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Synthesis and Reactivity of a Series of Analogous Rhenium Tris(imido), Bis(imido) Alkyne, and Imido Bis(alkyne) Complexes

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A reaction between Re_2O_7, $ArNH_2$ (Ar = 2,6-C_6H_3-*i*-Pr_2), NEt_3, and Me_3SiCl yields $Re(NAr)_3Cl$. Reduction of $Re(NAr)_3Cl$ in THF by 1 equiv of sodium amalgam gives $Hg[Re(NAr)_3]_2$ in ca. 50% yield. An X-ray study showed $Hg[Re(NAr)_3]_2$ to be composed of molecular units of $(ArN)_3Re—Hg—Re(NAr)_3$ having a linear Re—Hg—Re bond and nearly trigonal planar staggered $Re(NAr)_3$ units. Reduction of either $Hg[Re(NAr)_3]_2$ or $Re(NAr)_3Cl$ by 2 equiv of sodium amalgam in THF affords $Na(THF)_2Re(NAr)_3$ in high yield. An X-ray structure of $[N(PPh_3)_2][Re(NAr)_3]$ showed that the $[Re(NAr)_3]^-$ ion is a trigonal planar species in which the Re—N—C angles all are essentially linear. Compounds that contain the $[Re(NAr)_3]^-$ ion can be alkylated to give compounds of the type $Re(NAr)_3R$ and protonated to give $Re(NAr)_3H$. Reactions between $Re(NAr)_3H$ and π-acceptor ligands yield pseudotetrahedral compounds of the type $Re(NAr)_2(NHAr)(\eta^2\text{-L})$ [L = C_2H_2, C_2Me_2, $OCHCMe_3$, C_2H_4, or norbornene]. Addition of 2 equiv of pyHCl to $Re(NAr)_3Cl$ yields $Re(NAr)_2Cl_3(py)$. Reduction of $Re(NAr)_2Cl_3(py)$ with sodium amalgam in THF in the presence of MeC≡CMe or NpC≡CNp (Np = neopentyl) yields complexes of the type $Re(NAr)_2(\eta^2\text{-}C_2R_2)Cl$. Reduction of $Re(NAr)_2(\eta^2\text{-}C_2Np_2)Cl$ by 1 equiv of sodium amalgam yields $Hg[Re(NAr)_2(\eta^2\text{-}C_2Np_2)]_2$, while reduction by 2 equiv of sodium amalgam yields pentane-soluble $Na(THF)_2Re(NAr)_2(\eta^2\text{-}C_2Np_2)$. $Na(THF)_2Re(NAr)_2(\eta^2\text{-}C_2Np_2)$ reacts with MeI or $ClCH_2$-2,4,6-$C_6H_2Me_3$ to yield $Re(NAr)_2(\eta^2\text{-}C_2Np_2)R$ or with $[Et_2NH_2][OTf]$ in THF to give $Re(NAr)_2(\eta^2\text{-}C_2Np_2)H$. Addition of excess PMe_2Ph to $Re(NAr)_2(\eta^2\text{-}C_2Np_2)H$ yields $Re(NAr)_2(PMe_2Ph)_2H$. Addition of 4 equiv of pyridinium chloride in a 1:5 mixture of THF and pyridine to $Na(THF)_2Re(NAr)_3$ affords $Re(NAr)Cl_3(py)_2$ in high yield. $Re(NAr)Cl_3(py)_2$ is reduced by excess Zn dust in the presence of 2 equiv of dineopentylacetylene in refluxing THF to afford $Re(NAr)(\eta^2\text{-}C_2Np_2)_2Cl$. Reduction of $Re(NAr)(\eta^2\text{-}C_2Np_2)_2Cl$ by 1 or 2 equiv of sodium amalgam in THF yields $Hg[Re(NAr)(\eta^2\text{-}C_2Np_2)_2]_2$ or $Na(THF)_2Re(NAr)(\eta^2\text{-}C_2Np_2)_2$, respectively. The molecular structure of $Na(THF)_2Re(NAr)(\eta^2\text{-}C_2Np_2)_2$ shows that $[Na(THF)_2]^+$ is bound to the imido nitrogen atom (2.464(9) Å), not to rhenium (Re—Na = 3.17 Å), and the coordination about the rhenium center is distorted from the pseudotrigonal planar geometry expected for $[Re(NAr)(\eta^2\text{-}C_2Np_2)_2]^-$. $Na(THF)_2Re(NAr)(\eta^2\text{-}C_2Np_2)_2$ is alkylated smoothly by MeI or $ClCH_2$-2,4,6-$C_6H_2Me_3$ to afford $Re(NAr)(\eta^2\text{-}C_2Np_2)_2R$, while addition of $[Et_2NH_2][OTf]$ yields pale yellow $Re(NAr)(\eta^2\text{-}C_2Np_2)_2H$. Cyclic voltammograms (200 mV s^{-1}) were obtained for the chloride derivatives and sodium salts of the tris-, bis-, and mono(imido) complexes in a solution of 0.5 M $[NBu_4][PF_6]$ in THF. Extended Hückel calculations on $[Re(NH)_3]^-$, $[Re(NH)_2(C_2H_2)]^-$, and $Re(NH)(C_2H_2)_2]^-$ all clearly show that a 20-electron count on the metal is avoided by filling a ligand-centered nonbonding orbital.

Introduction

Recently, we discovered an unusual trigonal planar transition metal complex, $Os(NAr)_3$ (Ar = 2,6-C_6H_3-*i*-Pr_2).[1,2] $Os(NAr)_3$ is potentially a 20-electron compound if one assumes that all three linear imido ligands are six-electron donors. However, a simple molecular orbital analysis reveals that one combination of in-plane nitrogen p orbitals has C_3 symmetry, a symmetry that is not matched by any metal orbital. Therefore one electron pair remains in this ligand-centered nonbonding orbital. The situation is similar to that found in $W(\eta^2\text{-}C_2R_2)_3CO$,[3–7] a compound whose structure and stability was rationalized over 20 years ago in similar terms. An important requirement in order to stabilize trigonal planar geometries of the type found for $Os(NAr)_3$ is that the imido ligand substituent must be sterically bulky enough to prevent formation of imido-bridged species. The fact that $Os(N\text{-}t\text{-}Bu)_3$ is a dimer is evidence that steric factors can be important.[8]

An imido ligand is isoelectronic with an oxo ligand[9] and is related to a cyclopentadienyl ligand,[10] an alkylidyne ligand,[11] and an alkoxide ligand.[12] All can in principle bind to the metal through a σ orbital and two *identical*

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π orbitals; i.e., they are all "$2\pi,1\sigma$" ligands. In addition to the "donor-acceptor" bonding described by the Dewar-Chatt-Duncanson model,[13,14] the alkyne can form a second π-bond to the metal perpendicular to plane that contains the metal and the two alkyne carbon atoms ($\pi_\perp$). Recognition of the $\pi_\perp$ interaction led to a description of alkyne ligands as either "two-electron" or "four-electron" donors.[15,16] An alkyne ligand also can be viewed as a dianion,[17] a view that is consistent with protonolysis of some metal-alkyne complexes to yield olefins.[18] An alkyne ligand is not strictly a member of the class of $2\pi,1\sigma$ ligands since it cannot form two equivalent π-bonds to the metal; it might be called a "$1\pi,1\pi',1\sigma$" ligand. Nevertheless, it might be expected to behave in some situations in a manner that is related to the behavior of a true $2\pi,1\sigma$ ligand.

We were attracted to the challenge of synthesizing d^2 rhenium imido compounds analogous to Os(NAr)$_3$ in order to determine whether they would have the expected trigonal planar structure and also in order to compare their reactivity with that of Os(NAr)$_3$, which is relatively unreactive. In the process we became interested also in compounds that contain both imido and alkyne ligands,[10,19-21] since the alkyne ligand is related to the imido ligand (as noted above) and since a large family of oxo alkyne complexes are known that contain the [ReO(η^2-C$_2$R$_2$)$_2$] core.[22-25] We expected that differences between imido alkyne complexes and oxo alkyne complexes could be significant, in part because of the increased steric protection of the metal afforded by an imido ligand relative to an oxo ligand. In this paper we report the synthesis of d^2 tris(imido) complexes of rhenium and related imido alkyne complexes. A portion of this work has been published in a preliminary communication.[20]

Results

Tris(imido) Compounds. The reaction shown in eq 1, which is modeled after methods reported for synthesizing Re(NAr)$_2$Cl$_3$(py),[26] W(NAr)$_2$Cl$_2$(dme),[27] and Mo(NAr)$_2$Cl$_2$(dme),[28] affords good yields of Re(NAr)$_3$Cl (**1**). Protonolysis of one of the imido ligands in Re(NAr)$_3$Cl with

$$0.5Re_2O_7 + 3ArNH_2 + 6NEt_3 + 7Me_3SiCl \rightarrow Re(NAr)_3Cl + 3.5(Me_3Si)_2O + 6NEt_3HCl \quad (1)$$

pyridinium chloride affords Re(NAr)$_2$Cl$_3$(py), a reaction that can be reversed by adding triethylamine (eq 2).

$$Re(NAr)_3Cl \underset{2NEt_3}{\overset{2pyHCl}{\rightleftarrows}} Re(NAr)_2Cl_3(py) + ArNH_2 \quad (2)$$

Proton NMR spectra suggest that all imido ligands in **1** are equivalent and freely rotating about the N-C$_{ipso}$ bond on the NMR time scale at room temperature. We presume that **1** is a pseudotetrahedral species analogous to Re(N-t-Bu)$_3$Cl and related species.[29]

Re(NAr)$_3$Cl is reduced in THF by 1 equiv of sodium amalgam to give Hg[Re(NAr)$_3$]$_2$ (**2a**) in ca. 50% yield. An X-ray study showed **2a** to have the structure shown in Figure 1. (Relevant bond distances and angles are listed in Table I.) The crystal is composed of molecular units of (ArN)$_3$Re—Hg—Re(NAr)$_3$, with the crystallographically imposed molecular point group symmetry S_6. The Hg—Re distance of 2.621(1) Å is consistent with a single bond (less than the sum of the covalent radii); the Re—Hg—Re angle (180°) is imposed. The imido ligands are linear (Re—N—C = 173(1)°) with a Re═N distance of 1.76(1) Å, approximately the same as the average Os═N distance of 1.737 Å found in Os(NAr)$_3$.[2] The Hg—Re—N angle (97.4(4)°) is between that expected for a "capped" trigonal planar (90°) and a tetrahedral (109°) coordination geometry about rhenium. Since the structure of the free anion (vide infra) is trigonal planar, the Re—Hg bonds in **2a** are perhaps best viewed as being largely ionic bonds between Hg^{2+} and [Re(NAr)$_3$]$^-$ ions.

Reduction of either Hg[Re(NAr)$_3$]$_2$ or Re(NAr)$_3$Cl by 2 equiv of sodium amalgam in THF affords Na(THF)$_2$Re(NAr)$_3$ (**2b**) in high yield as a brown powder that is slightly soluble in pentane. It is not known whether the sodium ion is bound to one or more imido nitrogen atoms (cf. Li salts of anionic W(VI) and Mo(VI) imido complexes[30] and another structure reported later in this paper) or directly to rhenium. Since only 2 equiv of THF are present, **2b** seems unlikely to contain separated [Na(THF)$_2$]$^+$ and [Re(NAr)$_3$]$^-$ ions. We favor the proposal that the sodium is bound to at least one of the imido nitrogen atoms in the solid state in spite of the fact that NMR data in benzene are consistent with a highly symmetric structure on the NMR time scale. Other salts, [NEt$_4$][Re(NAr)$_3$] (**2c**) and [PPN][Re(NAr)$_3$] (**2d**) ([PPN]$^+$ = [Ph$_3$P═N═PPh$_3$]$^+$, have been prepared from **2b** by adding the appropriate salt to the reaction mixture in which **2b** is formed.

Ruby red crystals of **2d** were suitable for an X-ray diffraction study (Figure 2, Table II). The crystal is composed of well-separated ion pairs. The structure of the [Re(NAr)$_3$]$^-$ ion is analogous to that of [Os(NAr)$_3$]. There are some small differences. Each imido ligand in [Re(NAr)$_3$]$^-$ is crystallographically distinct (as required by a lack of molecular symmetry), and each rhenium—imido bond length is statistically different (Re—N(1) = 1.600(10) Å, Re—N(2) = 1.753(8) Å, Re—N(3) = 1.684(9) Å). Since all of the Re—N—C angles are essentially linear (Re—N(1)—C(11) = 168.8°, Re—N(2)—C(21) = 173.6°,

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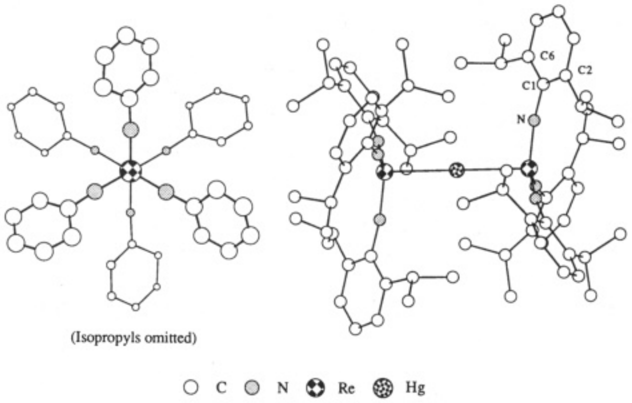


Figure 1. Molecular structure of $Hg[Re(NAr)_3]_2$ (**2a**).

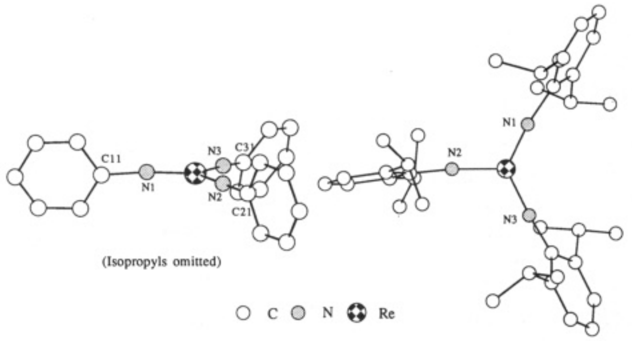


Figure 2. Molecular structure of $[N(PPh_3)_2][Re(NAr)_3]$ (**2d**).

Table I. Selected Bond Distances (Å) and Angles (deg) in $Hg[Re(NAr)_3]_2$ (2a)

angle		distance	
Re–Hg–Re	180.00	Hg–Re	2.621(1)
Hg–Re–N	97.4(4)	Re–N	1.76(1)
N–Re–N	118.4(2)		
Re–N–C(1)	173(1)		

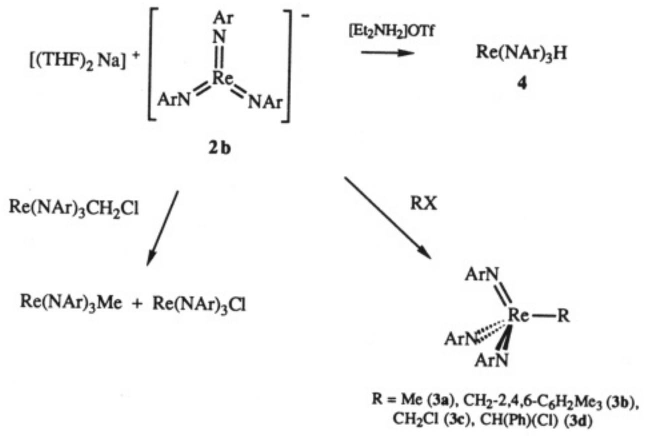
Table II. Selected Bond Distances (Å) and Angles (deg) in $[N(PPh_3)_2][Re(NAr)_3]$ (2d)

angle		distance	
N(1)–Re–N(2)	116.1(4)	Re–N(1)	1.60(1)
N(1)–Re–N(3)	128.0(4)	Re–N(2)	1.753(8)
N(2)–Re–N(3)	115.8(4)	Re–N(3)	1.684(9)
Re–N(1)–C(11)	168.8(8)		
Re–N(2)–C(21)	173.6(8)		
Re–N(3)–C(31)	173.2(8)		

Re—N(3)—C(31) = 173.2°), the Re═N bonding is best described in terms of the group theoretical analysis reported for $Os(NAr)_3$.[1,2] However, the relatively long Re—N(2) bond *might* indicate that the nonbonding electron pair is somewhat more localized on N(2) in the solid state. The geometry about rhenium in **2d** is trigonal planar (the N—Re—N angles sum to 360.0°), and the Re is only 0.029 Å out of the plane of the imido nitrogen atoms. The imido aryl groups are tilted at angles of 73, 95, and 68° with respect to the N_3 plane; the imido ligand with the longest Re═N bond is that in which the aryl ring is closest to being perpendicular to the ReN_3 plane.

