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Investigation of the Formation of Ligated Dinitrogen from Rhenium-Bound Aryldiazenide

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Chemical or electrochemical reduction of the cationic rhenium aryldiazenido complexes $[Cp'Re(L_1)(L_2)(p\text{-}N_2C_6H_4OMe)][BF_4]$ **(1b−7b)** generates the corresponding neutral dinitrogen complexes **1a−7a** of the type $Cp'Re(L_1)(L_2)(N_2)$ ((a) Cp′ = Cp; $L_1 = L_2$ = CO **(1a)**; (b) Cp′ = Cp*, L_1 = CO, $L_2 = PMe_3$ **(3a)** or $P(OMe)_3$ **(4a)**; and (c) Cp′ = Cp*, $L_1 = L_2$ = CO **(2a)**, PMe_3 **(5a)**, dmpe **(6a)**, or $P(OMe)_3$ **(7a)**). Evidence is presented in support of a proposed mechanism which involves one-electron reduction of the aryldiazenido complex cation in **1b−7b** to the neutral 19-electron intermediate, followed by C−N bond homolysis to give **1a−7a** plus the *p*-methoxyphenyl radical that proceeds to form anisole by hydrogen atom abstraction from the solvent. The cathodic reduction peak potentials observed for **1b−7b** by cyclic voltammetry are increasingly negative in the sequence of coligands $(PMe_3)_2$ (**5b**, −1.89 V) > dmpe (**6b**, −1.74 V) > $[P(OMe)_3]_2$ (**7b**, −1.41 V) > $(CO)(PMe_3)$ (**3b**, −1.24 V) > $(CO)[P(OMe)_3]$ (**4b**, −0.98 V) > $(CO)_2$ (**2b**, −0.62 V). The value for the dicarbonyl Cp* complex **2b** is more negative than for the corresponding Cp complex **1b** (−0.46 V). These potentials are a good indication of the success of chemical reduction: all **1b−7b** are reduced to **1a−7a** by Na/Hg in THF, whereas Cp_2Co, which has a smaller reduction potential than Na/Hg, only reduces **1b**, **2b**, and **4b**. The reaction of **2b** with $NaBH_4$ is shown by full spectroscopic characterization to produce the aryldiazene complex $Cp^*Re(CO)_2(p\text{-}NHNC_6H_4OMe)$, which is thermally unstable and yields the dinitrogen complex **2a** and anisole.

Introduction

The first examples of rhenium dinitrogen complexes were reported in 1969 by Chatt et al.[1] These octahedral rhenium(I) dinitrogen complexes, *trans*-$ReCl(N_2)(dppe)_2$, *trans*-$ReCl(N_2)(PMe_2Ph)_4$, and *trans*-$ReCl(N_2)(PPh_3)_2(PF_3)_2$, were prepared by the degradation of the chelated benzoyldiazenido complex $ReCl_2(PPh_3)_2(N_2COPh)$. The production of methyl benzoate in the reactions suggested that nucleophilic attack of methanol or methoxide ion on the carbonyl carbon atom may be involved in the production of the dinitrogen complexes.[2]

Since the initial discovery, numerous dinitrogen complexes of rhenium have been prepared by many different routes. For example, the rhenium hydrido dinitrogen complex $ReH(N_2)(dppe)_2$ resulted from the reaction of the ammonium salt $[NH_4]_2[ReH_9]$ with 2 equiv of dppe in 2-propanol under an atmosphere of dinitrogen.[3] Furthermore, the half-sandwich rhenium dinitrogen complex $CpRe(CO)_2(N_2)$ was synthesized by controlled oxidation of the corresponding hydrazine complex $CpRe(CO)_2(N_2H_4)$ with H_2O_2 in the presence of copper(II) salts[4] or by displacement of the labile THF ligand in $CpRe(CO)_2(THF)$ by dinitrogen under high pressure.[5]

Despite this, the original Chatt synthesis remained for more than a decade the only example in which an organodiazenido ligand was transformed into a dinitrogen ligand. However, it was observed several years ago in our laboratory that the aryldiazenido ligand in the cationic manganese complex $[(\eta^5\text{-}C_5H_4Me)Mn(CO)_2(N_2Ar)][BF_4]$ was converted into ligated dinitrogen by I^-, Br^-, and Cl^- to yield the neutral complex $(\eta^5\text{-}C_5H_4Me)Mn(CO)_2(N_2)$;[6] the only other product identified was the respective substituted arene, IAr, BrAr, or ClAr. The limited available experimental evidence obtained for these reactions was consistent with a nucleophilic displacement mechanism, though a radical process cannot be ruled out.

Interestingly, identical results were not obtained when these reactions were repeated with the analogous cationic aryldiazenido complexes of rhenium, and products varied with the experimental conditions. For example, reaction of the rhenium aryldiazenido complex $[CpRe(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ with I^- gave not only the expected dinitrogen complex $CpRe(CO)_2(N_2)$ but also the known[7] diiodo complex $CpRe(CO)_2I_2$. Treatment of the rhenium aryldiazenido complex with Br^- yielded the dinitrogen complex, the corresponding dibromo complex $CpRe(CO)_2Br_2$,[8] and the carbonyl substitution complex $CpReBr(CO)(p\text{-}N_2C_6H_4OMe)$. GC−MS analysis of the reaction mixtures resulting from these halide ion additions showed in each case the presence of the respective iodo and bromo arene compounds (IC_6H_4OMe or BrC_6H_4OMe) as well as the formation of anisole (C_6H_5-

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[6] (a) Barrientos-Penna, C. F.; Einstein, F. W. B.; Sutton, D.; Willis, A. C. *Inorg. Chem.* **1980**, *19*, 2740. (b) Barrientos-Penna, C. F.; Sutton, D. *J. Chem. Soc., Chem. Commun.* **1980**, 111.

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[8] Nesmeyanov, A. N.; Kolobova, N. E.; Makarov, Y. V.; Anisimov, K. N. *Bull. Acad. Sci. USSR., Div. Chem. Sci. (Engl. Trans.)* **1969**, 1687. King, R. B.; Reimann, R. H. *Inorg. Chem.* **1976**, *15*, 183.

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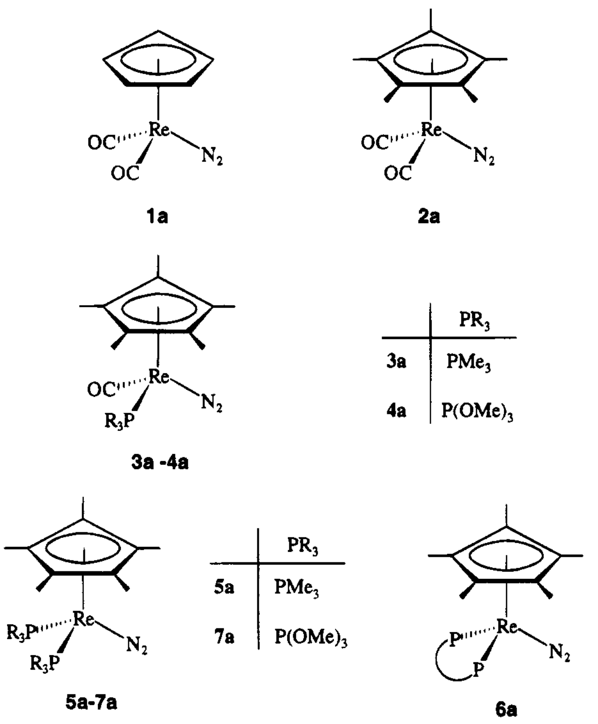
Chart 1



OMe).[9] Using Cl^- as the reagent produced only the carbonyl substitution complex CpReCl(CO)(*p*-$N_2C_6H_4$-OMe); the dichloro derivative $CpRe(CO)_2Cl_2$ and the dinitrogen complex were not formed. Furthermore, the reaction of the halide ion X^- ($X^- = I^-$, Br^-, or Cl^-) with the pentamethylcyclopentadienyl analog [Cp*Re$(CO)_2$(*p*-$N_2C_6H_4OMe$)][BF_4] yielded in all cases exclusively the respective carbonyl substitution complex Cp*ReX(CO)(*p*-$N_2C_6H_4OMe$) with no production of the expected dinitrogen complex.[9] These results, unlike those obtained for the related manganese complexes, could not be completely explained by a nucleophilic displacement mechanism but, instead, were suggestive of at least a competitive radical process.

It was clear from the synthetic results just presented that the chemistry associated with the conversion of the aryldiazenido ligand to the dinitrogen ligand, especially at a rhenium metal center, was complex and warranted further investigation. A general route to a wide variety of rhenium dinitrogen complexes has now been developed, the details of which are described in this paper. It is shown that chemical or electrochemical *reduction* of the cationic rhenium aryldiazenido complexes generates the corresponding neutral dinitrogen complexes of the type Cp′Re(L_1)(L_2)(N_2) ((a) Cp′ = Cp, $L_1 = L_2$ = CO (**1a**);[4-6] (b) Cp′ = Cp*, L_1 = CO, L_2 = PMe_3 (**3a**)[10] or $P(OMe)_3$ (**4a**);[10] and (c) Cp′ = Cp*, $L_1 = L_2$ = CO (**2a**),[10] PMe_3 (**5a**), dmpe (**6a**), or $P(OMe)_3$ (**7a**)) (Chart 1) cleanly, quickly, and in high yield. The mechanism of this conversion is discussed. While the dinitrogen complexes **1a**–**4a** have been described previously,[6,10] some of the characterizing data obtained for these compounds when they have been synthesized by methods used in this study are included for authentication purposes and for a ready comparison with those dinitrogen compounds **5a**–**7a** that have been synthesized for the first time in this work.

