Geometrical Isomers of Neutral (Pentamethylcyclopentadienyl)rhenium Complexes Resulting from Different Orientations of a Singly-Bent Aryldiazenido Ligand

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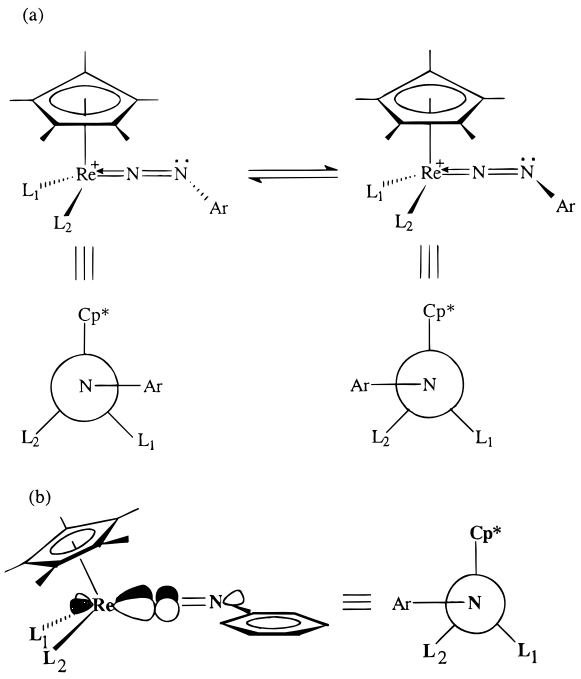
The variable temperature ^{1}H NMR spectra of Cp*ReH(CO)(*p*-$N_2C_6H_4OMe$) (**1**) and Cp*Re(CH$_3$)(CO)(*p*-$N_2C_6H_4OMe$) (**3**) and the variable temperature ^{31}P{^{1}H} NMR spectra of Cp*ReCl(PR$_3$)(*p*-$N_2C_6H_4OMe$) [R = Me (**4**), OMe (**5**), Ph (**7**)] are presented and discussed. The spectra of **1** and **3**−**5** show that at low temperature two isomers are present in each case and that these isomers interconvert on the NMR time scale. The isomers are interpreted to occur because the *p*-$N_2C_6H_4OMe$ ligand adopts two different orientations where the aryl group is oriented syn to either the X or Y ligand in these chiral complexes of general formula Cp*ReXY(*p*-$N_2C_6H_4OMe$). The bulky PPh$_3$ ligand in **7** results in an overwhelming preference for orientation only syn to the Cl group and thus only one observable isomer. The activation parameters for the conformational isomerization of the aryldiazenido ligand in these neutral complexes have been obtained from NMR line shape analyses and are compared with data obtained previously for related cationic rhenium aryldiazenido complexes.

Introduction

We have recently reported evidence for geometric isomers of *cationic* (pentamethylcyclopentadienyl)rhenium complexes resulting from different orientations of a singly-bent aryldiazenido ligand.[1] Thus, certain of the complexes [Cp*ReL$_1$L$_2$(N$_2$Ar)]$^+$ (where Cp* = η^5-C$_5$Me$_5$, L$_1$ = CO, L$_2$ = phosphine, and Ar = *p*-C$_6$H$_4$OMe) exhibit two ^{31}P{^{1}H} NMR resonances at low temperature that are interpreted to result from the two isomers shown in idealized form in Scheme 1a. At room temperature, rapid interconversion of the two isomers occurs as a consequence of the stereochemically nonrigid aryldiazenido ligand flipping between the two orientations by either a rotation or an inversion or perhaps some combination of the two. The existence of these isomers can be understood when the frontier orbital interaction between the singly-bent N$_2$Ar$^+$ fragment and the d^6 rhenium(I) fragment Cp*ReL$_1$L$_2$ is examined. As a result of the important overlap between the filled d$_\pi$ orbital on Re and the empty in-plane nitrogen p orbital on N$_2$Ar$^+$, the plane of the aryldiazenido ligand is oriented in a formal sense normal to the plane bisecting the L$_1$—Re—L$_2$ angle, as shown in Scheme 1b. Thus, the aryl ring may, in principle, be directed syn to either of the ligands L$_1$ or L$_2$. Furthermore, when the ligands L$_1$ and L$_2$ differ in their π donor−acceptor properties, the d orbital is rotated and the plane of the aryldiazenido ligand therefore is also rotated, so that now the C—N···Re—L$_1$ dihedral angle is near 90° (where L$_1$ is the better π acceptor) as in Scheme 2.[1,2]