$Re(NAr)_3{}^-$ is a powerful nucleophile and reducing agent. Its reactions are summarized in Scheme I. $Na(THF)_2Re(NAr)_3$ is alkylated within 1 min at −40 °C with MeI or $ClCH_2$-2,4,6-$C_6H_2Me_3$ to give the expected alkylation products **3a** and **3b**. Compound **2b** also reacts cleanly with dichloromethane and 1,1-dichlorotoluene to give the unusual chloroalkyl tris(imido)rhenium species **3c** and **3d**. Compounds of type **3** are all red-purple crystalline solids

Scheme I. Some Reactions of $Na(THF)_2Re(NAr)_3$ (2b)



that are soluble in pentane and have NMR spectra that are consistent with their having C_{3v} pseudotetrahedral structures. A 1:1 mixture of $Re(NAr)_3Cl$ and $Re(NAr)_3Me$ is formed in good yield (~85% isolated) when $Na(THF)_2Re(NAr)_3$ reacts with $Re(NAr)_3CH_2Cl$ in THF; the source of the proton is not known. $Re(NAr)_3Me$ is also formed in reactions aimed at preparing $[NMe_4][Re(NAr)_3]$. $[NEt_4][Re(NAr)_3]$ reacts with Me_3NO to afford $[NEt_4][Re(NAr)_3O]$, but **2b** does not react with CO_2, ethylene, or H_2. Only under forcing conditions (refluxing in THF for a week) will compounds of type **2** react with excess phosphine, but the products are not formed in high yield and so far have not been isolated. This result should be compared with the *rapid* reaction between $Os(NAr)_3$ and phosphines to give complexes of the type $Os(NAr)_2L_2$.[2]

Protonation of **2b–d** in THF with $[Et_2NH_2][OTf]$ yields $Re(NAr)_3H$ (**4**) quantitatively, a magenta compound that is slightly soluble in pentane. No absorptions corresponding to ν_{ReH} or ν_{NH} can be observed (above 3100 cm^{-1} or from 1500 to 2800 cm^{-1}) in IR spectra taken in Nujol mulls or C_6H_6, but a resonance is observed in the proton NMR spectrum at 7.22 ppm. The proton NMR spectra of this compound vary only slightly with temperature, the most significant change being a 0.4 ppm downfield shift of the 7.22 ppm resonance upon cooling a sample from +20 to −80 °C. The minimum relaxation time of the proton that gives rise to the resonance at 7.22 ppm (T_1(min)), as determined by the inversion-recovery method, was found to be 212 ms at −58 °C. These data do not prove that **4** is a d^0 Re(VII) hydride complex; an alternative formulation is $Re(NAr)_2(NHAr)$, or some variation in which the electron pair in the NH bond is interacting with the metal (an agostic interaction[31]). Similar agostic interactions involving CH electrons in alkylidene ligands in many d^0, and especially d^2, tantalum and tungsten complexes are well-known.[32,33] At this stage for convenience we will describe **4** as a hydride complex.

Upon adding CCl_4 to a benzene solution of **4** the resonance at 7.22 ppm disappears and $Re(NAr)_3Cl$ and $CHCl_3$ are formed, a reaction one would expect for $Re(NAr)_3H$, while reactions between **4** and π-acceptor ligands yield pseudotetrahedral compounds of the type

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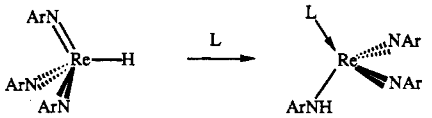
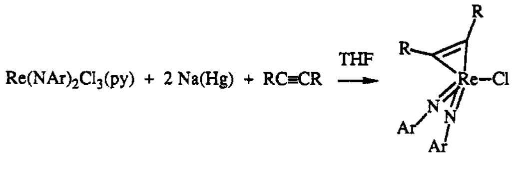


(3)

$Re(NAr)_2(NHAr)(\eta^2\text{-}L)$ [eq 3; L = C_2H_2 (**5a**), C_2Me_2 (**5b**), $OCHCMe_3$ (**5c**), C_2H_4 (**5d**), or norbornene (**5e**)], a type of reaction one could rationalize regardless of whether **4** is formulated as $Re(NAr)_2(NHAr)$ or as $Re(NAr)_3(H)$. NMR data for complexes of type **5** are consistent with a pseudotetrahedral core geometry in which the two atoms of L that are bonded to Re lie in the same plane as the Re and amido nitrogen atom; i.e., the $Re(N_{imido})_2$ core can be viewed as being isoelectronic with the 15-electron $TaCp_2$ core,[10,21] if the lone pairs on the imido ligands in **5f** are in orbitals that have significant metal character. Therefore the metal electron count is 18 in the absence of any donation of the electron pair on the NHAr ligand to the metal and rotation about the metal–amide bond should be relatively fast on the NMR time scale. ^{13}C NMR and ^1H NMR data for these complexes are consistent with these proposals. The amido proton resonances are found between 6.4 and 7.1 ppm in these compounds, and an IR absorption at approximately 3400 cm^{-1} can be assigned to ν_{NH}, consistent with the amido formulation. Compound **4** also reacts with PMe_3 to form $Re(NAr)_2(NHAr)(PMe_3)$ (**5f**), while no reaction between **4** and NEt_3, NEt_2H, or pyridine is observed, even in neat solution. Compounds **5** are analogous to the recently reported d^2 bis(imido) complexes of W(IV), Re(V), and Os(VI).[10,20,21]

Bis(imido) Alkyne Compounds. Since alkynes can behave as $2\pi,1\sigma$ ligands and can be viewed as dianions, we attempted to prepare bis(imido) alkyne complexes analogous to the tris(imido) complexes just described. A suitable starting material is $Re(NAr)_2Cl_3(py)$, which can be prepared by the published method[26] or by treating **1** with 2 equiv of pyridinium chloride in methylene chloride.[34] We often chose to use $Me_3CCH_2C{\equiv}CCH_2CMe_3$ (NpC≡CNp), since we have found that compounds containing NpC≡CNp can be prepared in higher yield and are more easily isolated than those containing 2-butyne or 3-hexyne. Dineopentylacetylene is also a good choice for steric reasons; steric hindrance near the metal is minimal, but alkyne coupling at some point during synthesis is still discouraged by the relatively bulky neopentyl groups.

Reduction of $Re(NAr)_2Cl_3(py)$ with sodium amalgam in THF in the presence of MeC≡CMe or NpC≡CNp yields complexes of the type $Re(NAr)_2(\eta^2\text{-}C_2R_2)Cl$ [R = Me (**6a**)[21] or Np (**6b**)] (eq 4). An alternative method is to add the alkyne to $Re(NAr)_2Cl(py)_2$ (eq 5).[21] Both compounds are dark red-orange. Proton and carbon NMR spectra for **6a** and **6b** show that the ends of the alkyne ligands are inequivalent and the methylene protons in **6b** are equivalent, consistent with a rigid pseudotetrahedral C_s structure in which the alkyne carbon atoms lie in a plane that contains the Re—Cl bond. This structure is analogous to that found for $ReO_2(\eta^2\text{-}C_2R_2)R$[35] and is the structure expected in a "metallocene-like" $Re(NAr)_2$ compound.[21] An absorption is found at 1769 cm^{-1} (ν_{CC}) in the IR spectrum of **6b**.



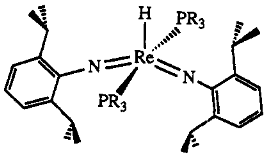
(4)

$$Re(NAr)_2(py)_2Cl + RC{\equiv}CR \xrightarrow[-2py]{THF} Re(NAr)_2(\eta^2\text{-}RC{\equiv}CR)Cl \quad (5)$$

Reduction of **6b** by 1 equiv of sodium amalgam yields red-orange, highly crystalline $Hg[Re(NAr)_2(\eta^2\text{-}C_2Np_2)]_2$ (**7a**) in 76% yield, while reduction by 2 equiv of sodium amalgam yields pine-green, pentane-soluble $Na(THF)_2Re(NAr)_2(\eta^2\text{-}C_2Np_2)$ (**7b**) in 92% yield. In compound **7a** the imido ligands are equivalent with diastereotopic isopropylmethyl groups, the ends of the alkyne ligands are inequivalent, and a plane of symmetry passes through the methylene carbon atoms of the alkyne. NMR data for **7b** in benzene are consistent with a C_{2v} structure, either a pseudotrigonal planar core in which ions are separated or a highly fluxional structure in which sodium is associated with the anion in some way, most likely by binding to a nitrogen atom. We prefer the latter description on the basis of the structure of a related compound reported below.

$Na(THF)_2Re(NAr)_2(\eta^2\text{-}C_2Np_2)$ (**7b**) appears to be a stronger nucleophile than $Na(THF)_2Re(NAr)_3$; **7b** reacts instantaneously with electrophiles, while reactions involving **2b** require more time (up to 1 min). **7b** reacts with MeI or $ClCH_2\text{-}2,4,6\text{-}C_6H_2Me_3$ to yield $Re(NAr)_2(\eta^2\text{-}C_2Np_2)Me$ (**8a**) or $Re(NAr)_2(\eta^2\text{-}C_2Np_2)(CH_2\text{-}2,4,6\text{-}C_6H_2Me_3)$ (**8b**), but it does not react smoothly with methylene chloride. **7b** also does not react readily with PMe_3, CO_2, ethylene, CO, or H_2, while no product could be identified upon attempted oxidation of **7b** with Me_3NO. **7b** is easily protonated with $[Et_2NH_2][OTf]$ in THF to give pale orange $Re(NAr)_2(\eta^2\text{-}C_2Np_2)H$ (**9**). What we will assume at this stage to be a hydride resonance is observed at 2.6 ppm in the proton NMR spectrum, but again no absorption could be observed in the IR spectrum that could be attributed to ν_{Re-H}. Addition of CCl_4 to $Re(NAr)_2(\eta^2\text{-}C_2Np_2)H$ in benzene-d_6 yields $CHCl_3$ and $Re(NAr)_2(\eta^2\text{-}C_2Np_2)Cl$ quantitatively. Cooling a sample of **9** in toluene-d_8 results in little change in the proton NMR spectrum. The minimum longitudinal relaxation time of the hydride ligand in **7b** was found to be 191 ms, similar to that found in $Re(NAr)_3H$. A plausible structure for **7b** is one in which the acetylene and hydride ligands lie in a plane that passes between the two imido ligands and in which the N–Re–N angle is ca. 135°.

$Re(NAr)_2(PMe_2Ph)_2H$ (**10**) forms rapidly upon adding excess PMe_2Ph to **9**. In this case a Re–H absorption is clearly observable in the IR spectrum at 1998 cm^{-1}. The hydride resonance is observed as a triplet at −10.28 ppm in **10**, while the phosphine methyl resonances are virtual



10

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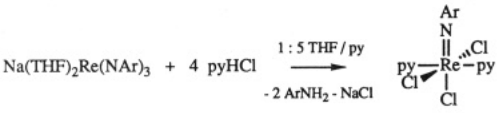
(34) Horton, A. D.; Schrock, R. R. *Polyhedron* **1988**, *7*, 1841.

(35) Felixberger, J. K.; Kuchler, J. G.; Herdtweck, E.; Paciello, R. A.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 946.

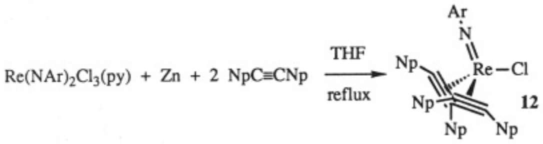
triplets, suggesting a *trans*-bis(phosphine) arrangement. Two sets of resonances are observed for the isopropyl groups. T_1(min) for **10** was found to be 166 ms at −52 °C, slightly shorter than T_1(min) in the other hydride complexes reported above. A plausible structure for **10** is a distorted trigonal bipyramid in which the imido nitrogen atoms and hydride lie in the equatorial plane and the N–Re–N angle is ca. 150° and in which the axial phosphines prevent free rotation of the imido aryl groups on the NMR time scale. Such a structure would be analogous to that observed for $Os(NAr)_2(PMe_2Ph)I_2$).[2] Addition of 2-butyne to **9** in benzene-d_6 in an NMR tube yields $Re(NAr)_2(\eta^2\text{-}C_2Me_2)H$, but **9** does not react readily with dimethylacetylene dicarboxylate or with CO (1 atm).

Imido Bis(alkyne) Compounds. Addition of 4 equiv of pyridinium chloride in a 1:5 mixture of THF and pyridine to $Na(THF)_2Re(NAr)_3$ (**2b**) affords $Re(NAr)Cl_3(py)_2$ (**11**) in high yield (eq 6). **2b** simply can be added to a rapidly stirred slurry of pyridinium chloride in THF/py in portions; the brown solution of $[Re(NAr)_3]^-$ turns to the grass green color of $Re(NAr)Cl_3(py)_2$ in a few minutes. Compound **11** is an analog of a series of complexes of the type $Re(Y)X_3(PR_3)_2$ (Y = imido or oxo).[36,37] The structure shown in eq 6 is consistent with NMR data and with known structures of compounds in this class.



(6)

$Re(NAr)Cl_3(py)_2$ is reduced by excess Zn dust in the presence of 2 equiv of alkyne in refluxing THF to afford **12** (eq 7) in high yield in approximately 3 days. NMR data for **12** are consistent with it being a rigid pseudotetrahedral C_s species analogous to the known structures of $Re(O)(\eta^2\text{-}C_2R_2)_2I$ compounds.[22,25] The alkyne ligands in **12** do not exchange with added alkyne and are not fluxional on the NMR time scale, as found also for alkynes in compounds of the type $Re(O)(\eta^2\text{-}C_2R_2)_2I$.[22]



12

(7)

Reduction of **12** by 1 or 2 equiv of sodium amalgam in THF yields $Hg[Re(NAr)(\eta^2\text{-}C_2Np_2)_2]_2$ (**13a**) or $Na(THF)_2Re(NAr)(\eta^2\text{-}C_2Np_2)_2$ (**13b**), respectively. Pentane-soluble, cherry red **13a** is formed in approximately 85% yield. NMR spectra suggest that it has the same symmetry as **12**, i.e., one set of resonances is observed for the isopropyl groups and four doublets are observed for the neopentyl methylene protons. Although **13a** could not be obtained analytically pure, the $[M]^+$ ion was observed by mass spectrometry (with the appropriate pattern consistent with the $HgRe_2$ core). **13b** is a purple, crystalline solid that is slightly soluble in pentane. Proton and carbon NMR data for **13b** in benzene are consistent with a trigonal planar rhenium center on the NMR time scale. $[NEt_4][Re(NAr)(\eta^2\text{-}C_2Np_2)_2]$ (**13c**) can be prepared as a navy blue solid by treating **13b** with NEt_4Cl, but it decomposes in toluene-d_8 solution overnight to give a yellow solution containing C_2H_4, NEt_3, and $Re(NAr)(\eta^2\text{-}C_2Np_2)_2H$ (vide infra) in a 1:1:1 ratio.