Results

Synthesis and Characterization of Dinitrogen Complexes. (a) Reactions Involving Hydride Sources. The hydride sources $LiAlH_4$ and $NaBH_4$ were reacted with the cationic rhenium aryldiazenido complexes [Cp*Re$(CO)_2$(*p*-$N_2C_6H_4OMe$)][BF_4] (**2b**) and [Cp*Re$(PMe_3)_2$(*p*-$N_2C_6H_4OMe$)][BF_4] (**5b**). Treatment of a solution of **5b** in methanol with either $LiAlH_4$ or $NaBH_4$ produced no reaction over several hours even after a large excess of the hydride source was added. By contrast, treatment of a solution of **2b** in methanol with excess solid $LiAlH_4$ afforded the known methoxycarbonyl complex Cp*Re(CO)(COOMe)(*p*-$N_2C_6H_4OMe$),[9] which was characterized by IR and ^1H NMR spectroscopy. This was most likely formed as a result of methoxide being generated "in situ" from the reaction of $LiAlH_4$ with methanol, and the compound could be synthesized quantitatively by addition of NaOMe to a solution of **2b** in methanol, as reported previously.[9] The dinitrogen complex **2a** was not formed in this reaction.

However, addition of excess $NaBH_4$, as a solid, to a solution of **2b** in methanol at room temperature instead resulted in the initial formation of a deep red solution. The reaction then progressed further, with loss of the red color and formation of a yellow solution containing the dinitrogen complex **2a**. Similar results were obtained when this reaction was repeated using acetone as the solvent, in agreement with earlier studies.[10-12] GC analysis of the reaction mixture indicated that anisole (C_6H_5OMe) was also a product. An IR spectrum of the red solution which was formed immediately after the addition of $NaBH_4$ to a solution of **2b** in acetone at room temperature showed the complete disappearance of **2b** and the presence of two new strong absorptions of similar intensity at 1917 and 1852 cm^{-1} assigned to ν(CO) of the intermediate species. IR spectra acquired every 5 min showed that the absorptions corresponding to the intermediate smoothly disappeared as the bands due to the dinitrogen complex **2a** gradually appeared, and **2a** was the final product.

The synthesis of the red solution was repeated at 195 K using acetone-d_6 as the solvent. A ^1H NMR spectrum of this solution acquired at 233 K demonstrated the disappearance of **2b** and the presence of resonances attributable to Cp* and *p*-methoxyphenyl groups plus a broad singlet at δ 15.68 integrating to one proton. No signal upfield from TMS (in the hydride region) was observed. The intermediate species was reprepared at 195 K by adding $NaBH_4$ to an acetone-d_6 solution of the dicarbonyl aryldiazenido complex **2b**-$^{15}N_\alpha$, which was specifically ^{15}N-labeled at the rhenium-bound nitrogen atom (N_α). A ^1H NMR spectrum of this solution acquired at 233 K exhibited, in addition to the typical resonances expected for the Cp* and the methoxyphenyl group, a doublet at δ 15.68 (J_{NH} = 69 Hz) integrating to one proton. A ^{15}N NMR spectrum of this solution obtained at this temperature also showed a doublet at δ −46.7 with the same coupling constant. The downfield doublet at δ 15.68 (J_{NH} = 69 Hz) observed in the low-temperature ^1H NMR spectrum and the doublet at

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δ −46.7 (J_{NH} = 69 Hz) detected in the low-temperature ^{15}N spectrum are confirmation of a one-bond $^{15}N-H$ coupling. Therefore, since the ^{15}N label was introduced at the rhenium-bound nitrogen atom (N_α) exclusively, the intermediate was unambiguously assigned as the aryldiazene complex $Cp^*Re(CO)_2(p\text{-}^{15}NH^{14}NC_6H_4OMe)$.

A $^{13}C\{^1H\}$ NMR spectrum of this complex recorded at 233 K in acetone-d_6 exhibited, in addition to the typical resonances for the Cp* and aryldiazene groups, a single resonance in the carbonyl region at δ 208.32 indicative of two symmetry-equivalent CO ligands. To verify that a second resonance was not hidden under the solvent resonance, the $^{13}C\{^1H\}$ NMR spectrum was reacquired at 233 K in methanol-d_4; the resulting spectrum was identical to that obtained previously using acetone-d_6.

(b) Reactions Involving the Triphenylmethyl Radical ($Ph_3C^\bullet$). Addition of excess Ph_3C, formed from the reduction of Ph_3CCl with zinc dust in THF, to a solution of the cationic dicarbonyl aryldiazenido complexes **1b** or **2b** in CH_2Cl_2 at room temperature afforded the corresponding neutral dinitrogen complexes **1a** and **2a**, respectively, in moderate yield. In both cases the production of the dinitrogen complex was accompanied by the formation of a white precipitate that was identified by melting point, ^1H NMR spectroscopy, and elemental analysis as $Ph_3COOCPh_3$, formed by oxidation of the Ph_3C radical. Using freshly distilled and scrupulously degassed solvents and high-purity Ar as the inert atmosphere prevented the formation of this peroxide.

A gas chromatogram of the volatiles, which were removed under vacuum prior to the purification of the dinitrogen complexes, indicated the presence of anisole. Notably, no evidence to support the formation of the radical combination products $Ph_3CC_6H_4OMe$ or Ph_3CCPh_3 was obtained. However, ^1H NMR spectroscopy and elemental analysis confirmed the presence of $[Ph_3C][BF_4]$.

Interestingly, the addition of even a large excess of the triphenylmethyl radical to a solution of the aryldiazenido complexes **3b**−**7b** in CH_2Cl_2 did not yield the dinitrogen complexes **3a**−**7a**. The starting aryldiazenido complexes were recovered quantitatively even after the mixtures were stirred for 24 h.

(c) Reactions Involving Cobaltocene or Sodium. Addition of excess cobaltocene (Cp_2Co) to a solution of the dicarbonyl aryldiazenido complexes **1b** and **2b** in acetone at room temperature gave the corresponding neutral dinitrogen complexes **1a** and **2a** in excellent yield. Unlike the triphenylmethyl radical chemistry mentioned above, Cp_2Co was also effective in reducing the cationic carbonyl trimethylphosphite aryldiazenido complex **4b** to the dinitrogen complex **4a** in good yield. Again, anisole, confirmed by gas chromatography, was also formed in each of these reactions. The salt $[Cp_2Co][BF_4]$ was also detected as a byproduct by ^1H NMR spectroscopy.

Notably, when this procedure was repeated for the remaining carbonyl trimethylphosphine or bis(phosphorus ligand) aryldiazenido complexes **3b** or **5b**−**7b**, the corresponding dinitrogen complexes were not produced.

Treatment of a solution of **2b** in liquid ammonia/THF with sodium metal did not give the dinitrogen complex **2a** but instead the known[9] neutral carbamoyl complex $Cp^*Re(CO)(CONH_2)(p\text{-}N_2C_6H_4OMe)$ was produced, identified by IR and ^1H NMR spectroscopy. This complex was confirmed to result when **2b** was added as a solid to liquid NH_3 in the absence of Na, as reported previously.[9] Ammonia is therefore a poor choice of solvent for the sodium reactions because it reacts with **2b** quickly and completely to form the carbamoyl complex before the addition of Na, and no further reaction ensues. Repeating the Na/NH_3 reduction with **5b** did not yield the dinitrogen complex **5a** either; instead, the dihydride complex *trans*-$Cp^*Re(PMe_3)_2H_2$ was produced and characterized by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.[13a] Sonication of a mixture of sodium metal and **2b** in THF afforded the dinitrogen complex **2a** in poor yield. However, addition of a solution of **2b** in THF to sodium amalgam at room temperature gave exclusively the dinitrogen complex **2a** in excellent yield. More importantly, treatment of any of the aryldiazenido complexes **1b** or **3b**−**7b** with Na/Hg afforded the neutral dinitrogen complexes **1a** or **3a**−**7a**, respectively, in good yield. Once again, anisole was determined by gas chromatography to accompany the production of the dinitrogen complexes.

Table 1. Cyclic Voltammetric Cathodic Peak Potentials for Complexes 1b−7b[a]

complex	E_p^c (V)
$[CpRe(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ **(1b)**	−0. 46
$[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ **(2b)**	−0.62
$[Cp^*Re(CO)(PMe_3)(p\text{-}N_2C_6H_4OMe)][BF_4]$ **(3b)**	−1.24
$[Cp^*Re(CO)\{P(OMe)_3\}(p\text{-}N_2C_6H_4OMe)][BF_4]$ **(4b)**	−0.98
$[Cp^*Re(PMe_3)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ **(5b)**	−1.89
$[Cp^*Re(dmpe)(p\text{-}N_2C_6H_4OMe)][BF_4]$ **(6b)**	−1.74
$[Cp^*Re\{P(OMe)_3\}_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ **(7b)**	−1.41

[a] Recorded for 1.0 mM solutions of the complexes in acetonitrile at a Pt electrode with 0.2 M TEAP as the supporting electrolyte; scan rate 0.2 V/s; potentials are vs. SCE.

(d) Electrochemical Reduction. The cyclic voltammograms of **1b**−**7b** in MeCN, recorded at a scan rate of 0.2 V/s, displayed in each case a single cathodic wave between −0.46 and −1.89 V vs. SCE but no observable return anodic wave, indicating a chemically irreversible process (Table 1).

