Cl_3(dppbe)$, and $Re(NC_3H_7)Br_3(dppbe)$, tables giving full details of crystal data and data collection parameters (Tables S1–S3), listings of positional parameters and their errors for the non-hydrogen positional parameters (Tables S4–S6), the positional parameters for the hydrogen atoms (Tables S7–S9), and the anisotropic thermal parameters (Tables S10–S12), complete listings of bond distances (Tables S13–S15) and bond angles (Tables S16–S18), and figures showing the atomic numbering schemes (39 pages); tables of observed and calculated structure factors (56 pages). Ordering information is given on any current masthead page.

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