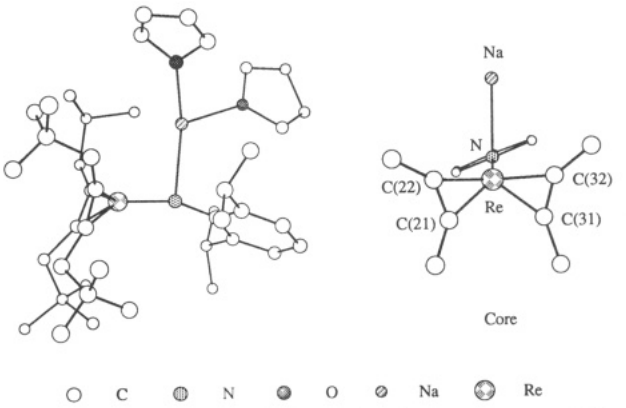


Figure 3. Two views of the molecular structure of $Na(THF)_2Re(NAr)(\eta^2\text{-}C_2Np_2)_2$ (**13b**).

Table III. Selected Bond Distances (Å) and Angles (deg) in $Na(THF)_2Re(NAr)(\eta^2\text{-}C_2Np_2)_2$ (13b)

	Distances		
Re–Na	3.174(5)	Re–C(31)	2.004(9)
Re–N	1.793(7)	Re–C(32)	2.015(9)
Na–N	2.463(9)	Re–C(21)	2.005(9)
Na–O(1)	2.26(1)	Na–O(2)	2.28(1)
Re–C(22)	1.989(9)		
	Angles		
Na–Re–N	50.6(3)	C(21)–Re–C(22)	38.1(4)
Re–Na–N	34.2(2)	C(21)–Re–C(31)	90.4(4)
Re–N–Na	95.2(3)	C(22)–Re–C(32)	128.7(4)
Re–N–C(11)	157.5(7)	C(21)–Re–C(32)	116.9(4)
Na–N–C(11)	107.3(6)	C(22)–Re–C(31)	121.8(4)
N–Re–C(22)	115.5(4)	Re–C(21)–C(28)	151.8(8)
N–Re–C(31)	120.5(4)	Re–C(22)–C(21)	71.6(6)
N–Re–C(21)	130.6(3)	Re–C(22)–C(23)	155.1(9)
N–Re–C(32)	110.1(3)	Re–C(21)–C(22)	70.2(6)
Re–Na–O(1)	128.5(3)	O(1)–Na–N	148.5(4)
Re–Na–O(2)	136.9(3)	O(2)–Na–N	109.2(4)
O(1)–Na–O(2)	94.5(4)		

The molecular structure of $Na(THF)_2Re(NAr)(\eta^2\text{-}C_2Np_2)_2$ (**13b**) is shown in Figure 3. Bond distances and angles are found in Table III. The $[Na(THF)_2]^+$ ion in **13b** is bound to the imido nitrogen atom (2.463(8) Å), but not to rhenium (Re–Na = 3.174(5) Å), and the coordination about the rhenium center is distorted from the pseudotrigonal planar geometry expected for $[Re(NAr)(\eta^2\text{-}C_2Np_2)_2]^-$. The alkyne ligands are tipped away from one another and the alkyne carbon atoms furthest from the sodium atom are closer together, although the rhenium–carbon distances are all within ~0.03 Å of one another (1.976–2.005 Å). The short metal–carbon distances are consistent with the four-electron donor alkyne formalism. The rhenium–nitrogen distance (1.793(7) Å) and Re–N–C_{ipso} angle (157.5(7)°) are consistent with the imido ligand's lone electron pair being bonded to sodium rather than rhenium. Overall the structure of **13b** is similar to that of $Na(MeCN)_2Re(O)(\eta^2\text{-}C_2Ph_2)_2$.[38]

$Na(THF)_2Re(NAr)(\eta^2\text{-}C_2Np_2)_2$ (**13b**) also behaves as a nucleophile. It is alkylated smoothly by MeI and $ClCH_2$-2,4,6-$C_6H_2Me_3$ to afford $Re(NAr)(\eta^2\text{-}C_2Np_2)_2Me$ (**14a**) and $Re(NAr)(\eta^2\text{-}C_2Np_2)_2(CH_2\text{-}2,4,6\text{-}C_6H_2Me_3)$ (**14b**). (NMR and IR data for **14a** and **14b** are analogous to those for the tris(imido) and bis(imido) alkyne analogs.) Addition of

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

[37] Chatt, J.; Garforth, J. D.; Johnson, N. P.; Rowe, G. A. *J. Chem. Soc.* **1964**, 1012.

[38] Spaltenstein, E.; Conry, R. R.; Critchlow, S. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1989**, *111*, 8741.

Table IV. Electrochemical Potentials for the Chloride Derivatives and the Sodium Salts[a]

derivative	$[Re(NAr)_3]$	$[Re(NAr)_2(\eta^2\text{-}C_2Np_2)]$	$[Re(NAr)(\eta^2\text{-}C_2Np_2)_2]$
Cl (reduction)	−1.83,[b] −2.56	−1.98	−2.14
anion (oxidation)	−0.56	−1.3	−1.6
Na (oxidation)	−0.56	−1.21	−1.43[b]

[a] The potentials are reported as V vs $FeCp_2$ internal reference in approximately 5 mM solutions in 0.5 M NBu_4PF_6/THF. [b] Process is electrochemically reversible at fast scan rates.

methylene chloride or trimethylamine oxide to **13b** leads to decomposition, and phosphines do not displace the alkyne ligands in **13b** readily at 25 °C. Addition of $[Et_2NH_2][OTf]$ to **13b** yields pale yellow $Re(NAr)(\eta^2\text{-}C_2Np_2)_2H$ (**15**). A hydride absorption can be observed in the IR spectrum at 1988 cm^{-1}, and the hydride resonance can be observed at 6.6 ppm in the ^1H NMR spectrum. T_1 = 193 ms for the hydride ligand at −55 °C. Addition of CCl_4 to **15** in benzene-d_6 yields $Re(NAr)(\eta^2\text{-}C_2Np_2)_2Cl$ and $CHCl_3$ quantitatively. Compound **15** is the most robust of any of the hydrides reported here. It does not react readily with alkynes, olefins, CO, or oxygen, and it reacts only very slowly with phosphines to give paramagnetic, pale green, and as yet unidentified products.

Electrochemistry. Cyclic voltammograms (200 mV s^{-1}) were obtained for the chloride derivatives and sodium salts of the tris-, bis-, and mono(imido) complexes in a solution of 0.5 M $[NBu_4][PF_6]$ in THF. The potentials are listed in Table IV and are reported as V vs SSCE, using the ferrocene/ferrocenium couple ($Fc/Fc^+ = +0.53$ V vs SSCE) as an internal standard.

The anions ($[Re(NAr)_3]^-$, $[Re(NAr)_2(\eta^2\text{-}C_2Np_2)]^-$, and $[Re(NAr)(\eta^2\text{-}C_2Np_2)_2]^-$) are progressively easier to oxidize ($E_{a,p}$ = −0.56, −1.21, −1.43 V; Table IV), although all oxidations are irreversible. This trend is consistent with the greater ease of oxidizing a metal in a lower formal oxidation state (Re(V), Re(III), Re(I), counting the alkynes as neutral ligands).

The cyclic voltammogram of $Re(NAr)_3Cl$ is one of the most interesting; it is shown in Figure 4. A quasi reversible one-electron reduction occurs at −1.83 V vs $FeCp_2$. The size of the current obtained in the reoxidation state depends upon the scan rate. A second, irreversible reduction is observed at −2.56 V ($E_{c,p}$), and an irreversible oxidation, on the return scan at $E_{a,p}$ = −0.56 V, the potential at which $Na(THF)_2Re(NAr)_3$ is irreversibly oxidized. The oxidation wave is also observed when a switching potential more positive than −2.4 V is employed, but the current is much smaller than when the second reduction is allowed to take place. Therefore, the product that is oxidized at −0.56 V ($[Re(NAr)_3]^-$) is being produced at both −1.83 and −2.56 V. At a switching potential of −2.2 V and fast scan rates i_a/i_c is near unity and decreases as the scan rate decreases, consistent with formation and reoxidation of $[Re(NAr)_3Cl]^-$ at fast scan rates. When the scan rate is decreased from 500 mV/s, the ratio i_{ox} (at −0.56 V) to i_c (at −1.83 V) increases until a scan rate of 50 mV/s is reached, at which point it begins to decrease; at a scan rate of 10 mV/s, no oxidation wave at −0.56 V is observed. We propose that $[Re(NAr)_3Cl]^-$ is formed at −1.83 V, loses Cl^- to give $[Re(NAr)_3]$, which is immediately reduced to $[Re(NAr)_3]^-$ (an ECE mechanism), or is further reduced at a more negative potential to $[Re(NAr)_3Cl]^{2-}$, which then dissociates Cl^- and forms $[Re(NAr)_3]^-$ (an EEC mechanism). At high scan rates, $[Re(NAr)_3Cl]^-$ is reoxidized before chloride dissociates to an appreciable extent. As the scan rate is decreased, the concentration of $[Re(NAr)_3Cl]^-$ builds up, chloride dissociates, and $[Re(NAr)_3]$ is reduced to $[Re(NAr)_3]^-$. However, as the scan rate is decreased even further, $[Re(NAr)_3]^-$ can diffuse away from the electrode, which reduces the amount available for reoxidation.

The cyclic voltammograms of $Re(NAr)_2(\eta^2\text{-}C_2Np_2)Cl$ and $Re(NAr)(\eta^2\text{-}C_2Np_2)_2Cl$ are similar to each other (Figures 5 and 6). The halide derivatives are reduced in an irreversible, two-electron EEC mechanism to $[Re(NAr)_{3-x}(\eta^2\text{-}C_2Np_2)_x]^-$ (x = 1 or 2), and this anion is reoxidized (and the product decomposes) on the return scan. Even at a scan rate of 1 V/s, the reduction of $Re(NAr)_2(\eta^2\text{-}C_2Np_2)Cl$ and $Re(NAr)(C_2Np_2)_2Cl$ are electrochemically irreversible. The two-electron reduction of $Re(NAr)(\eta^2\text{-}C_2Np_2)_2Cl$ is confirmed by holding the potential at −2.4 V vs $FeCp_2$ in a solution of $Re(NAr)(\eta^2\text{-}C_2Np_2)_2Cl$ using large Pt electrodes and observing the intense blue color of $[Re(NAr)(\eta^2\text{-}C_2Np_2)_2]^-$ as it is generated at the cathode. The disparity in the oxidation potentials of the electrochemically generated $[Re(NAr)(\eta^2\text{-}C_2Np_2)_2]^-$ and $Na(THF)_2Re(NAr)(\eta^2\text{-}C_2Np_2)_2$ may be attributed to the different cations in the two compounds. We have found a significant interaction of the sodium cation with the anion in the solid state (vide supra) and believe there is some interaction between the two in solution; in electrochemically generated $[NBu_4][Re(NAr)(\eta^2\text{-}C_2Np_2)_2]$, there can be no such interaction. The mechanism for reduction of the alkyne-containing compounds is likely to be analogous to that proposed for EEC reduction of $Re(NAr)_3Cl$, if one assumes that chloride dissociation from $[Re(NAr)(\eta^2\text{-}C_2Np_2)_2Cl]^-$ occurs at approximately the same rate as from $[Re(NAr)_3Cl]^-$. Thus the only kinetically available pathway for reduction of $Re(NAr)(\eta^2\text{-}C_2Np_2)_2Cl$ would be an EEC pathway because chloride dissociation from $[Re(NAr)(\eta^2\text{-}C_2Np_2)_2Cl]^-$ appears to be very slow relative to electron capture. Subsequent dissociation of chloride from $[Re(NAr)(\eta^2\text{-}C_2Np_2)_2Cl]^{2-}$ must be fast, since the reduction is irreversible.

Calculations. Extended Hückel MO calculations on $Os(NH)_3$ agreed qualitatively with SCF–Xα calculations.[2] Therefore the qualitative molecular orbital description also should be valid for $[Re(NH)_3]^-$. An MO diagram for $[Re(NH)_3]^-$ (on the basis of extended Hückel calculations) is shown in Figure 7. The HOMO is the rhenium d_{z^2} orbital, while the LUMO (omitted) is the doubly degenerate Re–N $\pi_\perp^*$ orbital. The HOMO and the LUMO are separated by 1.8 eV, which could account for the lack of reactivity of $[Re(NAr)_3]^-$ with nucleophiles. As in $Os(NAr)_3$, a ligand-centered nonbonding orbital (LCNBO; a_1''; HOMO(−1)) lowers the "20-electron" count at rhenium to 18 in $[Re(NH)_3]^-$. However, the HOMO(−2) (a_2''), which consists of the symmetric combination of nitrogen p_z orbitals and which is stabilized by Re $6p_z$,[2] is mainly ligand-centered due to the large separation of the orbital energies (p(N) vs p(Re)). This a_2'' orbital is 2% Re 6 p in the extended Hückel calculations and 4% Os 6p in the Xα calculations. However, some rhenium p character in this orbital must be inferred in order to electronically saturate the metal center.

The calculated MO diagram for $[Re(NH)_2(\eta^2\text{-}C_2H_2)]^-$ (Figure 8) is similar to that for $[Re(NH)_3]^-$. Again the HOMO is mainly Re d_{z^2} and the LUMO (omitted) is mainly

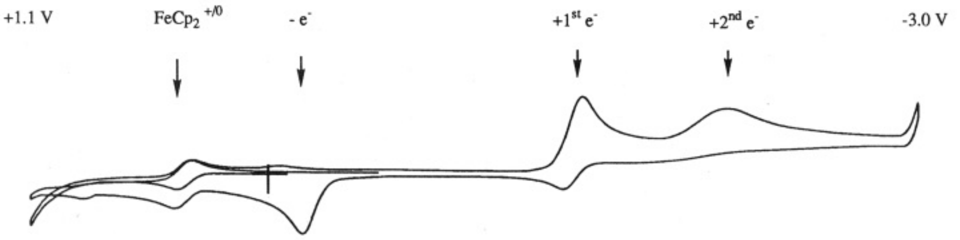


Figure 4. Voltammogram of $Re(NAr)_3Cl$, 5 mM in 0.5 M NBu_4PF_6/THF. Scan rate = 220 mV/s.

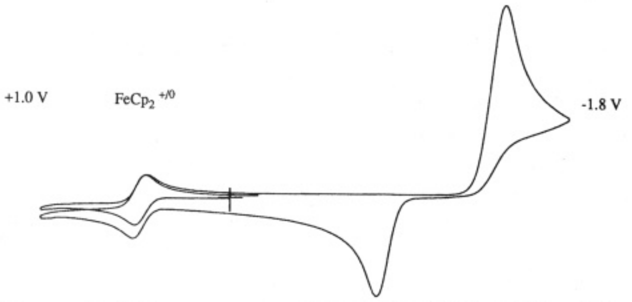


Figure 5. Voltammogram of $Re(NAr)_2(C_2Np_2)Cl$, 5 mM in 0.5 M NBu_4PF_6/THF. Scan rate = 200 mV/s.