The cyclic voltammograms of the cationic dicarbonyl aryldiazenido complexes **1b** and **2b** (Figure 1(a)) showed no signs of approaching electrochemical reversibility as the scan rate was increased to 1.0 V/s. However, at this scan rate a return anodic wave was clearly resolved for the cationic carbonyl phosphine and phosphite complexes **3b** and **4b** (Figure 1(b)). Unfortunately, it was not possible with the limited scan rates available with the electrochemical equipment at SFU to employ scan rates faster than 1.0 V/s to see whether a well-defined reversible wave form could be achieved for **3b**, **4b**, or any of the other cationic complexes. However, Richards and Bard successfully employed fast scan rate cyclic voltammetry and scanning electrochemical microscopy (SECM) to examine in more detail the electrochemical behavior of $[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ **(2b)**.[13b] The cyclic voltammogram of **2b** exhibited a reversible wave with a cathodic peak potential of −0.66 V with respect to a silver quasireference electrode at a scan rate of 10 V/s. The anodic wave was first resolved at this

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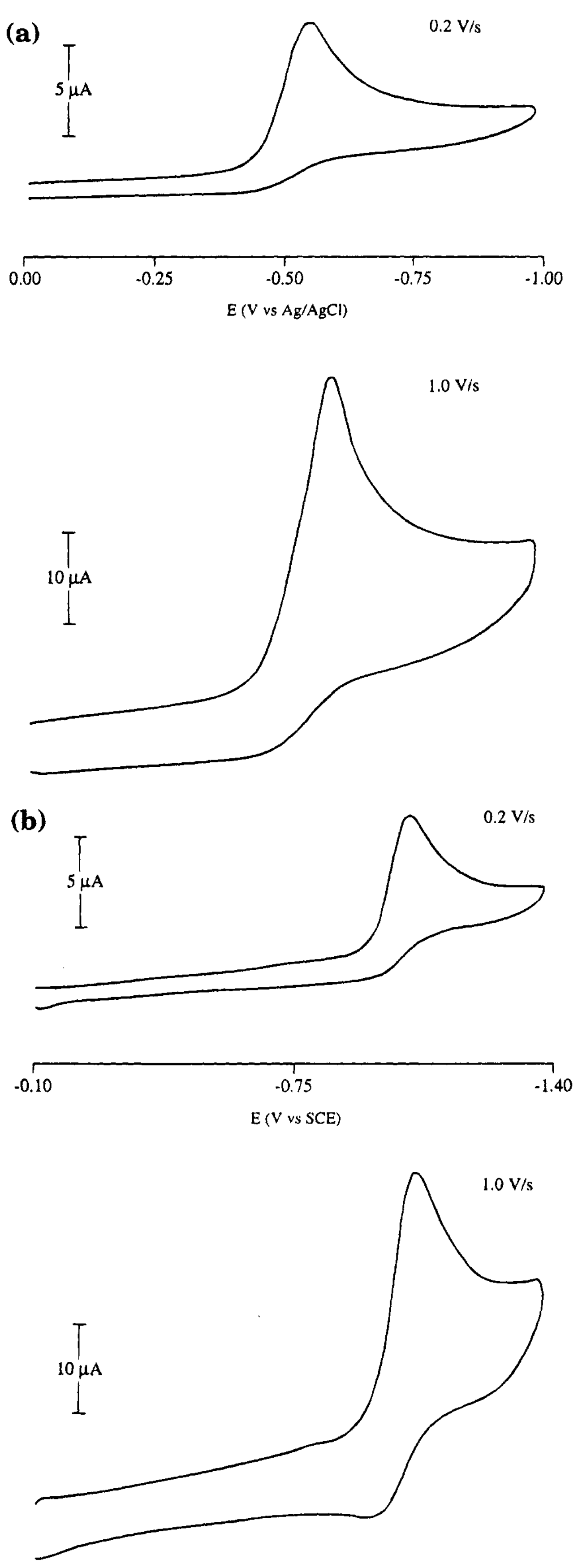

Figure 1. Cyclic voltammograms of (a) **2b** and (b) **3b** (1.0 mM MeCN solution; 0.2 M TEAP; Pt working electrode).

scan rate and became well-defined at 50 V/s. Digital simulation of these cyclic voltammograms assuming an electrochemical E_rC_i mechanism afforded a rate constant $k_c = 145 \pm 10$ s^{-1} for the decomposition of the reduced species to products. The validity of this rate constant was substantiated by SECM which also produced a value of 145 s^{-1} for k_c.[13b]

The controlled potential electrolysis (CPE) of solutions of the cationic aryldiazenido complexes **1b**–**3b** and **5b** in acetonitrile (5 mM) was performed at a large Pt gauze electrode with tetraethylammonium perchlorate (TEAP, 0.2 M) as the supporting electrolyte. When the amount of charge consumed at the end of the CPE experiment was monitored, a value for the number of electrons involved in the overall reduction reaction was determined for **1b**–**3b**.[13b] Exhaustive CPE of **1b**–**3b** (60 min) at a potential sufficiently more negative than their respective cathodic peak potentials vs. SCE (Table 1) indicated the consumption of 1 equiv of electrons in all cases. Monitoring the progress of the electrolysis of **1b**–**3b** by IR spectroscopy[13b] showed the clean production of the corresponding neutral dinitrogen complexes **1a**–**3a**, respectively, in good yield and complete disappearance of **1b**–**3b**. Upon completion of the electrolysis, solvent and volatiles were removed by vacuum, and a gas chromatogram of the condensate confirmed the presence of anisole. The results from the CPE studies of the cationic bis(trimethylphosphine) aryldiazenido complex **5b** were inconclusive, since **5b** proved to be very air-sensitive and was easily oxidized to the known trioxo complex Cp^*ReO_3[14] prior to or during the CPE measurements, despite all efforts to maintain an inert atmosphere in the CPE cell.

Discussion

Synthesis and Characterization of Dinitrogen Complexes. In this study, a wide variety of Cp and Cp* rhenium aryldiazenido complexes has been converted to the corresponding dinitrogen complexes of general formula $Cp'Re(L_1)(L_2)(N_2)$ ((a) Cp′ = Cp, $L_1 = L_2$ = CO (**1a**);[4-6] (b) Cp′ = Cp*, L_1 = CO, L_2 = PMe_3 (**3a**)[10] or $P(OMe)_3$ (**4a**);[10] and (c) Cp′ = Cp*, $L_1 = L_2$ = CO (**2a**),[10] PMe_3 (**5a**), dmpe (**6a**), or $P(OMe)_3$ (**7a**)) (Chart 1) by the use of $NaBH_4$, Ph_3C, Cp_2Co, Na/Hg, or electrochemical reduction. Some of these compounds have been made from aryldiazenido complexes previously by employing reagents that included, among others, $NaBH_4$, Bu^{n}Li, or iodide[6,10-12] but reagents used here, such as Na/Hg or Cp_2Co, are superior in terms of yield, mild conditions, or ease of workup. Individual reagents are discussed separately below. In addition, we did attempt to synthesize **3a**–**7a** by oxidative removal of a carbonyl ligand in **2a** with PhIO or Me_3NO in a coordinating solvent such as MeCN, followed by subsequent substitution of the ligated solvent by phosphine or phosphite, but this was not successful.

The dinitrogen complexes **1a**–**7a** were obtained as analytically and spectroscopically pure pale yellow solids that are very soluble in the majority of organic solvents. As solids, complexes **1a**–**4a** can be exposed to air for short periods of time without appreciable deterioration and can be stored indefinitely at 263 K under an atmosphere of N_2; solutions are more air-sensitive.[10] The bis(phosphorus ligand) dinitrogen complexes **5a** and **7a** and the bidentate phosphine dinitrogen complex **6a**, either in solution or as solids, are very air-sensitive, and

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Table 2. IR, ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR Data for the Dinitrogen Complexes 1a–7a

complex	IR (cm^{-1})[a]	^1H NMR $\delta(Cp^*)$[b]	$^{31}P\{^1H\}$ NMR[c]	$^{13}C\{^1H\}$ NMR $\delta(CO)$[b]
1a	2145 $\nu(NN)$; 1973, 1919 $\nu(CO)$	5.23 s		195.79 s
1a-$^{15}N_\alpha$	2110 $\nu(NN)$; 1973, 1919 $\nu(CO)$			
2a	2125 $\nu(NN)$; 1954, 1902 $\nu(CO)$	2.09 s		200.09 s
2a-$^{15}N_\alpha$	2092 $\nu(NN)$; 1954, 1902 $\nu(CO)$			
3a	2044 $\nu(NN)$; 1865 $\nu(CO)$	2.00 d ($J = 0.7$)	−29.86	207.18 d ($J = 7$)
3a-$^{15}N_\alpha$	2011 $\nu(NN)$; 1865 $\nu(CO)$			
4a	2078, 2066 $\nu(NN)$; 1877 $\nu(CO)$	2.04 d ($J = 0.8$)	139.12	204.96 d ($J = 12$)
4a-$^{15}N_\alpha$	2045, 2033 $\nu(NN)$; 1877 $\nu(CO)$			
5a	1975 $\nu(NN)$	1.88 t ($J = 0.7$)	−35.31	
5a-$^{15}N_\alpha$	1943 $\nu(NN)$			
5a-$^{15}N_\beta$	1943 $\nu(NN)$			
6a	1977 $\nu(NN)$	1.92 s	−16.88	
7a	2014 $\nu(NN)$	1.87 t ($J = 0.8$)	138.80	

[a] In hexane. [b] In $CDCl_3$ for **1a**–**4a** and in acetone-d_6 for **5a**–**7a**; referenced to TMS; J given in Hz; δ given in ppm. [c] In $CDCl_3$ for **1a**–**4a** and in acetone-d_6 for **5a**–**7a**; referenced to 85% H_3PO_4; δ given in ppm.

exposure to air for even short periods of time results in the oxidation of these complexes to the known trioxo complex Cp^*ReO_3.[14] The trioxo complex was confirmed by bubbling O_2 (g) through a solution of the dinitrogen complexes **5a**–**7a** in hexane for 5 min and then analyzing the product formed by ^1H NMR and mass spectroscopy. The mechanism for this conversion is not known, and is currently under investigation in our laboratory.

From the IR spectra of the dinitrogen complexes **1a**–**7a**, recorded in hexane, $\nu(NN)$ was observed as a strong absorption in the 2145–1975 cm^{-1} region (Table 2). The assignment of $\nu(NN)$ was confirmed by ^{15}N isotopic substitution at the rhenium-bound nitrogen atom (N_α) in **1a**–**5a**. In all cases an isotopic shift to lower wavenumber, by *ca.* 33 cm^{-1}, was observed for $\nu(NN)$. Data obtained in this study agree well with previously obtained values for **1a**–**4a**.[6,10] The two resolved $\nu(NN)$ absorptions reported[10] for the carbonyl trimethylphosphite dinitrogen complex **4a** and accounted for by the presence of conformational isomers brought about by the specific orientation of the Me group of the $P(OMe)_3$ ligand were observed for the material synthesized in this work by different procedures. In contrast to this result, the bis(trimethylphosphite) dinitrogen complex **7a** exhibited only a single IR absorption for $\nu(NN)$.

For complexes **1a**–**7a** the relative electronic properties of the Cp, Cp*, or phosphorus ligands are borne out by changes in $\nu(CO)$ or, more dramatically, by changes in $\nu(NN)$ (Table 2). The greater the σ-donor (or poorer the π-acceptor) ability of these ligands, the higher the degree of charge delocalization into the carbonyl or dinitrogen antibonding orbitals and the lower $\nu(CO)$ or $\nu(NN)$. Values for $\nu(NN)$ and, where applicable, for $\nu(CO)$, follow the order Cp > Cp* in comparable compounds, in agreement with the general view that Cp* is a better electron-donating ligand than Cp, and these findings are similar to those reported for the chromium dicarbonyl dinitrogen complexes (η-aryl)$Cr(CO)_2(N_2)$ (aryl = C_6H_6, $C_6H_3Me_3$, or C_6Me_6).[15a] Furthermore, the values follow the order of the coligands $(CO)[P(OMe)_3]$ **(4a)** > $(CO)(PMe_3)$ **(3a)** > $[P(OMe)_3]_2$ **(7a)** > dmpe **(6a)** ≈ $(PMe_3)_2$ **(5a)**, which correlates with increasing σ-donor ability (or decreasing π-acceptor ability) of the phosphorus ligand. Taken together, these results conform to the view that PMe_3 is a significantly better electron-donating ligand [$\Delta\nu(NN) = 81$ cm^{-1} on going from **2a** to **3a**] than $P(OMe)_3$ [$\Delta\nu(NN) =$ *ca.* 53 cm^{-1} on going from **2a** to **4a**].

The ^1H NMR spectra for complexes **1a**–**4a** exhibited the typical resonances expected for the Cp, Cp*, and phosphorus groups. The only observation of note was that the Cp* resonance in the carbonyl phosphine and phosphite complexes **3a** and **4a** was, as reported previously,[10] split into a doublet with J_{H-P} couplings of 0.7 and 0.8 Hz, respectively, which supports the presence of a single phosphorus ligand in these complexes (Table 2). For complexes **5a**–**7a**, the ^1H NMR spectra showed some notable features. The Cp* resonance for both the bis(trimethylphosphine) dinitrogen complex **5a** and for the bis(trimethylphosphite) dinitrogen complex **7a** appeared as a triplet, indicating that the Cp* methyls were observably coupled to two equivalent phosphorus ligands. Interestingly, for the bidentate phosphine dinitrogen complex **6a** only a singlet Cp* resonance was observed. In **5a** the resonance at δ 1.48 assigned to the PMe_3 protons was observed to be a virtual doublet integrating to 18H. The apparent coupling constant ($^2J_{H-P} + {}^4J_{H-P}$), given by the separation between the two outside peaks, was 7.4 Hz. In **7a** the resonance at δ 3.45 assigned to the $P(OMe)_3$ protons was also observed to be a virtual doublet, integrating to 18H with a coupling constant ($^3J_{H-P} + {}^5J_{H-P}$) of 11.5 Hz.

The $^{31}P\{^1H\}$ NMR spectra of complexes **3a**–**7a**, in each case, displayed a single resonance in the normal region for a coordinated phosphine or phosphite (Table 2), which also indicates that in the bis(phosphorus ligand) complexes **5a**–**7a** the phosphorus ligands are equivalent by symmetry. The $^{13}C\{^1H\}$ NMR spectra of complexes **1a**–**4a** showed a carbonyl carbon resonance in the region 195.79–207.18 ppm; a singlet was observed for **1a** and **2a** and a doublet for the phosphorus ligand complexes **3a** and **4a** with $J_{C-P} = 7$ and 12 Hz, respectively. The single resonance observed for $\delta(CO)$ for the dicarbonyl dinitrogen complexes **1a** and **2a** indicates that these two CO ligands are also symmetry equivalent. As has been indicated earlier,[10] the ^{15}N NMR spectra of some of these dinitrogen complexes, such as **1a** and **2a**, when labeled with ^{15}N at the α position show that the label is scrambled into the β position. The data provided here are for the pure $^{15}N_\alpha$ isotopomer synthesized and quickly isolated below ambient temperature; full details of the isomerization study will be included in a separate paper.[15b] Further characterization of the dinitrogen complexes **1a**–**7a** was provided by mass spectroscopy. In all cases the molec-

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[15] (a) Sellmann, D.; Maisel, G. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1972**, *27*, 465. (b) For a preliminary account see: Cusanelli, A.; Sutton, D. *J. Chem. Soc., Chem. Commun.* **1989**, 1719.

ular ion M^+ was observed as a weak peak and was always accompanied by a fragment corresponding to loss of the dinitrogen ligand.

Reactions Using $NaBH_4$. Several years ago, the reaction of the aryldiazenido complexes $[CpRe(CO)_2(p\text{-}N_2C_6H_4R)][BF_4]$ (R = Me, OMe, NEt_2) and $[CpRe(CO)_2\{N_2C_6H_3(3,5\text{-}Me_2)\}][BF_4]$ with $NaBH_4$ was reported from this laboratory.[16] The product in each case was the highly colored corresponding aryldiazene (NH=NAr) complex formed by nucleophilic attack of hydride at the metal-bound nitrogen N_α and was unambiguously identified as such by the NH resonance in the complex with R = NEt_2 which occurred as a doublet in the $^{15}N_\alpha$-labeled isotopomer. The aryldiazene complex was thermally unstable resulting in the production of the dinitrogen complex $CpRe(CO)_2(N_2)$ **(1a)** and the corresponding arene. When a Cp* analogue, namely $[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ **(2b)** was reacted with $NaBH_4$ the transient red product formed en route to the dinitrogen compound **2a** was considered by analogy to be the aryldiazene complex $Cp^*Re(CO)_2(p\text{-}NHNC_6H_4OMe)$.[11,12] It was not, however, characterized except for the IR spectrum (ν(CO) = 1914, 1850 cm^{-1} in acetone). Now, this compound has been completely characterized as part of this study.

The IR spectrum of the aryldiazene complex formed in situ from the addition of $NaBH_4$ to **2b** in acetone at low temperature showed two ν(CO) absorptions (1917 and 1852 cm^{-1} in acetone), which were lowered substantially from the corresponding positions in the aryldiazenido complex **2b** (2054 and 1995 cm^{-1} in acetone). The ν(NN) band for the aryldiazene complex was not observed in solution spectra, nor was the ν(NH) absorption. Notably, even ^{15}N isotopic substitution of the rhenium-bound nitrogen atom (N_α) in the aryldiazene complex $Cp^*Re(CO)_2(p\text{-}^{15}NH^{14}NC_6H_4OMe)$ did not lead to observable absorptions assignable to ν(NN) or ν(NH) in the solution spectra.

The ^1H NMR spectrum readily demonstrated the presence of the aryldiazene ligand. The NH resonance occurs well downfield (δ 15.68) and is at the lower end of the range (*ca.* δ 11–15) observed for many other aryldiazenes,[17-19] and the resonance was split into a sharp doublet ($J_{^{15}NH}$ = 69 Hz) in the spectrum of the $^{15}N_\alpha$ derivative $Cp^*Re(CO)_2(p\text{-}^{15}NH^{14}NC_6H_4OMe)$. This coupling constant is in agreement with $J_{^{15}NH}$ values reported for other aryldiazene complexes, such as $[PtCl(PEt_3)_2(p\text{-}^{15}NH^{14}NC_6H_4F)][BF_4]$ (J = 77 Hz),[17] $[RuCl(^{15}NH^{14}NPh)(CO)_2(PPh_3)_2][ClO_4]$ (J = 65 Hz),[18] and $[W(CO)_2(NO)(PPh_3)_2(^{15}NH^{14}NPh)][PF_6]$ (J = 63 Hz),[19] and is appropriate for metal-bound sp^2-hybridized nitrogen.

The actual bonding mode of the ligand (i.e., end-on (η^1) or side-on (η^2) bonded) cannot be unambiguously deduced. The observed single resonance at δ 208.32 in the carbonyl region in the $^{13}C\{^1H\}$ NMR spectrum at 233 K is not consistent with a η^2-aryldiazene with the NN axis parallel to the Cp* plane but would be consistent if the aryldiazene lies perpendicular to the Cp* plane and in a plane equating the two CO ligands, or is rotating. A η^1-aryldiazene ligand freely rotating about the Re–N bond would also result in equivalent carbonyl groups. Since the δ(NH) ^1H NMR resonance is observed in the region where δ(NH) for crystallographically-determined η^1-aryldiazene complexes resonates, it is likely that the aryldiazene is η^1 in this complex.[18] To date, all previously reported aryldiazene complexes have been shown or are believed to be η^1-bonded to the metal. It should be noted, however, that the closely related diphenyldiazene complex $CpRe(CO)_2(N_2Ph_2)$ is η^2-bonded in the crystal structure, and undergoes rapid η^1–η^2 interconversion in solution.[20]

It has been previously observed that reaction of the carbonyl trimethylphosphine complex $[Cp^*Re(CO)(PMe_3)(p\text{-}N_2C_6H_4OMe)][BF_4]$ **(3b)** with $NaBH_4$ resulted in no formation of an aryldiazene ligand; instead, there was substitution of PMe_3 to yield the hydrido complex $Cp^*ReH(CO)(p\text{-}N_2C_6H_4OMe)$.[10] Here, we find that replacement of *both* CO ligands by PMe_3 appears to render the complex inert to hydride attack, as neither the corresponding aryldiazene, dinitrogen or hydrido complex was observed. Treatment of the bis(trimethylphosphine) complex **5b** with $NaBH_4$ resulted in no reaction. It is reasoned that an increase in the electron-donating ability of the ligand, as each CO group is replaced by PMe_3, causes an increase of electron density at the metal center which in turn leads to greater metal d–π^*(NNAr) back-bonding (reflected in the trend in ν(NN) values). The result is that the rhenium center and the rhenium-bound nitrogen atom in **5b** are made less susceptible to nucleophilic attack by hydride.