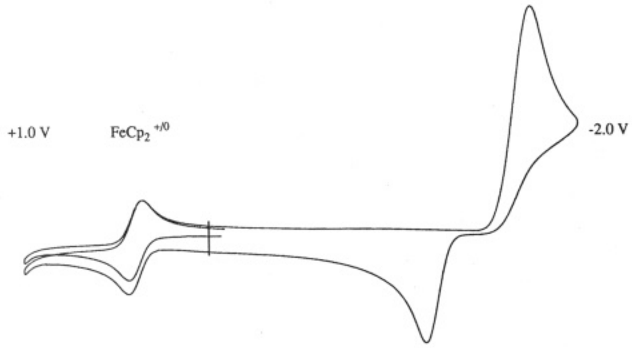
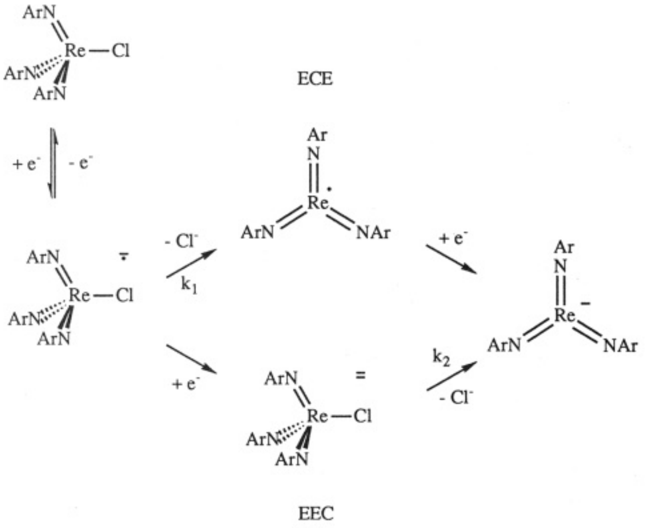


Figure 6. Voltammogram of $Re(NAr)(C_2Np_2)_2Cl$, 5 mM in 0.5 M NBu_4PF_6/THF. Scan rate = 200 mV/s.

Scheme II. EEC and ECE Pathways for Reduction of Re(NAr)$_3$Cl (1)



Re d_{yz} (Re–N $\pi_\perp$*). The HOMO–LUMO separation is 1.2 eV. The HOMO(−1) in this case is the Re(alkyne) backbonding orbital (Re–CC $\pi_\perp$). There is an orbital reminiscent of the C_3 symmetric LCNBO in this complex also; it is the HOMO(−2) (with b_1 symmetry) in the diagram. The metal–alkyne bonding is consistent with a four-electron donor description. However the b_1 LCNBO highlights the importance of an MO description, in contrast to counting the alkyne simply as a "two" or "four" electron donor. It also should be noted that the hybridization of the alkyne in-plane π bond upon coordination to the metal allows formation of the M–CC σ-bond (a_1; HOMO(−3)) using an sd hybrid orbital, rather than an in-plane sp hybrid, as in the imido bonding. Incorporation of more metal character in the (HOMO(−3)) a_1 orbital saturates the metal and achieves an 18-electron count.

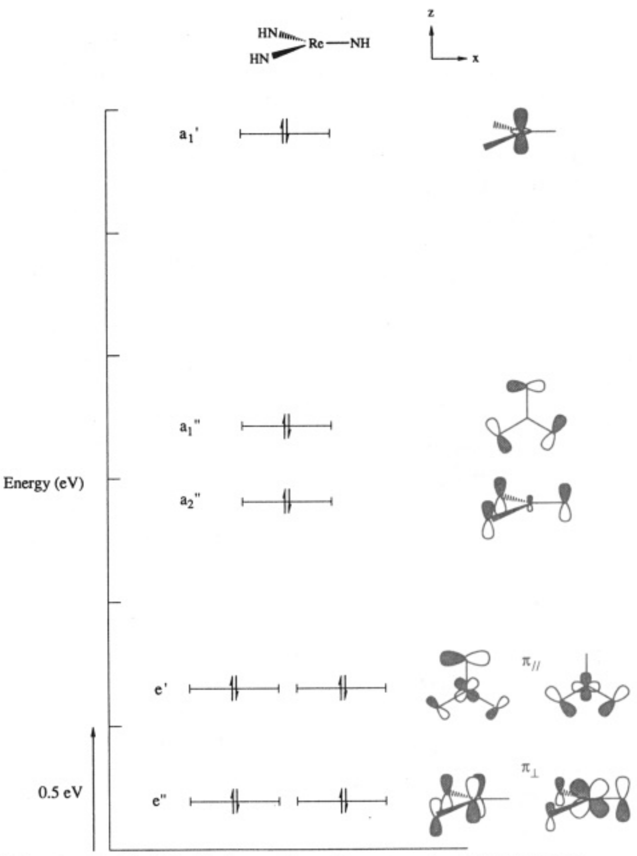


Figure 7. Orbital interaction diagram for $[Re(NH)_3]^-$.

In Figure 9 is shown the calculated MO diagram for $[Re(NH)(C_2H_2)_2]^-$; it again is similar to that for $[Re(NH)_3]^-$. The HOMO is Re d_{z^2}, and the LUMO is Re d_{xz} (Re–N $\pi_\parallel$*); they are separated by 2.5 eV. The orbital analogous to a C_3 symmetric LCNBO has moved down in energy (to HOMO(−3)) due to the lower energy of the alkyne π orbitals relative to nitrogen p orbitals. The HOMO(−2) is reminiscent of the a_2'' orbital in $[Re(NH)_3]^-$ in that the metal character in this orbital is small. This orbital consists mainly of alkyne to metal σ donation as well as some metal–nitrogen $\pi_\parallel$. There is some Re d_{xy} character in this orbital, but the hybridization of the alkyne σ-donor orbital prevents good spacial overlap with the metal d orbital, which is in the ML_3 plane, and the orbital is mainly ligand-centered (it is 5% Re d_{xy}). Again a 20-electron count is avoided by filling a LCNBO. Five

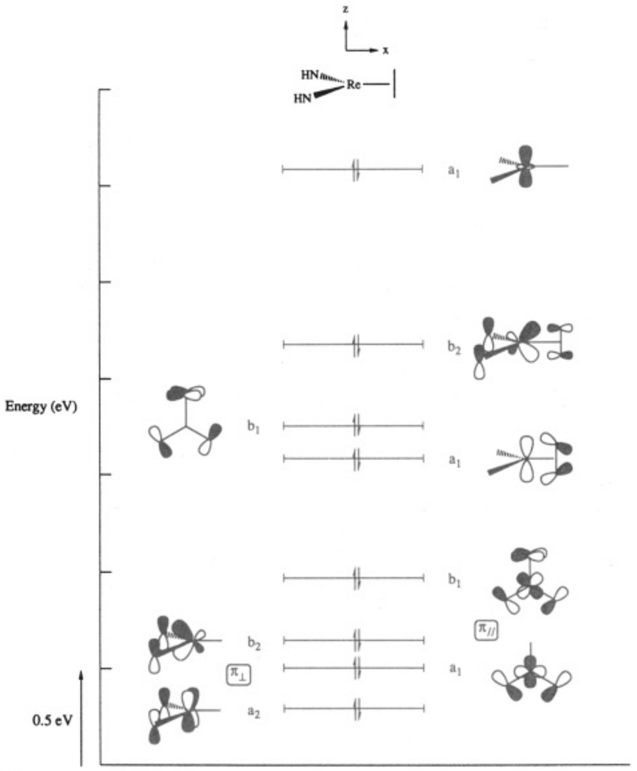


Figure 8. Orbital interaction diagram for $[Re(NH)_2(C_2H_2)]^-$.

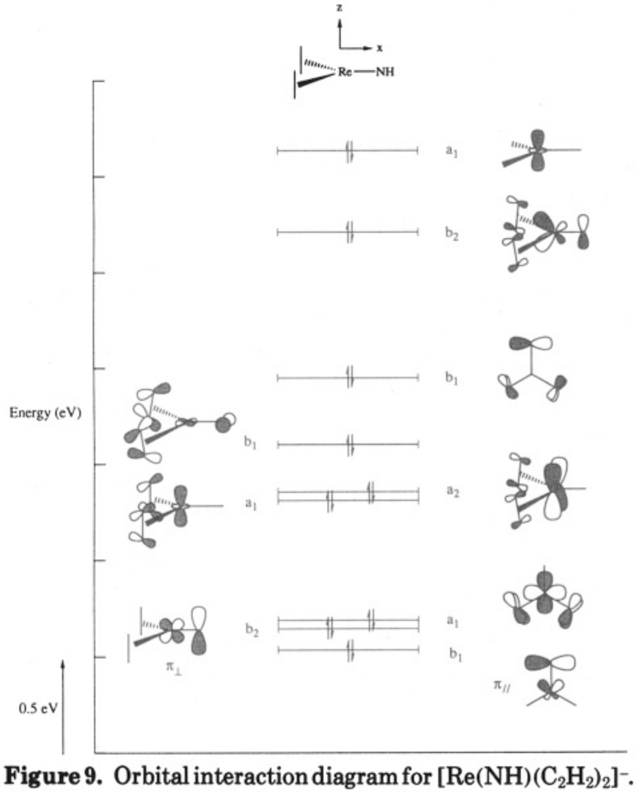
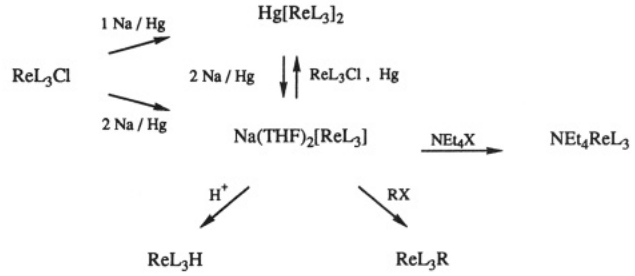


Figure 9. Orbital interaction diagram for $[Re(NH)(C_2H_2)_2]^-$.

π-bonds are formed, but the fifth (b_1) is so weakened by poor spacial overlap of the component orbitals that it is mainly ligand-centered. The sixth ligand-centered combination (also b_1) cannot overlap with any metal-based orbital.

Scheme III. Reactions of $Re(NAr)_3$, $[Re(NAr)_2(\eta^2\text{-}RC{\equiv}CR)]^-$, and $[Re(NAr)(\eta^2\text{-}RC{\equiv}CR)_2]$ Complexes That Are Analogous



Discussion

The original goal of this work was to synthesize and outline the reactivity of the rhenium tris(imido) anion. However, having found that $Re(NAr)_3H$ reacts with alkynes to form $Re(NAr)_2(NHAr)(\eta^2\text{-}C_2R_2)$, a secondary goal became the synthesis of mixed imido alkyne complexes in order to compare the reactivities of species containing $Re(NAr)_x(\eta^2\text{-alkyne})_{3-x}$ ($x = 1$–3) cores. We were somewhat surprised to find (as summarized in Scheme III) that chloride derivatives can all be reduced to give mercury derivatives or nucleophilic anions that can be alkylated or protonated. The greatest potential for differences between $Re(NAr)_x(\text{alkyne})_{3-x}$ cores for different values of x exists for compounds that formally contain the anion and those that appear to be hydride complexes. Formation of species that contain the metallocene-like bis(imido) core appears to be favorable and could more sharply distinguish the chemistry of complexes in which $x = 2$ or 3 from chemistry of complexes in which $x = 1$. What is also striking about the chemistry uncovered here is the paucity of facile alkyne coupling reactions, behavior that has been noted in related rhenium complexes[39] but that contrasts with the behavior of imido alkyne complexes of (e.g.) tantalum,[40,41] where alkyne coupling is common.

The importance of steric effects in preventing oligomerization of the metal centers in these compounds cannot be overemphasized. For instance, reduction of $Re(NAr')_3Cl$ ($Ar' = 2,6\text{-}C_6H_3Me_2$) using sodium amalgam results in formation of $[Re(NAr')_2(\mu\text{-}NAr')]_2$, which does not undergo further reduction.[42] $[Re(NAr')_3]^-$ has never been prepared. Likewise, rhenium *tert*-butylimido complexes readily form dimeric species.[29] Comparison of the reaction in which $Re(NAr)(\eta^2\text{-}C_2Np_2)_2Cl$ is reduced with reactions in which compounds of the type $ReO(\eta^2\text{-}C_2R_2)_2I$ are reduced leads to the same conclusion; oxo-bridged dimers are often formed in the oxo systems, even though a large amount of metal–ligand π-bonding is often maintained.[38] The chemistry of imido bis(alkyne) complexes is otherwise analogous to that of oxo bis(alkyne) complexes, as one might expect.

The reactivities of the $[ReL_3]^-$ species reported here are strikingly similar to those for $[CpMo(CO)_3]^-$, $[Re(CO)_5]^-$, $[CpFe(CO)_2]^-$, and other metal carbonyl anions.[43] For instance, $[Re(CO)_5]^-$ reacts with proton sources and alkylating agents and will oxidize mercury (in electrochemical experiments with mercury electrodes) to form $Hg[Re(CO)_5]_2$.[44,45] Each metal anion behaves as an 18-

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Table V. ^{13}C NMR Chemical Shifts (ppm, above) and ν_{CC} (cm^{-1}, below) for Dineopentylacetylene Complexes

	X				
	Cl	Hg	Na	H	Me
Re(NAr)$_2$(η^2-C$_2$Np$_2$)X	158.9, 143.4	154.2, 143.5	157.0	153.2, 136.9	151.0, 141.0
Re(NAr)(η^2-C$_2$Np$_2$)$_2$X	162.7, 154.7	167.9, 160.1	171.4	163.8, 155.7	160.7, 159.9
Re(NAr)$_2$(η^2-C$_2$Np$_2$)X	1769	1769	1744	1785	1780
Re(NAr)(η^2-C$_2$Np$_2$)$_2$X	1758, 1743	1743, 1725	1700, 1653	1758, 1748	1755, 1744

electron, σ-donor nucleophile.[43] For [Re(CO)$_5$]$^-$ it perhaps is not surprising that the fragment remains intact throughout the reaction sequences, but it is still surprising to us that the [ReL$_3$]$^-$ compounds (where L is either an imido or alkyne ligand) also behave strictly as σ-nucleophiles and do not react with π-acceptors or nucleophiles, except when bis(imido) complexes can be formed. This behavior contrasts with that of a d^2 compound such as Ta(OSiR$_3$)$_3$,[46,47] which interacts strongly with π bonding ligands.

We conclude that a surprising number of structural and chemical analogies between imido and alkyne ligands are valid, at least in the types of compounds we have explored here. However, the low electronegatively of an alkyne ligand relative to an imido ligand, the fact that an alkyne is not strictly a 2π,1σ ligand, and the fact that an alkyne can be displaced by another two-electron donor all are likely to limit the validity of the analogy between an imido and an alkyne ligand in extreme circumstances. Although the bis(imido) framework continues to show at least structural similarities to metallocenes, and now cyclopentadienyl imido complexes are also attracting attention as metallocene analogs,[48-50] the analogy between bis(alkyne) complexes and metallocenes, although valid to some extent in terms of an orbital analysis and known structures,[51-54] appears to be more tenuous.

Experimental Section

General Details. All manipulations were carried out under a dry dinitrogen atmosphere in a Vacuum/Atmospheres drybox, under a dry argon atmosphere using standard Schlenk techniques on a Schlenk line, or on a high-vacuum line. All solvents and liquid reagents were distilled under dry dinitrogen over sodium/benzophenone ketyl (THF, benzene, ether, pentane), molten sodium (toluene, pyridine, norbornene), or CaH$_2$ (dichloromethane, 2,6-diisopropylaniline, NEt$_3$, phosphines, pivaldehyde), and stored over sieves. Pentane was washed using 5% HNO$_3$/H$_2$SO$_4$ and dried over CaCl$_2$ prior to distillation, and tetraglyme was added to dissolve the ketyl. THF was further purified by vacuum transfer from sodium/benzophenone ketyl under high vacuum before use. Re$_2$O$_7$ (Alfa), Me$_3$SiCl, [N(PPh$_3$)$_2$]Cl, and 2,4,6-trimethylbenzyl chloride were purchased from commercial sources and used as received. [NBu$_4$]PF$_6$ (Strem) was recrystallized four times from hot ethanol, powdered, and dried under high vacuum at 120 °C for 2 days. Ferrocene and pyridinium chloride (Aldrich) were sublimed under high vacuum prior to use. Sodium metal was cut freshly just prior to use, and mercury (triply distilled, Aldrich) was filtered before use. MeI and all acetylenes were passed through activated alumina (high vacuum, 120 °C, 2 days) just prior to use. 2,2,7,7-Tetramethyloct-4-yne was prepared according to literature procedures[55] from acetylene (Matheson), butyl lithium (Alfa), and neopentyl iodide (Aldrich). All NMR data were recorded in C$_6$D$_6$ at approximately 22 °C on a Varian Unity 300-MHz spectrometer (all variable-temperature experiments, most ^{13}C experiments), a Varian XL-300 spectrometer, or a Bruker AM250 spectrometer. All chemical shifts are reported in ppm downfield from TMS (^{1}H, ^{13}C) or P(OMe)$_3$ (^{31}P, external reference, δ 141 ppm (H$_3$PO$_4$)), and *J*'s are in hertz. Deuterated solvents were stored over molecular sieves. Infrared spectra were recorded on a Perkin-Elmer 1400 spectrometer or a Mattson-Cygnus 100 FT-IR spectrometer as Nujol mulls between KBr plates. Microanalyses (C, H, N) were performed in our laboratory using a Perkin-Elmer PE2400 microanalyzer.

Extended Hückel Calculations. Molecular orbital calculations were performed on the CAChe Worksystem, a product developed by Tektronix, using the Alvarez collected parameters. The parameters used for the extended Hückel calculation of the three compounds are as follows: Re–N = 1.73 Å, Re–C = 1.99 Å, N–H = 1.07 Å, C–H = 1.09 Å, L–Re–L = 120, Re–N–H = 180°, Re–C–H = 150°. The Cartesian coordinates of the models can be found in the supplementary material.

Electrochemistry. All electrochemical experiments were performed using an EG&G PARC Model 175 universal programmer and a Model 173 potentiostat, and data were recorded on a EG&G RE0089 X-Y recorder. THF solutions of the appropriate compound (3–5 mM), 0.5 M in NBu$_4$PF$_6$, were used with internal ferrocene (approximately 0.6 mM) as a reference. A three-electrode system was used: a Pt disk electrode, a Pt mesh counter electrode, and a silver wire pseudoreference electrode. The Fc$^{+/0}$ couple was measured in a typical solution versus an SSCE ($E^{\circ\prime}$ = +0.53 V vs SSCE). All potentials reported here are reported as volts vs SSCE. All experiments were performed in the drybox, except the measurement of the ferrocene couple vs SSCE.

Re(NAr)$_3$Cl (1). Re$_2$O$_7$ (12.5 g, 25.8 mmol) was added to 200 mL of dichloromethane, and the slurry was chilled to −40 °C. To this slurry was added sequentially at −40 °C 2,6-diisopropylaniline (29.2 mL, 155 mmol), NEt$_3$ (50.5 mL, 361 mmol), and (slowly) Me$_3$SiCl (52.4 mL, 413 mmol). The reaction mixture was allowed to warm to room temperature and was stirred under nitrogen for 3 days. The solution was evaporated to dryness in vacuo, and the resulting maroon solid was extracted with ether (500 mL). The mixture was filtered through Celite and the precipitate washed with ether until the filtrate was no longer red. The solvent was removed in vacuo, and the resulting solid was washed with cold pentane and dried to afford 38.5 g (99%) of dark red crystals: ^{1}H NMR δ 7.04 (d, 6, H$_m$), 6.92 (t, 3, H$_p$), 3.68 (sept, 6, C*H*Me$_2$), 1.09 (d, 36, CH*Me*$_2$). Anal. Calcd for C$_{36}$H$_{51}$N$_3$ClRe: C, 57.85; H, 6.87; N, 5.62. Found: C, 58.16; H, 7.04; N, 5.59.

[Re(NAr)$_3$]$_2$Hg (2a). To a cold (−40 °C) solution of Re(NAr)$_3$Cl (5.00 g, 6.69 mmol) in 40 mL of THF was added freshly-prepared sodium amalgam (0.154 g, 6.69 mmol of Na in 31 g of mercury). The mixture was shaken vigorously for 5 min

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and stirred for an additional 1.5 h. The solution was decanted away from the mercury and filtered through Celite. The solvent was removed from the filtrate in vacuo. The residue was extracted with 400 mL of hot toluene. The extract was filtered and concentrated in vacuo to give 2.53 g (47%) of dark red microcrystals upon addition of pentane. An analytically pure sample was recrystallized from toluene by adding pentane and cooling to −40 °C: ^{1}H NMR δ 7.05 (d, 2, H_m), 6.98 (t, 1, H_p), 3.99 (sept, 2, $\mathrm{C}H\mathrm{Me}_2$), 1.15 (d, 12, $\mathrm{CH}Me_2$). Anal. Calcd for $\mathrm{C_{72}H_{102}N_6HgRe_2}$: C, 53.23; H, 6.33; N, 5.17. Found: C, 53.51; H, 6.41; N, 5.01.

[Re(NAr)$_3$][Na(THF)$_2$] (2b). To a cold (−40 °C) solution of $\mathrm{Re(NAr)_3Cl}$ (0.50 g, 0.67 mmol) in 10 mL of THF was added freshly-prepared sodium amalgam (18 mg, 78 μmol of Na in 15 g of Hg). The mixture was shaken vigorously for 5 min, during which time the color changed from red-purple to red-orange. The mixture was stirred at ambient temperature for 2 h. The solution was decanted from the Hg and the solvent removed in vacuo. The product was then extracted with 40 mL of toluene, and the extract was filtered through Celite. The solvent was removed from the filtrate in vacuo to yield 0.57 g (97%) of brown microcrystals which were recrystallized at −40 °C from THF with added pentane: ^{1}H NMR δ 7.08 (9, $\mathrm{H_{aryl}}$), 4.14 (sept, 6, $\mathrm{C}H\mathrm{Me}_2$) 3.00 (m, 8, $\mathrm{O[C}H_2\mathrm{CH_2]_2}$), 1.25 (d, 36, $\mathrm{CH}Me_2$) 1.13 (m, 8, $\mathrm{O[CH_2C}H_2\mathrm{]_2}$). Anal. Calcd for $\mathrm{C_{44}H_{67}O_2N3_NaRe}$: C, 60.11; H, 7.68; N, 4.78. Found: C, 60.44; H, 7.82; N, 4.73.

[NEt$_4$][Re(NAr)$_3$] (2c). $\mathrm{Re(NAr)_3Cl}$ (5.0 g, 6.7 mmol) and $\mathrm{NEt_4Cl}$ (1.1 g, 6.7 mmol) were dissolved in THF (30 mL), and the solution was chilled to −40 °C. This red solution was then added to cold 0.5% Na/Hg (64 g, 14 mmol), and the mixture was shaken vigorously for a few minutes and stirred for 12 h, during which time it became brown. The solution was decanted and filtered through Celite, and the filtrate was concentrated in vacuo. The resulting brown powder was washed with toluene (5 × 10 mL) and ether (5 × 10 mL) and dried to give 4.9 g (88%) of a tan powder. Red needles were obtained by crystallization from cold THF with added ether: ^{1}H NMR ($\mathrm{C_6D_5Br}$) δ 6.9–6.7 (m, 9, $\mathrm{H}_{m,p}$), 4.09 (sept, 6, $\mathrm{C}H\mathrm{Me}_2$), 2.11 (q, 8, $\mathrm{C}H_2\mathrm{CH_3}$), 1.16 (d, 36, $\mathrm{CH}Me_2$), 0.31 (t, 12, $\mathrm{NCH_2C}H_3$).

[N(PPh$_3$)$_2$][Re(NAr)$_3$] (2d). $\mathrm{Re(NAr)_3Cl}$ (1.0 g, 1.3 mmol) and $\mathrm{[N(PPh_3)_2]Cl}$ (0.384 g, 0.669 mmol) were dissolved in THF (20 mL). The solution was chilled to −40 °C and added to cold 0.5% Na/Hg (13 g, 2.8 mmol). The reaction mixture was shaken vigorously for a few minutes and stirred for 12 h. The solution was decanted and filtered through Celite, and the filtrate was concentrated in vacuo. The resulting solid was washed with toluene and extracted with cold THF. A few milliliters of toluene was added, and this solution was concentrated in vacuo to give 536 mg (64% based on PPNCl) of ruby red crystals. Due to the compound's low solubility in benzene, it is difficult to assign peaks in the aromatic region: ^{1}H NMR δ 7.2–6.9 (m, 39, $\mathrm{H_{aryl}}$), 4.8 (sept, 6, $\mathrm{C}H\mathrm{Me}_2$), 1.5 (d, 36, $\mathrm{CH}Me_2$). Anal. Calcd for $\mathrm{C_{72}H_{81}N_4P_2Re}$: C, 69.15; H, 6.53; N, 4.48. Found: C, 69.34; H, 6.53; N, 4.39.

[NEt$_4$][Re(NAr)$_3$O]. **1b** (0.50 g, 0.64 mmol) and $\mathrm{Me_3NO}$ (0.050 g, 0.64 mmol) were added to toluene (10 mL), and the slurry was stirred for 30 min, during which time the color changed from brown to bright orange. The slurry was filtered, and the precipitate was washed with toluene and then extracted with THF. The THF extract was concentrated in vacuo to yield 0.49 g (95%) of a pure orange powder: ^{1}H NMR ($\mathrm{CD_2Cl_2}$) δ 6.94 (d, 6, H_m), 6.71 (t, 3, H_p), 3.58 (sept, 6, $\mathrm{C}H\mathrm{Me}_2$), 3.22 (q, 8, $\mathrm{NC}H_2\mathrm{CH_3}$), 1.27 (tt, 12, $J_{\mathrm{NH}} = 1.7$, $\mathrm{NCH_2}CH_3$), 1.03 (d, 36, $\mathrm{CH}Me_2$); ^{13}C NMR ($\mathrm{CD_2Cl_2}$) δ 145.3 (C_i), 130.4 (C_o), 111.4 (C_m), 110.3 (C_p), 42.80 ($\mathrm{N}C\mathrm{H_2CH_3}$), 17.94 ($C\mathrm{HMe_2}$), 13.56 ($\mathrm{CH}Me_2$), −2.29 ($\mathrm{NCH_2}C\mathrm{H_3}$); IR (cm^{-1}) 839 ($\nu_{\mathrm{ReO}}$). Anal. Calcd for $\mathrm{C_{44}H_{71}N_4Re}$: C, 61.58; H, 8.34; N, 6.53. Found: C, 61.92; H, 8.70; N, 6.34.

Re(NAr)$_3$CH$_3$ (3a). **1b** (0.5 g, 0.6 mmol) was dissolved in THF (10 mL), and MeI (37 μL, 0.6 mmol) was added to the stirred solution. The solution turned dark red immediately. The white precipitate was filtered off, and the filtrate was concentrated in vacuo. The resulting solid was extracted with pentane, and the extract was filtered through Celite and cooled to −40 °C to yield 0.41 g (94%) red crystals: ^{1}H NMR δ 7.1–6.95 (m, 9, $\mathrm{H_{aryl}}$), 3.71 (sept, 6, $\mathrm{C}H\mathrm{Me}_2$), 2.72 (s, 3, $\mathrm{Re}Me$), 1.15 (d, 36, $\mathrm{CH}Me_2$); ^{13}C NMR δ 153.5 (C_i), 140.8 (C_o), 125.9 (C_p), 122.3 (C_m), 28.8 ($C\mathrm{HMe_2}$), 23.5 ($\mathrm{CH}Me_2$), 8.64 ($\mathrm{Re}Me$). Anal. Calcd for $\mathrm{C_{37}H_{55}N_3Re}$: C, 61.04; H, 7.61; N, 5.77. Found: C, 61.27; H, 7.97; N, 5.68.

Re(NAr)$_3$(CH$_2$-2,4,6-C$_6$H$_2$Me$_3$) (3b). To a solution of **1b** (0.5 g, 0.06 mmol) in THF (8 mL) was added 2,4,6-$\mathrm{Me_3C_6H_2CH_2Cl}$ (0.1 g, 0.06 mmol) in THF (2 mL). The brown mixture immediately turned red. After 20 min the reaction was taken to dryness in vacuo and the residue was extracted with pentane. Cooling the pentane extract to −40 °C gave 0.5 g (98%) of red crystals. Attempts to analyze this compound were hindered by the presence of small amounts of the dibenzyl coupling product: ^{1}H NMR δ 7.08–6.95 (m, 9, $\mathrm{H_{aryl}}$), 6.77 (s, 2, H_m in benzyl ligand), 4.63 (s, 2, $\mathrm{C}H_2\mathrm{Ar}$), 3.50 (sept, 6, $\mathrm{C}H\mathrm{Me}_2$), 2.46 (s, 6, $\mathrm{CH_2}$-2,6-Me_2-4-$\mathrm{MeC_6H_2}$), 2.27 (s, 3, $\mathrm{CH_2}$-4-Me-2,6-$\mathrm{Me_2C_6H_2}$), 1.08 (d, 36, $\mathrm{CH}Me_2$); ^{13}C NMR δ 153.8 (C_i), 141.8 (C_o), 140.4 ($\mathrm{CH_2Ar}_i$), 136.3 ($\mathrm{CH_2Ar}_o$), 135.2 ($\mathrm{CH_2Ar}_p$), 129.2 $\mathrm{CH_2Ar}_m$), 126.6 (C_p), 122.7 (C_m), 30.50 (t, $J = 133$, $C\mathrm{H_2Ar}$), 28.49 ($C\mathrm{HMe_2}$), 23.84 ($\mathrm{CH}Me_2$), 20.80 ($\mathrm{CH_2}$-4-Me-2,6-$\mathrm{Me_2C_6H_2}$), 20.57 ($\mathrm{CH_2}$-2,6-Me_2-4-$\mathrm{MeC_6H_2}$).

Re(NAr)$_3$(CH$_2$Cl) (3c). Dichloromethane (1 mL) was added to a solution of **2c** (571 mg, 669 mmol) in THF (5 mL). The solution turned blood-red. The reaction was taken to dryness in vacuo, and the resulting purple solid was extracted with ether. The extract was filtered through Celite and concentrated to dryness. The solid was dissolved in pentane, and the solution was filtered through Celite. The filtrate was cooled to afford the purple product in 85% yield (435 mg): ^{1}H NMR δ 7.38–7.10 (m, 9, $\mathrm{H_{aryl}}$), 5.67 (s, 2, $\mathrm{C}H_2\mathrm{Cl}$), 3.81 (sept, 6, $\mathrm{C}H\mathrm{Me}_2$), 1.24 (d, 36, $\mathrm{CH}Me_2$); ^{13}C NMR δ 153.50 (C_i), 141.7 (C_o), 127.1 (C_p), 122.6 (C_m), 40.80 (t, $J_{\mathrm{CH}} = 154$, $C\mathrm{H_2Cl}$), 28.76 ($C\mathrm{HMe_2}$), 23.48 ($\mathrm{CH}Me_2$). Anal. Calcd for $\mathrm{C_{37}H_{53}N_3ClRe}$: C, 58.36; H, 7.02; N, 5.52. Found (eight attempts to analyze crystalline samples yielded results in these ranges): C, 57.45–61.40; H, 7.02–7.87; N, 4.98–6.24. The reasons why apparently pure samples could not be analyzed successfully is not known.