Reactions Using Triphenylmethyl or Cobaltocene. The cationic dicarbonyl aryldiazenido complexes $[Cp'Re(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ (Cp′ = Cp **(1b)** or Cp* **(2b)**) were converted to the corresponding neutral dinitrogen complexes **1a** and **2a** at room temperature by reaction with a THF solution containing an excess of the triphenylmethyl radical. However, this reagent was completely ineffective when reacted with the phosphorus-substituted aryldiazenido complexes **3b**–**7b**. Reactions with Cp_2Co also resulted in the instantaneous formation of the dinitrogen complexes **1a** and **2a** in excellent yield, and this reagent was also effective in the case of the trimethylphosphite complex **4b**. However, it was not capable of reducing the remaining aryldiazenido complexes **3b** or **5b**–**7b** to the dinitrogen complexes.

The formation of anisole and $[Ph_3C][BF_4]$ or $[Cp_2Co][BF_4]$, respectively, in the reactions with Ph_3C or Cp_2Co is consistent with an electron transfer mechanism, resulting in the formation of a 19-electron neutral aryldiazenido complex intermediate $Cp'Re(CO)(L)(N_2Ar)$ (L = CO or $P(OMe)_3$). This is then visualized to decompose by CN bond homolysis to give the dinitrogen complex and an aryl radical which rapidly abstracts a hydrogen atom from the solvent to give anisole. No quantitative determination of the yields of anisole, $[Ph_3C][BF_4]$, or $[Cp_2Co][BF_4]$ was carried out. An attempt to observe by ESR the intermediate 19-electron radical in solution in the reaction of Ph_3C with the

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aryldiazenido complex **2b** was unsuccessful at room temperature and at 195 K.

Reactions Using Sodium Amalgam. The results with Ph_3C and Cp_2Co suggested that the inability to reduce the majority of the phosphine-substituted complexes such as **5b**–**7b** resulted from the complexes having reduction potentials for the reduction to the neutral aryldiazenido complex intermediate that are considerably more negative than are accessible with these reagents. Therefore, the use of the more powerful reductant sodium was examined. In agreement, sodium amalgam in THF was effective in reducing all of the aryldiazenido complexes **1b**–**7b** to the dinitrogen complexes **1a**–**7a**. We now consider this to be the most convenient and preferred reagent for production of all these rhenium dinitrogen complexes from the aryldiazenido complexes in excellent yield.

Electrochemical Methods. The suggestion that a one-electron chemical reduction was responsible for the conversion of the cationic aryldiazenido ligand to the neutral dinitrogen moiety was quantitatively corroborated by electrochemical measurements conducted on the complexes **1b**–**7b**. The cyclic voltammograms of these complexes displayed in each case a single irreversible cathodic wave, which was an indication of the relative reduction potential required to convert **1b**–**7b** to the corresponding neutral aryldiazenido complexes (Table 1).

The values of the cathodic peak potential reflect the expected electronic properties of the Cp, Cp*, or phosphorus ligands. For example, the Cp dicarbonyl complex **1b** has a smaller negative value for the potential (−0.46 V) than the Cp* analogue **2b** (−0.62 V). Furthermore, the potentials for the remaining aryldiazenido complexes follow the order of the coligands $(PMe_3)_2$ (**5b**, −1.89 V) > dmpe (**6b**, −1.74 V) > $[P(OMe)_3]_2$ (**7b**, −1.41 V) > $(CO)(PMe_3)$ (**3b**, −1.24 V) > $(CO)[P(OMe)_3]$ (**4b**, −0.98 V). Taken together, these results suggest that an increase in the σ-donor ability (or decrease in the π-acceptor ability) of an ancillary ligand leads to an increasingly negative value for the potential. These results satisfactorily account for the ability of sodium amalgam to reduce all of the aryldiazenido complexes and for Cp_2Co and Ph_3C to reduce only selected ones. The reduction potential of Cp_2Co is reported to be only *ca.* −0.9 V vs. SCE in CH_2Cl_2,[21] whereas the reduction potential of sodium is *ca.* −3.0 V vs. SCE.[22] The reduction potential of Ph_3C, to the best of our knowledge, has not been reported in the literature. The fact that Ph_3C was capable of reducing only the dicarbonyl complexes **1b** and **2b** suggests that the reduction capacity of Ph_3C is of the order of the potential determined for the Cp* dicarbonyl aryldiazenido complex **2b** (*ca.* −0.62 V).

Further evidence to support an electron transfer mechanism for the observed transformation of the aryldiazenido moiety to the respective dinitrogen derivative is provided by the results of fast scan rate cyclic voltammetry (CV) and scanning electrochemical microscopy (SECM) conducted by Richards and Bard and reported elsewhere.[13b] These measurements provide a first-order rate constant of $k_c = 145\ s^{-1}$ for the decomposition of the 19-electron intermediate in the case of $Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)$. The CPE study lends further support to an electrochemical E_rC_i mechanism. Exhaustive controlled potential electrolysis of **2b** (60 min) at −0.62 V versus SCE indicated the consumption of 1 equiv of electrons. This result is clearly consistent with the production of the neutral 19-electron complex and its subsequent decomposition. In addition, exhaustive CPE of the Cp dicarbonyl complex **1b** and the Cp* carbonyl trimethylphosphine complex **3b** also established these reactions to be clean one-electron processes, and in all three cases IR monitoring showed the conversion of the aryldiazenido complex to the dinitrogen complex and GC analysis revealed anisole as a product, demonstrating the similarity of the chemical and electrochemical processes.

Conclusion

We have shown that chemical or electrochemical reduction of the cationic rhenium aryldiazenido complexes $[Cp'Re(L_1)(L_2)(p\text{-}N_2C_6H_4OMe)][BF_4]$ (**1b**–**7b**) generates the corresponding neutral dinitrogen complexes **1a**–**7a** of the type $Cp'Re(L_1)(L_2)(N_2)$ ((a) Cp′ = Cp, $L_1 = L_2 = CO$ (**1a**); (b) Cp′ = Cp*, $L_1 = CO$, $L_2 = PMe_3$ (**3a**) or $P(OMe)_3$ (**4a**); and (c) Cp′ = Cp*, $L_1 = L_2 = CO$ (**2a**), PMe_3 (**5a**), dmpe (**6a**), or $P(OMe)_3$ (**7a**)). Evidence has been presented in support of a proposed mechanism that involves one-electron reduction of the aryldiazenido complex cation in **1b**–**7b** to the neutral 19-electron intermediate $Cp'Re(L_1)(L_2)(p\text{-}N_2C_6H_4OMe)$, followed by C−N bond homolysis to give **1a**–**7a** plus the *p*-methoxyphenyl radical that, in turn, yields anisole by hydrogen atom abstraction from the solvent. The measured cathodic wave peak potentials of **1b**–**7b** have been found to be a good indication of whether chemical reduction by the various reductants studied is successful in producing **1a**–**7a**. The mechanism of $NaBH_4$ reduction of **2b** has been shown to be different from the one-electron reduction. The intermediate aryldiazene complex $Cp^*Re(CO)_2(p\text{-}NHNC_6H_4OMe)$ is formed first and is thermally unstable, yielding the dinitrogen complex **2a** and anisole. This is not a general reaction for all of the aryldiazenido complexes studied, however. For example, no reaction occurs between $NaBH_4$ and the bis PMe_3 complex **5b**.

Experimental Section

General Methods. All manipulations were performed under nitrogen or argon by using standard Schlenk, drybox, or vacuum line techniques unless stated otherwise. Drybox manipulations were carried out in a nitrogen-filled Vacuum Atmospheres HE-493 Dri-Lab with attached Dri-Train.

All NMR data were recorded on a Bruker AMX 400 instrument at operating frequencies of 400.1, 162.0, 100.6, 40.5, and 28.9 MHz for ^1H, ^{31}P, ^{13}C, ^{15}N, and ^{14}N nuclei, respectively. ^1H and ^{13}C NMR chemical shifts are reported in ppm downfield (positive) of tetramethylsilane. ^{31}P NMR chemical shifts are referenced to 85% H_3PO_4. ^{14}N and ^{15}N NMR chemical shifts are referenced to external nitromethane ($MeNO_2$). Acetone-d_6 and methanol-d_4 were used as solvents for all the low-temperature NMR work. The term "virtual doublet" refers to

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the non-first-order multiplet (filled-in doublet)[23] which is seen in some of the ^{1}H NMR spectra; the apparent coupling constant is given by the separation between the two outside peaks. Electron spin resonance (ESR) spectra were recorded both at room temperature and at low temperature on a Varian E-4 instrument. Gas chromatography of the solutions after chemical and electrochemical reductions were complete was performed on a Hewlett-Packard 5890 A Series gas chromatograph containing a DB-1 capillary column and equipped with a Hewlett-Packard 3392 A integrator. Identification of the chromatographic peak for anisole was made by comparison with that of the authentic compound.