HRe(NAr)$_3$ (4). Dimethylammonium triflate (0.63 g, 3.0 mmol) was added to a solution of **2b** (2.5 g, 3.0 mmol) in THF (20 mL). The solution quickly turned deep magenta. After 2 h the mixture was filtered and the filtrate was concentrated to dryness to afford a dark red solid. The solid was extracted with pentane, and the extract was filtered and concentrated to give 2.2 g (88%) of a magenta powder: ^{1}H NMR δ 7.24 (s, 1, $\mathrm{Re}H$), 7.08 (m, 6, H_m), 7.00 (m, 3, H_p), 3.91 (sept, 6, $\mathrm{C}H\mathrm{Me}_2$), 1.20 (d, 36, $\mathrm{CH}Me_2$); ^{13}C NMR ($\mathrm{C_7D_8}$) δ 153.9 (C_i), 141.1 (C_o), 127.2 (C_p), 122.6 (C_m), 28.71 ($C\mathrm{HMe_2}$), 23.19 ($\mathrm{CH}Me_2$). Anal. Calcd for $\mathrm{C_{36}H_{52}N_3Re}$: C, 60.64; H, 7.35; N, 5.89. Found: C, 60.81; H, 7.42; N, 5.75.

A reaction between **2b** and $\mathrm{CCl_4}$ (~4 equiv) in $\mathrm{C_6D_6}$ yielded $\mathrm{Re(NAr)_3Cl}$ and $\mathrm{CHCl_3}$ over a 20-min period.

Re(NAr)$_2$(NHAr)(η^2-C$_2$H$_2$) (5a). $\mathrm{HRe(NAr)_3}$ (0.25 g, 0.35 mmol) was dissolved in toluene (6 mL) in a vial with a sealed septum cap. Acetylene (8 mL, 0.36 mmol) was added via syringe. The solution went from magenta to red over a period of 2 h. The reaction was taken to dryness and the residue extracted with ether. Pentane was added to give 0.15 g (59%) of an orange powder: ^{1}H NMR δ 10.11 (d, 1, $J = 1.8$ $H_{\mathrm{A}}\mathrm{CCH_B}$), 9.08 (s, 1, $\mathrm{H_ACC}H_{\mathrm{B}}$), 7.17 (m, 3, $\mathrm{H}_{m,p}$), 7.03 (m, 6, $\mathrm{H}_{m,p}$), 6.50 (br s, 1, NHAr), 3.62 (sept, 2, $\mathrm{C}H\mathrm{Me}_2$), 3.56 (sept, 4, $\mathrm{C}H\mathrm{Me}_2$), 1.35 (d, 12, $\mathrm{CH}Me_{\mathrm{A}}\mathrm{Me_B}$), 1.34 (d, 12, $\mathrm{CHMe_A}Me_{\mathrm{B}}$), 1.32 (d, 12, NHAr–$\mathrm{CH}Me_2$); ^{13}C NMR δ 153.2 (d, $J = 213$, $\mathrm{H_A}C\mathrm{CH_B}$), 152.6 ($\mathrm{C}_i$), 149.2 ($\mathrm{C}_i$), 144.9 ($\mathrm{C}_o$), 142.4 ($\mathrm{C}_o$), 139.6 (d, $J = 218$, $\mathrm{H_AC}C\mathrm{H_B}$), 125.7 ($\mathrm{C}_p$), 124.9 ($\mathrm{C}_p$), 123.7 ($\mathrm{C}_m$), 122.6 ($\mathrm{C}_m$), 28.43 ($C\mathrm{HMe_2}$), 27.94 ($C\mathrm{HMe_2}$), 24.01 ($\mathrm{CH}Me_{\mathrm{A}}\mathrm{Me_B}$), 23.81 (NHAr–$\mathrm{CH}Me_2$), 23.35 ($\mathrm{CHMe_A}Me_{\mathrm{B}}$); IR (cm^{-1}) 3338 ($\nu_{\mathrm{NH}}$), 1604 ($\nu_{\mathrm{CC}}$). Anal. Calcd for $\mathrm{C_{38}H_{54}N_3Re}$: C, 61.76; H, 7.36; N, 5.69. Found: C, 61.33; H, 7.58; N, 6.06.

Re(NAr)$_2$(NHAr)(η^2-C$_2$Me$_2$) (5b). The procedure was analogous to that for **5a** employing $\mathrm{HRe(NAr)_3}$ (0.25 g, 0.35 mmol) and 2-butyne (27 μL, 0.35 mmol) in toluene (6 mL); yield 0.22 g (83%): ^{1}H NMR δ 7.24 (m, 3, $\mathrm{H}_{m,p}$), 7.11 (m, 7, NAr_m, $\mathrm{N}H\mathrm{Ar}$), 3.81 (sept, 2, C*H*Me$_2$), 3.56 (sept, 4, C*H*Me$_2$), 2.74 (s, 3, *Me*$_A$CCMe$_B$), 2.48 (s, 3, Me$_A$CC*Me*$_B$), 1.23 (d, 12, CH*Me*$_A$Me$_B$), 1.22 (d, 12, CHMe$_A$*Me*$_B$), 1.11 (d, 12, NHAr–CH*Me*$_2$); ^{13}C NMR δ 152.6 (C$_i$), 150.6 (C$_i$), 150.4 (Me$_A$*C*CMe$_B$), 144.2 (C$_o$), 143.6 (Me$_A$C*C*Me$_B$), 143.4 (C$_o$), 125.9 (C$_p$), 124.6 (C$_p$), 123.9 (C$_m$), 122.6 (C$_m$), 28.23 (*C*HMe$_2$), 27.94 (*C*HMe$_2$), 24.19 (NHAr–CH*Me*$_2$), 23.76 (CH*Me*$_A$Me$_B$), 23.67 (CHMe$_A$*Me*$_B$), 18.00 (*Me*$_A$CCMe$_B$), 7.99 (Me$_A$CC*Me*$_B$); IR (cm^{-1}) 3425 (ν_{NH}). Anal. Calcd for C$_{40}$H$_{58}$N$_3$Re: C, 62.63; H, 7.62; N, 5.48. Found: C, 62.52; H, 7.98; N, 5.15.

Re(NAr)$_2$(NHAr)(η^2-OCH-*t*-Bu) (5c). This compound was prepared in a manner analogous to that used to prepare **5b**: ^{1}H NMR δ 7.20–7.10 (m, 3, H$_{aryl}$), 7.08–6.95 (m, 6, H$_{aryl}$), 6.43 (br s, 1, N*H*Ar), 5.79 (s, 1, OC*H*-*t*-Bu), 3.94 (sept, 2, C*H*$_A$Me$_2$), 3.84 (sept, 2, C*H*$_B$Me$_2$), 3.71 (sept, 2, NHAr–C*H*Me$_2$), 1.29 (d, 6, CH*Me*$_A$Me$_B$), 1.27 (d, 12, NHAr–CH*Me*$_2$), 1.16 (d, 6, CHMe$_A$*Me*$_B$), 1.14 (d, 6, CH*Me*$_C$Me$_D$), 1.06 (d, 6, CHMe$_C$*Me*$_D$), 1.06 (s, 9, OCH-*t*-*Bu*); ^{13}C NMR δ 152.6 (C$_i$), 151.7 (C$_{i'}$), 145.8 (C$_o$), 145.3 (C$_o$), 144.6 (C$_i$), 141.4 (C$_{o'}$), 126.0 (C$_p$), 125.2 (C$_{p'}$), 124.8 (C$_p$), 123.0 (C$_m$), 122.6 (C$_m$), 122.6 (C$_{m'}$), 101.4 (O*C*H-*t*-Bu), 37.0 (*C*Me$_3$), 45.5, 38.8, 37.4, 31.6, 31.3, 28.9 (C*C*HMe$_2$), 28.2 (C*C*$_A$HMe$_2$), 28.0 (C*C*$_B$HMe$_2$), 24.7, 24.6, 23.7, 23.6, 23.2, 22.6 (CCH*Me*$_2$). Anal. Calcd for C$_{41}$H$_{62}$N$_3$ORe: C, 61.62; H, 7.82; N, 5.26. Found: C, 61.20; H, 7.92; N, 5.20.

Re(NAr)$_2$(NHAr)(η^2-C$_2$H$_4$) (5d). This compound was prepared in a manner analogous to that used to prepare **5a** from HRe(NAr)$_3$ (1.5 g, 2.1 mmol) in ether (20 mL) and ethylene (53 mL, 2.1 mmol) in a flask with a sealed septum cap; yield 1.2 g (75%) of an orange powder from pentane: ^{1}H NMR δ 7.2–7.05 (m, 3, H$_{m,p}$), 7.00 (s, 6, H$_{m,p}$), 6.86 (bs, 1, NHAr), 3.67 (sept, 2, C*H*Me$_2$), 3.57, (t, 2, *J* = 12, *H*$_2$CCH$_2$), 3.52 (sept, 4, C*H*Me$_2$), 2.27 (t, 2, *J* = 12, H$_2$CC*H*$_2$), 1.2–1.05 (overlapping doublets, CH*Me*$_2$); ^{13}C NMR δ 153.2 (C$_i$), 149.4 (C$_i$), 144.7 (C$_o$), 142.4 (C$_o$), 139.6 (d, *J* = 218, H$_A$*C*CH$_B$), 125.7 (C$_p$), 124.9, (C$_p$), 123.7 (C$_m$), 122.6 (C$_m$), 28.43 (*C*HMe$_2$), 27.94 (N*C*HMe$_2$), 24.01 (CH*Me*$_A$Me$_B$), 23.81 (CH*Me*$_2$), 23.35 (CHMe$_A$*Me*$_B$).

Re(NAr)$_2$(NHAr)(η^2-norbornene) (5e). HRe(NAr)$_3$ (0.25 g, 0.35 mmol) was dissolved in toluene (5 mL), and norbornene (0.030 g, 0.35 mmol) in ether (1 mL) was added with stirring. The red solution was stirred overnight and was concentrated in vacuo. The residue was extracted with pentane, and the filtered extract was cooled to give 0.11 g (42%) of large ruby red crystals: ^{1}H NMR δ 7.22–7.10 (m, 3, H$_{aryl}$), 7.08–6.95 (m, 6, H$_{aryl}$), 6.64 (br s, 1, NHAr), 4.97 (d, 1, *J* = 7.7, C*H*$_\alpha$), 3.80 (sept, 2, C*H*$_A$Me$_2$), 3.79 (sept, 2, C*H*$_B$Me$_2$), 3.63 (sept, 2, C*H*$_M$e$_2$), 3.06 (d, 1, *J* = 7.8, C*H*$_{\alpha'}$), 2.78 (s, 1, C*H*$_\beta$), 2.21 (s, 1, CH$_{\beta'}$), 1.78 (m, 1, NBE), 1.52 (m, 1, NBE), 1.27–1.14 (overlapping doublets, 36, CH*Me*$_2$), 0.95 (d, 1, NBE*H*$_{7A}$), 0.48 (d, 1, NBE*H*$_{7B}$); ^{13}C NMR δ 153.8 (C$_i$), 153.0 (C$_i$), 149.7 (C$_i$), 144.7 (C$_o$), 142.4 (C$_o$), 141.6 (C$_o$), 126.0 (C$_p$), 125.2 (C$_p$), 124.8 (C$_p$), 123.1 (C$_m$), 122.9 (C$_m$), 122.8 (C$_m$), 72.5 (C$_\alpha$), 60.0 (C$_\alpha$), 45.5, 38.8, 37.4, 31.6, 31.3, 28.9 (norbornene), 28.4 (*C*$_A$HMe$_2$), 28.0 (*C*$_B$HMe$_2$), 24.4 and 24.3 (CH*Me*$_2$), 23.7 (CH*Me*$_A$Me$_B$), 23.1 (CHMe$_A$*Me*$_B$). Anal. Calcd for C$_{43}$H$_{62}$N$_3$Re: C, 63.98; H, 7.74; N, 5.21. Found: C, 64.19; H, 8.24; N, 5.01.

Re(NAr)$_2$(NHAr)(PMe$_3$) (5f). HRe(NAr)$_3$ (0.50 g, 0.7 mmol) was dissolved in ether (10 mL), and PMe$_3$ (73 μL, 0.7 mmol) was added via syringe. The red solution turned green. After 1 h it was filtered and the filtrate was concentrated to dryness in vacuo. The resulting green solid was extracted with pentane. Concentrating and cooling the pentane extract gave 0.50 g (84%) of green crystals: ^{1}H NMR δ 9.63 (br d, 1, J_{PH} = 5, N*H*Ar), 7.20–7.10 (m, 8, H$_{m,p}$), 6.90 (t, 1, H$_p$), 3.73 (sept, 4, C*H*Me$_2$), 3.68 (sept, 2, NHAr–C*H*Me$_2$), 1.29 (d, 12, NHAr–CH*Me*$_2$), 1.25 (d, 9, J_{PH} = 10.5, P*Me*$_3$), 1.22 (d, 12, CH*Me*$_A$Me$_B$), 1.17 (d, 12, CHMe$_A$*Me*$_B$); ^{13}C NMR δ 156.6 (C$_i$), 155.6 (C$_i$), 141.4 (C$_o$), 137.5 (C$_o$), 124.2 (C$_p$), 123.7 (C$_m$), 122.8 (C$_m$), 120 (C$_p$), 30.86 (*C*HMe$_2$), 28.25 (*C*HMe$_2$), 24.27 (NHAr–CH*Me*$_2$), 23.86 (CH*Me*$_A$Me$_B$), 23.65 (CHMe$_A$*Me*$_B$), 20.64 (P*Me*$_3$); IR (cm^{-1}) 3410 (ν_{NH}). Anal. Calcd for C$_{39}$H$_{61}$N$_3$PRe: C, 59.36; H, 7.79; N, 5.33. Found: C, 59.37; H, 7.98; N, 5.32.

Re(NAr)$_2$(η^2-C$_2$Np$_2$)Cl (6). Re(NAr)$_2$Cl$_3$(py) (5.00 g, 6.9 mmol) was added to a chilled (−40 °C) THF solution of dineopentylacetylene (1.48 mL, 6.9 mmol) over freshly prepared sodium amalgam (318 mg, 13.9 mmol Na; 74 g Hg), and THF was added to bring the reaction volume to 40 mL. The solution was shaken vigorously for 2 min and allowed to warm to room temperature over a period of 2 h while it was stirred vigorously. The orange-brown mixture was allowed to settle, the solution was decanted, filtered through Celite, and concentrated to dryness in vacuo. The solid was extracted with pentane, and the extract was filtered and cooled −40 °C to give 2.14 g (61%) of red cubes in two crops: ^{1}H NMR δ 7.0 (s, 3, H$_{m,p}$), 3.93 (s, 2, C*H*$_2$-*t*-Bu), 3.67 (sept, 4, C*H*Me$_2$), 3.33 (s, 2, C*H'*$_2$-*t*-Bu), 1.18 (d, 24, CH*Me*$_2$), 1.10 (s, 9, CH$_2$-*t*-*Bu*), 0.85 (s, 9, CH$_2$-*t*-*Bu'*); ^{13}C NMR δ 158.9 (Np*C*CNp′), 152.3 (C$_i$), 143.4 (NpC*C*Np′), 143.1 (C$_o$), 127.5 (C$_p$), 122.7 (C$_p$), 49.03 (*J* = 133, *t*-Bu*C*H$_2$), 40.87 (*J* = 135, *t*-Bu*C'H*$_2$), 34.26 (Me$_3$*C*CH$_2$), 33.45 (Me$_3$*C*CH$_2$), 30.32 (*Me*$_3$CCH$_2$), 30.12 (*Me'*$_3$CCH$_2$), 28.78 (*C*HMe$_2$), 23.98 (CH*Me*$_2$), 23.41 (CH*Me'*$_2$); IR (cm^{-1}) 1769 (ν_{CC}). Anal. Calcd for C$_{36}$H$_{56}$N$_2$ClRe: C, 58.55: H, 7.64; N, 3.79. Found: C, 58.66; H, 7.66; N, 3.68.

[Re(NAr)$_2$(η^2-C$_2$Np$_2$)]$_2$Hg (7a). To 10 mL of cold (−40 °C) THF over freshly-prepared sodium amalgam (16 mg, 0.68 mmol of Na; 16 g of Hg) was added Re(NAr)$_2$(η^2-C$_2$Np$_2$)Cl (0.50 g, 0.68 mmol). The mixture was shaken vigorously for 2 min and stirred overnight. The cherry red solution was decanted and filtered, and the filtrate was concentrated to dryness in vacuo. The residue was extracted with ether, and the extract was filtered through Celite and concentrated to dryness. The extraction was repeated with 30 mL of pentane to give 0.400 g (76%) of red cubes: ^{1}H NMR δ 7.01 (m, 6, H$_{aryl}$), 3.78 (sept, 4, C*H*Me$_2$), 3.65 (s, 2, C*H*$_2$-*t*-Bu), 3.35 (s, 2, C*H'*$_2$-*t*-Bu), 1.21 (d, 12, CH*Me*$_A$Me$_B$), 1.16 (d, 12, CHMe$_A$*Me*$_B$), 1.06 (s, 9, C*Me*$_3$), 1.03 (s, 9, C*Me'*$_3$); ^{13}C NMR δ 154.2 (*C*═C), 144.5 (C$_o$), 143.5 (C═*C*), 126.4 (C$_p$), 122.7 (C$_m$), 54.2 (*C*H$_2$-*t*-Bu), 46.5 (*C'*H$_2$-*t*-Bu), 34.9 (CH$_2$*C*Me$_3$), 34.5 (CH$_2$*C'*Me$_3$), 30.7 (CH$_2$C*Me*$_3$), 30.2 (CH$_2$C*Me'*$_3$), 28.1 (*C*HMe$_2$), 23.8 (CH*Me*$_A$Me$_B$), 23.7 (CHMe$_A$*Me*$_B$); IR (cm^{-1}) 1769 (ν_{CC}). Anal. Calcd for C$_{72}$H$_{112}$N$_4$HgRe$_2$: C, 53.82; H, 7.03; N, 3.49. Found: C, 53.72; H, 7.31; N, 3.09.

[Re(NAr)$_2$(η^2-C$_2$Np$_2$)][Na(THF)$_2$] (7b). To 5 mL of cold (−40 °C) THF over freshly-prepared sodium amalgam (36 mg, 1.57 mmol of Na; 9 g of Hg) was added a solution of Hg[Re(NAr)$_2$(η^2-C$_2$Np$_2$)]$_2$ (1.20 g, 75 μmol) in 10 mL of THF. The mixture was shaken vigorously for 2 min and then stirred overnight at ambient temperature. The solution was decanted and filtered through Celite. The filtrate was concentrated to dryness in vacuo, and the residue was extracted with 40 mL of pentane. The extract was filtered through Celite, concentrated in vacuo to 10 mL, and cooled to −40 °C to yield 1.2 g (92%) of green needles in two crops: ^{1}H NMR δ 7.19 (2, t, H$_p$), 7.10 (4, H$_m$), 3.97 (sept, 4, C*H*Me$_2$), 3.55 (s, 4, C*H*$_2$-*t*-Bu), 3.25 (m, 8, O[C*H*$_2$CH$_2$]$_2$), 1.38 (s, 18, CH$_2$-*t*-*Bu*), 1.32 (d, 24, CH*Me*$_2$), 1.26 (m, 8, O[CH$_2$C*H*$_2$]$_2$); ^{13}C NMR δ 157.0 (*C*═C), 151.2 (C$_i$), 140.0 (C$_o$), 122.4 (C$_m$), 120.7 (C$_p$), 68.0 (O[*C*H$_2$CH$_2$]$_2$), 49.2 (*C*H$_2$-*t*-Bu), 33.3 (CH$_2$*C*Me$_3$), 31.2 (CH$_2$C*Me*$_3$), 28.2 (*C*HMe$_2$), 25.5 (O[CH$_2$*C*H$_2$]$_2$), 23.5 (CH*Me*$_2$). IR (cm^{-1}) 1744 (ν_{CC}). Anal. Calcd for C$_{44}$H$_{72}$O$_2$N$_2$NaRe: C, 60.72; H, 8.34; N, 3.22. Found: C, 61.12; H, 8.51; N, 3.54.

Re(NAr)$_2$(η^2-C$_2$Np$_2$)CH$_3$ (8a). Na(THF)$_2$Re(NAr)$_2$(η^2-C$_2$Np$_2$) (100 mg, 115 μmol) was dissolved in THF (10 mL). The reaction was chilled to −40 °C, and MeI (7.20 μL, 115 μmol) was added. The solution turned pale yellow-orange immediately. The solvent was removed in vacuo. The resulting solid was extracted with pentane, and the extract was filtered and concentrated in vacuo to yield 82 mg (99%) of an orange powder: ^{1}H NMR δ 7.03 (s, 6, H$_{aryl}$), 3.76 (sept, 4, C*H*Me$_2$), 3.49 (s, 2, C*H*$_2$-*t*-Bu), 3.24 (s, 2, C*H'*$_2$-*t*-Bu), 2.71 (s, 3, Re*Me*), 1.22 (d, 12, CH*Me*$_A$Me$_B$), 1.20 (d, 12, CHMe$_A$*Me*$_B$), 1.02 (s, 9, CH$_2$-*t*-*Bu*), 0.97 (s, 9, CH$_2$-*t*-*Bu'*); ^{13}C NMR δ 152.8 (Np*C*C′Np′), 151.0 (C$_i$), 142.8 (C$_o$), 141.0 (NpC*C'*Np′), 125.6 (C$_p$), 122.6 (C$_m$), 45.87 (*J* = 132, *t*-Bu*C*H$_2$), 38.78 (*J* = 132, *t*-Bu′*C'*H$_2$), 33.95 (Me$_3$*C*CH$_2$), 33.11 (Me$_3$*C'*CH$_2$), 30.24 (*Me*$_3$CCH$_2$), 30.18 (*Me'*$_3$CCH$_2$), 28.51 (*C*HMe$_2$), 23.85 (CH*Me*$_A$Me$_B$), 23.48 (CHMe$_A$*Me*$_B$) 1.86 (*J* = 132, Re*Me*); IR (cm^{-1}) 1780 (ν_{CC}). Anal. Calcd for C$_{37}$H$_{59}$N$_2$Re: C, 61.88; H, 8.28; N, 3.90. Found: C, 62.01; H, 8.36; N, 3.73.

$Re(NAr)_2(\eta^2\text{-}C_2Np_2)(CH_2\text{-}2,4,6\text{-}C_6H_2Me_3)$ (8b). This compound was prepared in a fashion analogous to that used to prepare 8 using $Na(THF)_2Re(NAr)_2(\eta^2\text{-}C_2Np_2)$ (97 mg, 111 μmol) in THF (7 mL), that had been chilled to −40 °C, and 2,4,6-trimethylbenzyl chloride (19 mg, 111 μmol). The yield was 92 mg (99%) of an orange powder. The coupling product that was present in **8b** as an impurity prevented satisfactory analysis: ^{1}H NMR δ 7.03 (m, 6, H_{aryl}), 6.65 (s, 2, H_{aryl}), 4.35 (s, 2, $C\mathit{H}_2Ar$), 3.51 (sept, 4, $C\mathit{H}Me_2$), 3.29 (s, 2, $C\mathit{H}_2$-*t*-Bu), 3.05 (s, 2, $C\mathit{H}'_2$-*t*-Bu), 2.15 (s, 3, Me_p), 2.02 (s, 6, Me_o), 1.25 (d, 12, $CH\mathit{Me}_AMe_B$), 1.17 (s, 9, CH_2-*t-Bu*), 1.09 (d, 12, $CHMe_A\mathit{Me}_B$), 0.91 (s, 9, CH_2-*t*-Bu′); ^{13}C NMR δ 152.9 (C_i), 145.9 (NC_o), 143.8 (Np*C*C′Np′), 142.5 (C_o), 141.3 (NpC*C′*Np′), 137.4 (C_p), 129.2 (C_m), 126.9 (C_p), 122.9 (C_m), 46.0 (*t*-Bu$\mathit{C}H_2$), 40.9 (*t*-Bu′$\mathit{C}'H_2$), 33.5 ($Me_3\mathit{C}CH_2$), 32.02 ($Me_3\mathit{C}'CH_2$), 30.3 (Me_3CCH_2), 30.2 (Me'_2CCH_2), 30.1 (Re–$\mathit{C}H_2$), 27.7 ($\mathit{C}HMe_2$), 24.4 ($CH\mathit{Me}_AMe_B$), 24.3 ($CHMe_A\mathit{Me}_B$) 24.0 (Me_p), 20.6 (Me_m).

$Re(NAr)_2(\eta^2\text{-}C_2Np_2)H$ (9). Solid diethylammonium triflate (77 mg, 345 μmol) was added to a rapidly stirred solution of $Na(THF)_2Re(NAr)_2(C_2Np_2)$ (300 mg, 345 μmol) in THF (10 mL). The dark emerald green solution turned pale orange at the end point. The reaction was concentrated to dryness in vacuo and the product crystallized from pentane at −40 °C; yield 240 mg (99%): ^{1}H NMR δ 7.04 (s, 6, H_{aryl}), 3.85 (sept, 4, $C\mathit{H}Me_2$), 3.64 (s, 2, $C\mathit{H}_2$-*t*-Bu), 3.39 (s, 2, $C\mathit{H}'_2$-Bu′), 2.60 (slightly broad s, 1, Re*H*), 1.24 (d, 12, $CH\mathit{Me}_AMe_B$), 1.22 (d, 12, $CHMe_A\mathit{Me}_B$); ^{13}C NMR δ 153.2 (Np*C*C′Np′ and C_i), 141.4 (C_o), 136.9 (NpC*C′*Np′), 125.9 (C_p), 122.6 (C_m), 49.76 (J = 132, *t*-Bu$\mathit{C}H_2$), 45.52 (J = 132, *t*-Bu′$\mathit{C}'H_2$), 33.84 ($Me_3\mathit{C}CH_2$), 32.84 ($Me_3\mathit{C}'CH_2$), 30.30 (Me_3CCH_2), 30.21 (Me'_3CCH_2), 28.43 ($\mathit{C}HMe_2$), 23.28 ($CH\mathit{Me}_AMe_B$), 23.16 ($CHMe_A\mathit{Me}_B$); IR (cm^{-1}) 1795 (ν_{CC}). Anal. Calcd for $C_{36}H_{57}N_2Re$: C, 61.41; H, 8.16; N, 3.98. Found: C, 61.27; H, 8.19; N, 3.80.

The reaction between **9** and CCl_4 (~4 equiv) in C_6D_6 yielded $Re(NAr)_2(\eta^2\text{-}C_2Np_2)Cl$ and $CHCl_3$ in ~20 min.

$Re(NAr)_2(PMe_2Ph)_2H$ (10). Dimethylphenylphosphine (32.7 μL, 230 μmol) was added to a rapidly stirred solution of **9** (80 mg, 115 mmol). The solution turned to midnight blue immediately. The reaction was concentrated to dryness in vacuo, and the residue was extracted with ether. The extract was filtered through Celite and evaporated, and the product was crystallized from pentane with cooling to −40 °C to afford 90 mg (96%) of dark blue crystals: ^{1}H NMR δ 7.75 (m, 4, H_o), 7.15–6.95 (m, 12, $H_{m,p}$), 3.85 (sept, 2, $C\mathit{H}_AMe_2$), 3.49 (sept, 2, $C\mathit{H}_BMe_2$), 1.44 (virtual triplet, 12, J_{PH} = 2.7, PMe), 1.28 (d, 12, $CH_A\mathit{Me}_2$), 1.11 (d, 12, $CH_B\mathit{Me}_2$), −10.28 (t, 1, J_{PH} = 11.4, Re*H*); IR (cm^{-1}) 1998 (ν_{ReH}). Anal. Calcd for $C_{40}H_{57}N_2P_2Re$: C, 59.02; H, 7.06; N, 3.44. Found: C, 59.16; H, 6.98; N, 3.49.

$Re(NAr)Cl_3(py)_2$ (11). $Na(THF)_2Re(NAr)_3$ (13.4 g, 22.8 mmol) was added in ~500-mg portions as a solid to a rapidly stirred slurry of pyridinium chloride (12.1 g, 105 mmol) in a mixture of THF (50 mL) and pyridine (200 mL). The solution was allowed to stir for an additional 10 min after addition of the last portion of the Re complex. The solution was then concentrated in vacuo to a volume of ~30 mL. A large portion of pentane (approximately 300 mL) was then added in order to precipitate a mixture of the product and excess pyHCl, which was washed well with pentane. The resulting green solid was dried in vacuo for 3 h (it is important to remove *all* of the pyridine) and loaded into a paper Soxhlet thimble. A 300-mL Schlenk flask was charged with approximately 150 mL of benzene, equipped with the Soxhlet apparatus, thimble, and a condenser, and heated to reflux for 5 days. The resulting grass green solution was concentrated to approximately 50 mL, and 200 mL of pentane was added to precipitate the product as a fine bright green powder which was dried in vacuo overnight; yield 13.4 g (94%). The analytical sample of $Re(NAr)Cl_3(py)_2$ contained 1 equiv of benzene: ^{1}H NMR (CD_2Cl_2) δ 9.08 (d, 4, H_o), 7.75 (m, 3, H_p), 7.56 (t, 4, py), 7.06 (d, 2, H_m), 3.67 (sept, 2, $C\mathit{H}Me_2$), 0.82 (d, 12, $CH\mathit{Me}_2$); ^{13}C NMR δ 157.4 (C_o), 151.7 (C_p), 150.7 (C_i), 141.2 (C_o), 132.0 (C_m), 128.6 (C_p), 124.7 (C_p), 28.07 ($\mathit{C}HMe_2$), 24.07 ($CH\mathit{Me}_2$). Anal. Calcd for $C_{28}H_{33}N_3Cl_3Re$: C, 47.76; H, 4.72; N, 5.97. Found: C, 47.41; H, 5.00; N, 5.92.