The details for the preparation and purification of the cationic rhenium aryldiazenido complexes have been provided elsewhere.[10,24] Methanol and acetone were distilled from calcium sulfate under nitrogen and used immediately. Hexamethylphosphoramide (HMPA) (Aldrich Chemical Co.) was distilled from calcium hydride and stored over 4 Å molecular sieves, which had been activated by drying under vacuum at 573 K for several days. Anisole (Fisher Scientific Co.) was used as received. Sodium metal (BDH Chemicals Ltd.) was washed with hexane prior to use and was freshly cut. Mercury (Aldrich) was cleaned by filtration through fine filter paper and distilled under vacuum. Ammonia gas (Linde Union Carbide) was used as purchased. Sodium borohydride (BDH) and lithium aluminum hydride (Alfa Products, Ventron Division) were used as purchased and were stored under nitrogen. The triphenylmethyl radical ($Ph_3C^\bullet$) was synthesized by zinc reduction of triphenylchloromethane (Ph_3CCl)[25] which was prepared by reaction of triphenylmethanol (Ph_3COH) (Aldrich) with acetyl chloride.[26] Cobaltocene (Cp_2Co) was prepared by reaction of anhydrous cobalt(II) chloride (Alfa) with sodium cyclopentadienide prepared from sodium and dicyclopentadiene (Aldrich)[27] and was sublimed under vacuum onto a dry ice-cooled cold finger before use.

Preparation of CpRe(CO)$_2$(N$_2$) (1a) and 1a-^{15}N$_\alpha$. A 5-fold stoichiometric excess of Cp_2Co was dissolved in a minimum amount of acetone (5 mL) and then added *via* syringe to a solution of the cationic dicarbonyl complex **1b** or **1b**-$^{15}N_\alpha$ (100 mg, 0.189 mmol) in acetone (10 mL) at room temperature. The IR spectrum of this mixture recorded immediately after the cobaltocene addition showed the total disappearance of the cationic complex and only the presence of absorptions due to the dinitrogen complex **1a** or **1a**-$^{15}N_\alpha$. Diethyl ether (20 mL) was added to precipitate $[Cp_2Co][BF_4]$, and the mixture was stirred for 30 min. The solution was filtered through a short column of Celite, and the solvent was removed under vacuum to give a pale brown oil. The oil was absorbed by a small amount of neutral alumina and dried under vacuum, and the mixture was chromatographed on alumina. Elution with hexane afforded **1a** or **1a**-$^{15}N_\alpha$ as a pale yellow colored microcrystalline solid in 87% yield (55 mg, 0.16 mmol). IR (hexane): 2145 cm^{-1} ν(NN) (2110 cm^{-1} for $^{15}N_\alpha$-labeled complex); 1973, 1919 cm^{-1} ν(CO). ^{1}H NMR ($CDCl_3$): δ 5.23 (s, 5H, Cp). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 93.72 (s, Cp), 195.79 (s, CO). ^{15}N NMR (acetone-d_6): δ −120.9 (s, $^{15}N_\alpha$). ^{14}N NMR (acetone-d_6): δ −120 (s, $^{14}N_\alpha$), −26 (s, $^{14}N_\beta$). MS (EI): *m/z* 336 (337 in **1a**-$^{15}N_\alpha$) (M$^+$), 308 (M$^+$ − N$_2$). Anal. Calcd: C, 25.06; H, 1.49; N, 8.35. Found: C, 24.97; H, 1.71; N, 8.43.

Preparation of Cp*Re(CO)$_2$(N$_2$) (2a) and 2a-^{15}N$_\alpha$. A 5-fold stoichiometric excess of Cp_2Co was dissolved in a minimum amount of acetone (5 mL) and then added *via* syringe to a solution of the cationic dicarbonyl complex **2b** or **2b**-$^{15}N_\alpha$ (100 mg, 0.167 mmol) in acetone (10 mL) at room temperature. The IR spectrum of this mixture recorded immediately after the cobaltocene addition showed the total disappearance of the cationic complex and only the presence of absorptions corresponding to the dinitrogen complex **2a** or **2a**-$^{15}N_\alpha$. Purification following the procedure used for complex **1a** gave **2a** or **2a**-$^{15}N_\alpha$ as a pale yellow colored microcrystalline solid in 89% yield (60 mg, 0.15 mmol). IR (hexane): 2125 cm^{-1} ν(NN) (2092 cm^{-1} for $^{15}N_\alpha$-labeled complex); 1954, 1902 cm^{-1} ν(CO). ^{1}H NMR ($CDCl_3$): δ 2.09 (s, 15H, Cp*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 10.38 (s, $C_5\mathit{Me}_5$), 96.27 (s, C_5Me_5), 200.09 (s, CO). ^{15}N NMR (acetone-d_6): δ −110.8 (s, $^{15}N_\alpha$). ^{14}N NMR (acetone-d_6): δ −110 (s, $^{14}N_\alpha$), −26 (s, $^{14}N_\beta$). MS (EI): *m/z* 406 (407 in **2a**-$^{15}N_\alpha$) (M$^+$), 378 (M$^+$ − N$_2$). Anal. Calcd: C, 35.55; H, 3.70; N, 6.91. Found: C, 35.52; H, 3.74; N, 6.98.

Preparation of Cp*Re(CO)(PMe$_3$)(N$_2$) (3a) and 3a-^{15}N$_\alpha$. A sodium amalgam was prepared by adding small freshly cut pieces of sodium metal (5-fold stoichiometric excess) to a pool of mercury (5 mL) under argon with gentle stirring. The orange-brown solution of the cationic carbonyl phosphine complex **3b** or **3b**-$^{15}N_\alpha$ (100 mg, 0.155 mmol) in THF (10 mL) was then added *via* syringe to the sodium amalgam at room temperature, and the mixture was vigorously stirred for 30 min. An IR spectrum of the resulting yellow-brown solution recorded at this time showed the total disappearance of the cationic complex and only the presence of absorptions corresponding to the dinitrogen complex **3a** or **3a**-$^{15}N_\alpha$. The solution was filtered through a short column of Celite, and the solvent was removed under vacuum to give a pale brown oil. The oil was absorbed by a small amount of neutral alumina and dried under vacuum, and the mixture was chromatographed on alumina. Elution with hexane afforded **3a** or **3a**-$^{15}N_\alpha$ as a pale yellow colored microcrystalline solid in 82% yield (58 mg, 0.13 mmol). IR (hexane): 2044 cm^{-1} ν(NN) (2011 cm^{-1} for $^{15}N_\alpha$-labeled complex); 1865 cm^{-1} ν(CO). ^{1}H NMR ($CDCl_3$): δ 1.57 (d, 9H, PMe$_3$, J_{H-P} = 8.7 Hz), 2.00 (d, 15H, Cp*, J_{H-P} = 0.7 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 10.76 (s, $C_5\mathit{Me}_5$), 20.67 (d, PMe$_3$, J_{C-P} = 33 Hz), 93.29 (s, C_5Me_5), 207.18 (d, CO, J_{C-P} = 7 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −29.86 (s, PMe$_3$). ^{15}N NMR (acetone-d_6): δ −91.3 (s, $^{15}N_\alpha$). ^{15}N NMR (CD_3CN): δ −93.2 (s, $^{15}N_\alpha$). ^{14}N NMR (acetone-d_6): δ −91 (s, $^{14}N_\alpha$), −30 (s, $^{14}N_\beta$). MS (EI): *m/z* 454 (M$^+$), 426 (M$^+$ − N$_2$). Anal. Calcd: C, 37.08; H, 5.30; N, 6.16. Found: C, 36.92; H, 5.42; N, 6.28.

Preparation of Cp*Re(CO){P(OMe)$_3$}(N$_2$) (4a) and 4a-^{15}N$_\alpha$. A procedure similar to that described for the preparation of **2a** was used. The carbonyl phosphite dinitrogen complex **4a** or **4a**-$^{15}N_\alpha$ was obtained in 79% yield as a pale yellow microcrystalline solid (57 mg, 0.11 mmol). IR (hexane): 2078, 2066 cm^{-1} ν(NN) (2045, 2033 cm^{-1} for $^{15}N_\alpha$-labeled complex); 1877 cm^{-1} ν(CO). ^{1}H NMR ($CDCl_3$): δ 2.04 (d, 15H, Cp*, J_{H-P} = 0.8 Hz), 3.52 (d, 9H, P(OMe)$_3$, J_{H-P} = 12.1 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 10.31 (s, $C_5\mathit{Me}_5$), 51.27 (s, P(OMe)$_3$), 94.15 (s, C_5Me_5), 204.96 (d, CO, J_{C-P} = 12 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 139.12 (s, P(OMe)$_3$). ^{15}N NMR (acetone-d_6): δ −99.4 (s, $^{15}N_\alpha$). ^{15}N NMR (CD_3CN): δ −100.8 (s, $^{15}N_\alpha$). ^{14}N NMR (acetone-d_6): δ −99 (s, $^{14}N_\alpha$), −29 (s, $^{14}N_\beta$). MS (EI): *m/z* 502 (M$^+$), 474 (M$^+$ − N$_2$). Anal. Calcd: C, 33.46; H, 4.78; N, 5.57. Found: C, 33.37; H, 4.89; N, 5.69.