$Re(NAr)(\eta^2\text{-}C_2Np_2)_2Cl$ (12). $Re(NAr)Cl_3(py)_2$ (4.25 g, 6.79 mmol) was added to a solution of dineopentylacetylene (3.04 mL, 14.3 mmol) in THF over zinc powder (444 mg, 6.79 mmol), and THF was added to bring the solution volume to 80 mL in a 100-mL Schlenk flask. The flask was equipped with a condenser, and the reaction was heated to reflux and stirred vigorously for 60 h. During this time the solution turned from bright lime green to golden brown. The solvents were removed in vacuo, and the brown residue was extracted with ether. The extract was filtered though Celite and again taken to dryness in vacuo. The residue was recrystallized from pentane at −40 °C to give 4.00 g (81%) of a bright yellow powder or pale yellow crystals in two crops: ^{1}H NMR δ 7.0–6.9 (m, 3, H_{aryl}), 3.97 (d, 2, J = 12.4, $C\mathit{H}_AH_{A'}$-*t*-Bu), 3.89 (d, 2, J = 12.4, $CH_A\mathit{H}_{A'}$-*t*-Bu), 3.79 (d, 2, J = 13.5, $C\mathit{H}_BH_{B'}$-*t*-Bu), 3.63 (d, 2, J = 13.5, $CH_B\mathit{H}_{B'}$-*t*-Bu), 3.50 (sept, 4, $C\mathit{H}Me_2$), 1.20 (d, 12, $CH\mathit{Me}_2$), 1.01 (s, 18, CH_2-*t*-Bu), 0.94 (s, 18, CH_2-*t-Bu′*); ^{13}C NMR δ 162.7 (Np*C*CNp′), 154.7 (NpC*C*Np′), 150.4 (C_i), 144.2 (C_o), 127.2 (C_p), 122.8 (C_p), 46.72 (J = 132, *t*-Bu$\mathit{C}H_2$), 39.54 (J = 129, *t*-Bu′$\mathit{C}'H_2$), 34.24 ($Me_3\mathit{C}CH_2$), 34.13 ($Me_3\mathit{C}'CH_2$), 30.48 (Me_3CCH_2), 30.37 (Me'_3CCH_2), 28.50 ($\mathit{C}HMe_2$), 23.89 ($CH\mathit{Me}_2$); IR (cm^{-1}) 1758, 1771 (ν_{CC}). Anal. Calcd for $C_{36}H_{61}NClRe$: C, 59.27; H, 8.43; N, 1.92. Found: C, 59.14; H, 8.63; N, 1.81.

$[Re(NAr)(\eta^2\text{-}C_2Np_2)_2]_2Hg$ (13a). $Re(NAr)(\eta^2\text{-}C_2Np_2)_2Cl$ (0.50 g, 0.68 mmol) was added to 6 mL of cold (−40 °C) THF over freshly-prepared sodium amalgam (16 mg, 0.68 mmol of Na; 4 g of Hg). The mixture was shaken vigorously for 2 min and stirred overnight, during which time the solution changed from yellow to dark red. The solution was decanted and filtered, and the filtrate was taken to dryness in vacuo. The product was extracted into pentane, and the extract was filtered through Celite and concentrated to dryness to give 0.48 g of a red powder, which was not analytically pure: ^{1}H NMR δ 7.01 (m, 3, H_{aryl}), 4.15 (d, 2, $C(\mathit{H}_A)_2$-*t*-Bu), 3.98 (d, 2, $C(\mathit{H}_B)_2$-*t*-Bu), 3.88 (d, 2, $C(\mathit{H}_{A'})_2$-*t*-Bu), 3.72 (d, 2, $C(\mathit{H}_{B'})_2$-*t*-Bu), 3.63 (sept, 4, $C\mathit{H}Me_2$), 1.32 (d, 12, $CH\mathit{Me}_2$), 1.03 (bs, 36, $C\mathit{Me}_3$); ^{13}C NMR δ 167.9 ($\mathit{C}{=}C$), 160.1 ($\mathit{C}{=}C$), 152.0 (C_i), 144.5 (C_o), 124.8 (C_p), 122.4 (C_m), 52.5 ($\mathit{C}H_2$-*t*-Bu), 45.9 ($\mathit{C}'H_2$-*t*-Bu), 3.48 ($CH_2\mathit{C}Me_3$), 33.9 ($CH_2\mathit{C}'Me_3$), 30.9 ($CH_2C\mathit{Me}_3$), 30.7 ($CH_2C\mathit{Me}'_3$), 27.9 ($\mathit{C}HMe_2$), 24.0 ($CH\mathit{Me}_2$); IR (cm^{-1}) 1743, 1725 (ν_{CC}); mass spectrum (EIMS) 1590 (M^+).

$[Re(NAr)(\eta^2\text{-}C_2Np_2)_2][Na(THF)_2]$ (13b). Freshly-prepared sodium amalgam (0.018 g of Na, 15 g of Hg) was added to a cold (−40 °C) solution of **12** (0.50 g, 0.67 mmol) in 10 mL of THF. The mixture was shaken vigorously for 20 min, during which time the color changed from yellow to red-orange, and finally to purple. After the mixture was stirred for 48 h, the solution was decanted from the mercury and the solvents were removed in vacuo. The residue was extracted with toluene, the extract was filtered through Celite, and the solvent was removed from the extract in vacuo. The solid was extracted with ether and filtered through Celite, and the product was crystallized upon addition of pentane and cooling to −40 °C to yield 0.50 g (85%) of purple microcrystals: ^{1}H NMR δ 6.98 (m, 3, H_p), 3.82 (d, 4, $C\mathit{H}_2$-*t*-Bu), 3.58 (sept, 4, $C\mathit{H}Me_2$), 3.25 (m, 8, $O[C\mathit{H}_2CH_2]_2$), 3.20 (d, 4, $C\mathit{H}'_2$-*t*-Bu), 1.26 (m, 8, $O[CH_2C\mathit{H}_2]_2$), 1.24 (s, 36, CH_2-*t-Bu*), 1.21 (d, 12, $CH\mathit{Me}_2$); ^{13}C NMR δ 171.4 ($\mathit{C}{=}C$), 158 (C_i), 140.2 (C_o), 122.5 (C_m), 119.4 (C_p), 68.0 ($O[\mathit{C}H_2CH_2]_2$), 48.5 ($\mathit{C}H_2$-*t*-Bu), 32.7 ($CH_2\mathit{C}Me_3$) 31.1 ($CH_2C\mathit{Me}_3$), 27.7 ($\mathit{C}HMe_2$), 25.5 ($O[CH_2\mathit{C}H_2]_2$), 23.6 ($CH\mathit{Me}_2$); IR (cm^{-1}) 1744 (ν_{CC}). Anal. Calcd for $C_{44}H_{77}O_2NNaRe$: C, 61.36; H, 9.01; N, 1.63. Found: C, 60.96; H, 8.98; N, 1.43.

$Re(NAr)(\eta^2\text{-}C_2Np_2)_2CH_3$ (14a). $Na(THF)_2Re(NAr)(\eta^2\text{-}C_2Np_2)_2$ (100 mg, 116 μmol) was dissolved in THF (10 mL), and the solution was chilled to −40 °C. Methyl iodide (7.3 μL, 116 μmol) was added. The solution turned pale yellow immediately. The solvent was removed in vacuo, and the resulting solid was extracted into pentane. The extract was filtered, and the filtrate was taken to dryness in vacuo. The yellow residue was dissolved in pentane, and the solution was concentrated to yield 80 mg (98%) of a yellow powder: ^{1}H NMR δ 6.93 (m, 3, H_{aryl}), 3.90 (d, 2, J = 12.9, $C\mathit{H}_AH_{A'}$-*t*-Bu), 3.77 (s, 2, J = 12.9, $CH_A\mathit{H}_{A'}$-*t*-Bu), 3.46 (sept, 2, $C\mathit{H}Me_2$), 3.47 (d, 2, J = 12.9, $C\mathit{H}_BH_{B'}$-*t*-Bu), 3.36 (d, 2, J = 12.9,

$CH_BH_{B'}$-*t*-Bu), 2.77 (s, 3, Re–CH_3), 1.19 (d, 12, $CHMe_2$), 0.99 (s, 18, CH_2-*t-Bu*), 0.97 (s, 18, CH_2-*t-Bu'*); ^{13}C NMR δ 160.7 (Np*C*CNp'), 159.9 (NpC*C*Np'), 150.3 (C_i), 144.3 (C_o), 124.7 (C_p), 122.4 (C_p), 46.12 (J = 126, *t*-BuCH_2), 39.08 (J = 130, *t*-Bu'$C'H_2$), 34.10 (Me_3CCH_2), 33.95 ($Me_3C'CH_2$), 30.59 (Me_3CCH_2), 30.35 (Me'_3CCH_2), 28.19 ($CHMe_2$), 23.66 ($CHMe_2$), 8.87 (J = 127, Re–CH_3). IR (cm^{-1}) 1755, 1744 cm^{-1} (ν_{CC}). Anal. Calcd for $C_{37}H_{64}NRe$: C, 62.67; H, 9.10; N, 1.98; Found: C, 62.48; H, 9.06; N, 1.80.

Re(NAr)(η^2-C_2Np_2)$_2$(CH_2-2,4,6-$C_6H_2Me_3$) (14b). The synthesis of **14b** was analogous to that of **14a**; yield 80 mg (98%). Contamination with the dibenzyl coupling product again prevented satisfactory analysis: ^1H NMR δ 6.99 (s, 2, H_{aryl}), 6.95–6.85 (m, 6, H_{aryl}), 4.21 (s, 2, CH_2Ar), 3.99 (d, 2, J = 13.5, $CH_AH_{A'}$-*t*-Bu), 3.93 (s, 2, J = 13.5, $CH_AH_{A'}$-*t*-Bu), 3.48 (sept, 2, $CHMe_2$), 3.38 (d, 2, J = 13.4, CH_BH_B'-*t*-Bu), 2.72 (d, 2, J = 13.4, $CH_BH_{B'}$-*t*-Bu), 2.40 (s, 6, Me_o), 2.20 (s, 3, Me_p), 1.09 (d, 12, $CHMe_2$), 0.93 (s, 18, CH_2-*t-Bu*), 0.89 (s, 18, CH_2-*t-Bu'*); ^{13}C NMR δ 163.4 (Np*C*CNp'), 161.0 (NpC*C*Np'), 150.4 (C_i), 145.6 (C_i), 144.9 (C_o), 137.1 (C_o), 133.1 (C_p), 128.9 (C_m), 125.5 (C_p), 123.0 (C_m), 45.5 (*t*-BuCH_2), 37.08 (*t*-Bu'$C'H_2$), 34.5 (Me_3CCH_2), 34.4 ($Me_3C'CH_2$), 30.9 (Me_3CCH_2), 30.8 (Me'_3CCH_2), 27.6 ($CHMe_2$), 26.8 (CH_2Ar), 24.3 ($CHMe_2$), 2.16 (C_m), 21.0 (C_p).

Re(NAr)(η^2-C_2Np_2)$_2$H (15). Solid diethylammonium triflate (130 mg, 581 μmol) was added to a rapidly stirring solution of Na(THF)$_2$Re(NAr)(η^2-C_2Np_2)$_2$ (500 mg, 581 μmol) in THF (10 mL). The dark purple solution quickly turned pale yellow upon addition of the last bit of acid. The reaction was concentrated to dryness in vacuo, and the residue was extracted with pentane and filtered. The pentane was removed in vacuo, and the resulting pale yellow solid was again extracted with pentane, filtered, and concentrated to dryness to afford 400 mg (99%) of analytically pure yellow product: ^1H NMR δ 6.96 (s, 3, H_{aryl}), 6.47 (s, 1, Re*H*), 3.74 (d, 2, J = 13.5, $CH_AH_{A'}$-*t*-Bu), 3.68 (s, 4, $CH_BH_{B'}$-*t*-Bu), 3.56 (sept, 2, $CHMe_2$), 3.53 (d, 2, J = 13.5, $CH_AH_{A'}$-*t*-Bu), 1.23 (d, 12, $CHMe_2$), 1.08 (s, 18, CH_2-*t-Bu*), 1.07 (s, 18, CH_2-*t-Bu'*); ^{13}C NMR δ 163.8 (Np*C*CNp'), 155.8 (NpC*C*Np'), 150.9 (C_i), 143.6 (C_o), 124.6 (C_p), 122.4 (C_p), 49.09 (J = 127, *t*-BuCH_2), 47.03 (J = 126, *t*-Bu'$C'H_2$), 33.56 (Me_3CCH_2), 33.22 ($Me_3C'CH_2$), 30.48 (Me_3CCH_2), 30.32 (Me'_3CCH_2), 28.24 ($CHMe_2$), 23.31 ($CHMe_2$); IR (cm^{-1}) 1988 (ν_{ReH}), 1748, 1758 cm^{-1} (ν_{CC}). Anal. Calcd for $C_{36}H_{62}NRe$: C, 62.20; H, 8.99; N, 2.02. Found: C, 62.30; H, 9.02; N, 2.06.

15 reacted with CCl_4 (~4 equiv) in C_6D_6 to give Re(NAr)(η^2-C_2Np_2)$_2$Cl and $CHCl_3$ in ~20 min.

X-ray Structure of [N(PPh_3)$_2$][Re(NAr)$_3$] (2d). Data were collected at −72 °C on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). Of the 15 850 reflections that were collected, 14 966 were unique; equivalent reflections were merged. The intensities of three representative reflections measured after every 60 min of X-ray exposure time remained constant throughout data collection (no decay correction was applied). An empirical absorption correction, using the program DIFABS, was applied, resulting in transmission factors ranging from 0.57 to 1.2. The structure was solved by the Patterson method and refined by full-matrix least squares by using TEXSAN. The non-hydrogen atoms were refined anisotropically. Hydrogens were included in calculated positions (d_{C-H} = 0.95 Å). Crystal data may found in Table VI.

Table VI. Crystal Data for Compounds 2a, 2d, and 13b

	2a	**2d**	**13b**
emp formula	$HgRe_2N_6C_{72}H_{102}$	$ReP_2N_4C_{72}H_{81}$	$ReNaNO_2C_{44}H_{77}$
fw	1624.64	1250.61	861.29
cryst syst	cubic	triclinic	triclinic
a, Å	19.548	13.045(4)	10.652(5)
b, Å		13.726(3)	11.128(2)
c, Å		20.075(5)	19.900(6)
α, deg		106.68(2)	87.76(2)
β, deg		97.25(2)	79.35(3)
γ, deg		103.67(2)	82.29(2)
V, Å^3	7470	3272	2297
space group	$Pa\bar{3}$	$P\bar{1}$	$P\bar{1}$
Z	4	2	2
ρ(calcd), g/cm^3	1.444	1.269	1.245
μ, cm^{-1}	53.66	19.7	27.20
final R_1, R_2	3.4, 3.6	6.6, 6.1	6.7, 6.3
max peak in final diff map, e/Å^3	0.43	1.84	1.53
min peak in final diff map, e/Å^3	−0.39	−1.55	−2.80

X-ray Structure of Na(THF)$_2$Re(NAr)(η^2-C_2Np_2)$_2$ (13b). Data were collected at −72 °C on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). Of the 11 095 reflections that were collected, 10 517 were unique; equivalent reflections were merged. The intensities of three representative reflections measured after every 60 min of X-ray exposure time remained constant throughout data collection (no decay correction was applied.) An empirical absorption correction, using the program DIFABS, was applied, resulting in transmission factors ranging from 0.77 to 1.09. The structure was solved by the Patterson method and refined by full-matrix least squares by using TEXSAN. The non-hydrogen atoms were refined anisotropically. Hydrogens were included in calculated positions (d_{C-H} = 0.95 Å). Crystal data may found in Table VI.

X-ray Structure of Hg[Re(NAr)$_3$]$_2$ (2a). Details were reported in the supplementary material of the preliminary communication.

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Supplementary Material Available: Labeled ORTEP drawings, tables of final positional parameters and final thermal parameters for **2d** and **13b**, and listings of Cartesian coordinates, orbital energies, and orbital compositions for the models [Re(NH)$_3$]$^-$, [Re(NH)$_2$(C_2H_2)]$^-$, and [Re(NH)(C_2H_2)$_2$]$^-$ employed in extended Hückel calculations (26 pages). Ordering information can be found on any current masthead page.

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