Preparation of Cp*Re(PMe$_3$)$_2$(N$_2$) (5a), 5a-^{15}N$_\alpha$, and 5a-^{15}N$_\beta$. A procedure similar to that described for the preparation of **3a** was used. The bis(trimethylphosphine) dinitrogen complex, **5a**, **5a**-$^{15}N_\alpha$, or **5a**-$^{15}N_\beta$ (synthesized from [Cp*Re(PMe$_3$)$_2$(p-N^{15}NC$_6$H$_5$)][BF$_4$]), was obtained in 74% yield as a pale yellow microcrystalline solid (53 mg, 0.11 mmol). IR (hexane): 1975 cm^{-1} ν(NN) (1943 cm^{-1} for $^{15}N_\alpha$- or $^{15}N_\beta$-labeled complex). ^{1}H NMR (acetone-d_6): δ 1.48 (virtual doublet, 18H, PMe$_3$, J_{app} = 7.4 Hz), 1.88 (t, 15H, Cp*, J_{H-P} = 0.7 Hz). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ −35.31 (s, PMe$_3$). ^{15}N NMR (acetone-d_6): δ −82.1 (s, $^{15}N_\alpha$), −51.7 (s, $^{15}N_\beta$). ^{14}N NMR (acetone-d_6): δ −82 (s, $^{14}N_\alpha$), −49 (s, $^{14}N_\beta$). MS (EI): *m/z* 502 (M$^+$), 474 (M$^+$ − N$_2$). Anal. Calcd: C, 38.31; H, 6.58; N, 5.59. Found: C, 38.01; H, 6.92; N, 5.87.

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Preparation of $Cp^*Re(dmpe)(N_2)$ (6a). A procedure similar to that described for the preparation of **3a** was used. The bidentate phosphine dinitrogen complex **6a** was obtained in 79% yield as a pale yellow microcrystalline solid (57 mg, 0.11 mmol). IR (hexane): 1977 cm^{-1} $\nu(NN)$. ^1H NMR (acetone-d_6): δ 1.33 (d, 6H, $PMe_2CH_2CH_2Me_2P$, $J_{H-P} = 7.9$ Hz), 1.35 (m, 4H, $PMe_2CH_2CH_2Me_2P$), 1.42 (d, 6H, $PMe_2CH_2CH_2Me_2P$, $J_{H-P} = 7.8$ Hz), 1.92 (s, 15H, Cp*). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ −16.88 (s, dmpe). MS (EI): *m/z* 500 (M^+), 472 ($M^+ - N_2$). Anal. Calcd: C, 38.46; H, 6.21; N, 5.61. Found: C, 38.22; H, 6.37; N, 5.81.

Preparation of $Cp^*Re\{P(OMe)_3\}_2(N_2)$ (7a). A procedure similar to that described for the preparation of **3a** was used. The bis(trimethylphosphite) dinitrogen complex **7a** was obtained in 71% yield as a pale yellow microcrystalline solid (54 mg, 0.090 mmol). IR (hexane): 2014 cm^{-1} $\nu(NN)$. ^1H NMR (acetone-d_6): δ 1.87 (t, 15H, Cp*, $J_{H-P} = 0.8$ Hz), 3.45 (virtual doublet, 18H, $P(OMe)_3$, $J_{app} = 11.5$ Hz). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 138.80 (s, $P(OMe)_3$). MS (EI): *m/z* 598 (M^+), 570 ($M^+ - N_2$). Anal. Calcd: C, 32.15; H, 5.53; N, 4.69. Found: C, 31.79; H, 5.78; N, 4.93.

Reaction of $[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ (2b) with $LiAlH_4$. A 2-fold stoichiometric excess of $LiAlH_4$ was added as a solid to a solution of the cationic dicarbonyl complex **2b** (50 mg, 0.083 mmol) in methanol (10 mL) at room temperature. Upon addition, an immediate reaction occurred, with considerable gas evolution, and the color of the solution changed from red-brown to yellow. The solution was then filtered through a short column of Celite. Removal of the solvent under vacuum and subsequent extraction with hexane (3 × 20 mL) gave the methoxycarbonyl complex $Cp^*Re(CO)(COOMe)(p\text{-}N_2C_6H_4OMe)$ as a yellow solid in 89% yield (40 mg, 0.074 mmol). The dinitrogen complex **2a** was not formed in this reaction. IR (MeOH): 1937 cm^{-1} $\nu(CO)$; 1632 cm^{-1} $\nu(NN)$; 1614 $\nu(COOMe)$. ^1H NMR ($CDCl_3$): δ 2.10 (s, 15H, Cp*), 3.66 (s, 3H, COOMe), 3.82 (s, 3H, OMe), 6.93 (d, 2H, C_6H_4), 7.45 (d, 2H, C_6H_4).

Reaction of $[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ (2b) with $NaBH_4$. A 2-fold stoichiometric excess of $NaBH_4$ was added as a solid to a solution of the cationic dicarbonyl complex **2b** (50 mg, 0.083 mmol) in acetone (10 mL) at room temperature. An instantaneous reaction took place, and the color of the solution changed from red-brown to deep red. An IR spectrum of this solution demonstrated the total disappearance of **2b** and the presence of minor absorptions corresponding to the dinitrogen complex **2a** which were also accompanied by major absorptions at 1917 and 1852 cm^{-1}. The solution was stirred for 1 h, during which time the color of the solution changed from red to yellow. An IR spectrum then obtained showed only the presence of **2a**. The solvent was removed under vacuum to give a yellow oil. The oil was then absorbed by a small amount of neutral alumina and dried under vacuum, and the mixture was then chromatographed on alumina. Elution with hexane afforded **2a** in 47% yield (16 mg, 0.039 mmol).

Low-Temperature ^1H, $^{13}C\{^1H\}$, and ^{15}N NMR Experiments: Reaction of $[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ (2b) or 2b-$^{15}N_\alpha$ with $NaBH_4$. A solution of the cationic dicarbonyl complex **2b** or **2b**-$^{15}N_\alpha$ in acetone-d_6 was transferred to an NMR tube (5 mm tube for ^1H and $^{13}C\{^1H\}$; 10 mm tube for ^{15}N) which was kept in a Schlenk tube under a positive pressure of argon. The Schlenk tube containing the NMR solution was then cooled to 195 K in a dry ice−acetone bath. With a strong purge of argon, addition of a 2-fold stoichiometric excess of solid $NaBH_4$ directly to the NMR tube lead to the formation of a deep red solution. The NMR tube was quickly removed from the cold temperature bath and placed into the Bruker AMX 400 spectrometer whose cooling unit had been previously set to 233 K. The NMR sample was equilibrated for 30 min at this temperature before spectral acquisition. An identical procedure was used for obtaining spectra for each of the NMR active nuclei. The species responsible for the red solution was assigned as the neutral aryldiazene complex $Cp^*Re(CO)_2(p\text{-}NHNC_6H_4OMe)$. IR (acetone): 1917, 1852 cm^{-1} $\nu(CO)$. ^1H NMR (acetone-d_6, 233 K): δ 2.02 (s, 15H, Cp*), 3.83 (s, 3H, OMe), 6.97 (d, 2H, C_6H_4), 7.60 (d, 2H, C_6H_4), 15.68 (broad singlet, 1H, NH) (d, 1H, $^{15}N_\alpha H$, $J_{H\text{-}N} = 69$ Hz). $^{13}C\{^1H\}$ NMR (acetone-d_6, 233 K): δ 10.15 (s, C_5Me_5), 55.58 (s, OMe), 99.35 (s, C_5Me_5), 115.13, 120.99, 149.80, 160.03 (s, C_6H_4), 208.32 (s, CO). $^{13}C\{^1H\}$ NMR (methanol-d_4, 233 K): δ 10.19 (s, C_5Me_5), 55.61 (s, OMe), 99.41 (s, C_5Me_5), 115.32, 121.22, 149.97, 160.65 (s, C_6H_4), 208.79 (s, CO). ^{15}N NMR (acetone-d_6, 233 K): δ −46.7 (d, $^{15}N_\alpha H$, $J_{N-H} = 69$ Hz).

Reaction of $[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ (2b) with HMPA. The cationic dicarbonyl complex **2b** (50 mg, 0.083 mmol) was added directly to neat hexamethylphosphoramide (HMPA) (10 mL) at room temperature. An IR spectrum recorded immediately after the addition showed the presence of absorptions corresponding to the starting material **2b** as well as the newly formed dinitrogen complex **2a**. The solution was stirred for 24 h. No apparent color change was noted. An IR spectrum obtained at this time displayed the complete disappearance of the cationic complex and only the presence of absorptions due to **2a**. The dinitrogen complex was extracted with diethyl ether (2 × 20 mL), and the extractions were filtered through a column of Celite. The solvent was removed under vacuum to give a pale brown oil. The oil was then absorbed by a small amount of neutral alumina and dried under vacuum, and the mixture was chromatographed on alumina. Elution with hexane afforded **2a** in 35% yield (12 mg, 0.029 mmol).

Reaction of $[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ (2b) with PMe_3. A 10-fold stoichiometric excess of neat PMe_3 was added *via* syringe to a solution of the cationic dicarbonyl complex **2b** (50 mg, 0.083 mmol) in acetone (10 mL) at room temperature. The solution was stirred for 30 min. No apparent color change was noted after this time. An IR spectrum of this solution showed the total disappearance of the cationic complex and only the presence of absorptions corresponding to the dinitrogen complex **2a**. The solvent was then removed under vacuum, and the remaining pale brown oil was extracted with diethyl ether (2 × 20 mL). The ether extractions were concentrated to *ca.* 2 mL under vacuum and chromatographed on a neutral alumina column. Elution with hexane produced **2a** in 42% yield (14 mg, 0.035 mmol).

Reaction of $[CpRe(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ (1b) with Ph_3C. A solution of the triphenylmethyl (trityl) radical (Ph_3C) was prepared by reduction of the corresponding chloride Ph_3CCl with zinc dust in THF. A 10-fold stoichiometric excess of the yellow triphenylmethyl radical solution was then added by cannula to an orange-brown solution of the cationic dicarbonyl complex **1b** (50 mg, 0.095 mmol) in CH_2Cl_2 (10 mL) at room temperature. The resulting orange solution was stirred for 30 min. An IR spectrum measured at this time showed the total disappearance of **1b** and the presence of absorptions corresponding exclusively to the dinitrogen complex **1a**. The solvent was then removed under vacuum, and the remaining pale brown oil was extracted with diethyl ether (2 × 20 mL). The ether extractions were concentrated to *ca.* 2 mL under vacuum and chromatographed on a neutral alumina column. Elution with hexane yielded **1a** in 58% yield (18 mg, 0.055 mmol).

Reaction of $[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ (2b) with Ph_3C. A procedure identical to that described for the Cp analog **1b** was used. The dinitrogen complex **2a** was obtained in 63% yield (21 mg, 0.052 mmol).

Reaction of $[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ (2b) with Na/THF. A stoichiometric amount of sodium metal was added in small pieces to a solution of the cationic dicarbonyl complex **2b** (50 mg, 0.083 mmol) in THF (10 mL) at room temperature. The solution was then sonicated for 60 min. During this time the red-brown solution of **2b** became yellow-brown. An IR spectrum of this solution showed the complete disappearance of **2b** and the presence of minor absorptions corresponding to the dinitrogen complex **2a**. Major absorptions at 1929 and 1615 cm^{-1} were present as well. Attempts to isolate this unknown neutral species were not successful due to its low stability to silica gel or neutral alumina columns. A partially purified sample obtained by extraction with hexane gave unsatisfactory ^{1}H NMR and mass spectra. Column chromatography using hexane as the elutant gave **2a** in 17% yield (6 mg, 0.014 mmol).

Reaction of [Cp*Re(CO)$_2$(*p*-N$_2$C$_6$H$_4$OMe)][BF$_4$] (2b) with Na/NH$_3$. A two-necked flask was equipped with a dry ice condenser containing a dry ice–acetone mixture. The flask was also fitted with an ammonia gas line, so as to provide the solvent for the reaction by condensation, and a gas line to maintain a nitrogen atmosphere. The cationic dicarbonyl complex **2b** (50 mg, 0.083 mmol) was then added to the colorless liquid ammonia (100 mL). To this solution was added a minimum amount of THF (10 mL) to completely solubilize **2b**. A stoichiometric amount of sodium metal, as monitored by the color of the mixture (blue color indicates excess sodium), was then added in small pieces to the reaction flask. The mixture was stirred for 30 min. The ammonia was then allowed to escape, and the remaining THF solution was filtered through a short column of Celite. Removal of the solvent under vacuum and subsequent extraction with hexane (3 × 20 mL) gave the neutral carbamoyl complex Cp*Re(CO)(CONH$_2$)(*p*-N$_2$C$_6$H$_4$OMe) as a yellow solid in 78% yield (34 mg, 0.065 mmol). The dinitrogen complex **2a** was not formed in this reaction. IR (CH$_2$Cl$_2$): 1931 cm^{-1} ν(CO); 1625 cm^{-1} ν(NN); 1586 cm^{-1} ν(CONH$_2$). ^{1}H NMR (CDCl$_3$): δ 2.12 (s, 15H, Cp*), 3.83 (s, 3H, OMe), 6.95 (d, 2H, C$_6$H$_4$), 7.29 (d, 2H, C$_6$H$_4$); $\delta_{\text{N-H}}$ was not observed.

Reaction of [Cp*Re(PMe$_3$)$_2$(*p*-N$_2$C$_6$H$_4$OMe)][BF$_4$] (5b) with Na/NH$_3$. The bis(trimethylphosphine) complex **5b** (50 mg, 0.072 mmol) was taken up in THF (10 mL) and then added to liquid ammonia (100 mL) as described above for **2b**. A stoichiometric amount of sodium metal, as monitored by the color of the mixture, was added in small pieces to the reaction flask. The mixture was stirred for 30 min. The ammonia was then allowed to escape, and the remaining THF solution was filtered through a short column of Celite. The solvent was removed under vacuum, and the remaining yellow-brown oil was extracted with diethyl ether (2 × 20 mL). The ether extractions were concentrated to *ca.* 2 mL under vacuum and chromatographed on a neutral alumina column. Elution with hexane gave *p*-anisidine (NH$_2$C$_6$H$_4$OMe). This was verified by GC–MS and by comparison of its ^{1}H NMR spectrum to that of an authentic sample. Using diethyl ether as the elutant afforded the dihydrido complex *trans*-Cp*Re(PMe$_3$)$_2$H$_2$[13a] as a yellow solid in 58% yield (20 mg, 0.042 mmol). (The dinitrogen complex **2a** was not formed in this reaction). ^{1}H NMR (benzene-d_6): δ 2.04 (s, 15H, Cp*), 1.50 (virtual doublet, 18H, PMe$_3$, $J_{\text{app}} = 7.5$ Hz), −11.89 (t, 2H, ReH, $J_{\text{H-P}} = 43.5$ Hz). ^{31}P{^{1}H} NMR (benzene-d_6): δ −37.57 (s, PMe$_3$).

Electrochemical Methods. Acetonitrile was distilled from calcium hydride under a nitrogen atmosphere and used immediately. The supporting electrolyte was electrometric grade tetraethylammonium perchlorate (TEAP) (Anachemia Science Inc.), which was purified by recrystallization from distilled water (2 times) and then dried under vacuum for 2 days.

Cyclic Voltammetry. Experiments were performed in a single-compartment cell. The working electrode was a stationary, mirror-polished, platinum (Pt) disk which measured 1 mm in diameter (Pine Instrument Co.). The Pt disk was surrounded by a cylindrical Teflon collar of 2.5 mm thickness. Before each experiment, the electrode was dipped sequentially in concentrated HNO$_3$, then in saturated FeSO$_4$ in 2 M H$_2$SO$_4$, and finally rinsed thoroughly with distilled water; this procedure provided a consistent electrode surface. A Pt wire was used as the counter electrode. The reference electrode was either a silver wire in a saturated solution of silver chloride (Ag/AgCl) or a standard calomel electrode (SCE). Results are reported with respect to SCE.

The sample solutions were thoroughly deaerated with oxygen-free N$_2$, and an N$_2$ atmosphere was maintained throughout the voltammetric measurements. All experiments were carried out at room temperature and used solutions of 0.2 M TEAP (as the supporting electrolyte) in MeCN. Concentrations of analytes were 1.0 mM for all experiments. The scan rate was 0.2 V/s unless stated otherwise. The CV apparatus consisted of a Princeton Applied Research EG&G 175 programmer and an EG&G 170 potentiostat. Electrical responses were recorded on a Hewlett-Packard 7046A X-Y recorder. CV measurements were carried out as follows. An acetonitrile solution containing the electrolyte was placed in the cell and then deaerated with a continuous stream of nitrogen gas until a cyclic voltammogram of the solution showed no fluctuations in the current. A solution of the particular cationic rhenium aryldiazenido complex in a minimum amount of degassed acetonitrile was injected into the cell. A cyclic voltammogram of the solution using a potential range of +2.0 to −2.0 V was then recorded.

Controlled Potential Electrolysis. A two-compartment cell was used. A sintered-glass disk of fine porosity separated the counter and working compartments. The working electrode was a Pt gauze. A Pt counter electrode was positioned above the working electrode to obtain a uniform potential distribution. An Ag/AgCl or SCE reference electrode was positioned close to the working electrode. The CPE apparatus consisted of a Princeton Applied Research EG&G 175 programmer, an EG&G 170 potentiostat, and a EG&G 179 coulometer. CPE measurements and analysis of the products were carried out as follows. The electrolyte solution was placed in the working electrode compartment of the cell. A small amount of the same solution was added to the counter electrode compartment until the solution levels were equalized. The solution in the working compartment was then deaerated with nitrogen gas while being stirred continuously. Preelectrolysis was carried out until the background current became negligible. A 0.5 mL sample of the electrolyte solution was extracted by syringe, and an IR spectrum was collected. The spectrum would serve as a background for subsequent IR spectra. A solution of the particular cationic rhenium aryldiazenido complex in a minimum amount of degassed acetonitrile was then injected into the working compartment. A sample of the electrolysis solution was withdrawn, and an IR spectrum was recorded. The spectrum was then corrected by subtracting the background spectrum and was used as a reference from which to monitor the electrolysis. The electrolysis then proceeded at a given potential. At specific time intervals aliquots of the solution were withdrawn and analyzed by IR spectroscopy.

Preparation of the Dinitrogen Complexes 1a–3a by CPE. Controlled potential electrolysis (CPE) was carried out on the cationic rhenium aryldiazenido complexes **1b** (53 mg, 0.10 mmol), **2b** (60 mg, 0.10 mmol), and **3b** (65 mg, 0.10 mmol) using the procedure just described at the appropriate reduction potential (as determined by CV). An IR spectrum recorded after the bulk electrolysis was complete showed the total disappearance of the cationic complex and only the presence of absorptions corresponding to the respective dinitrogen complexes **1a**–**3a**. For **1a**: IR (MeCN containing TEAP) 2141 cm^{-1} ν(NN); 1956, 1894 cm^{-1} ν(CO). For **2a**: IR (MeCN containing TEAP) 2121 cm^{-1} ν(NN); 1939, 1879 cm^{-1} ν(CO). For **3a**: IR (MeCN containing TEAP) 2027 cm^{-1} ν(NN); 1834 cm^{-1} ν(CO). The solvent was removed under vacuum and the remaining solid was extracted with diethyl ether (3 × 20 mL). The ether extractions were concentrated to *ca.* 2 mL under vacuum, and chromatographed on a neutral alumina column. Elution with hexane yielded **1a** in 73% yield (24 mg, 0.073 mmol), **2a** in 78% yield (32 mg, 0.078 mmol), and **3a** in 74% yield (34 mg, 0.074 mmol).

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