In this paper, we report the results of a search for further examples of such geometric isomers resulting from the specific orientation of the singly-bent aryldiazenido ligand. In particular, we wished to know whether the ability to detect such isomers extended to *neutral* complexes and to NMR probes other than ^{31}P, since in previous work all of the complexes were cationic and distinguishable resonances were not detected in the ^{1}H NMR nor (in most cases) the ^{13}C NMR spectra. As a result, isomers have now been detected by ^{1}H NMR

Scheme 1. (a) Idealized Conformers of [Cp*ReL$_1$L$_2$(N$_2$Ar)]$^+$ That Arise from the Two Possible Orientations of the Aryldiazenido Ligand. (b) Diagram To Show the Important Overlap of the Filled Rhenium d$_\pi$ Orbital with the Empty In-Plane Nitrogen p Orbital

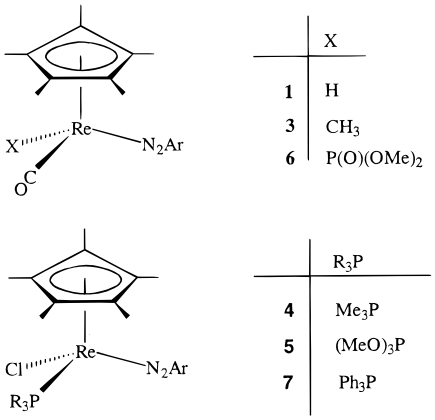


⊗ Abstract published in *Advance ACS Abstracts,* November 15, 1995.

(1) Cusanelli, A.; Batchelor, R. J.; Einstein, F. W. B.; Sutton, D. *Organometallics* **1994**, *13*, 5096.

(2) Yan, X.; Einstein, F. W. B.; Sutton, D. *Can. J. Chem.* **1995**, *73*, 939.

Chart 1



for Cp*ReX(CO)(N_2Ar) [X = H (**1**), Me (**3**)]. In addition, isomers have been observed by $^{31}P\{^1H\}$ NMR for the neutral compounds Cp*ReCl(L)(N_2Ar) [L = PMe_3 (**4**) or $P(OMe)_3$ (**5**)] (Chart 1).

Results

The hydrido complex Cp*ReH(CO)(*p*-$N_2C_6H_4OMe$) (**1**) was synthesized by a minor modification of the published method,[3] in that the complex [Cp*Re(CO)$_2$(*p*-$N_2C_6H_4OMe$)][BF_4] was treated with aqueous NaOH in acetone rather than CH_2Cl_2, since we encountered some formation of the chloro complex Cp*ReCl(CO)(*p*-$N_2C_6H_4$-OMe) (**2**) with the latter. The room temperature ^1H NMR spectrum of **1** in benzene-d_6 exhibits singlet resonances for the OMe, Cp*, and hydride ligand protons, in agreement with data reported previously.[3] The room temperature spectrum in acetone-d_6 is similar. Low temperature spectra were not measured in the previous study. Now, we find that at 220 K there are two resolved hydride resonances at δ −6.60 and −6.68 in an approximate ratio of 54:46. As the temperature is increased, these resonances broaden, coalesce at 258 K, and subsequently sharpen to a single resonance at δ −6.55 at 293 K.

The methyl complex Cp*Re(CH_3)(CO)(*p*-$N_2C_6H_4OMe$) (**3**) was synthesized by reacting the chloro complex Cp*ReCl(CO)(*p*-$N_2C_6H_4OMe$) (**2**)[4] with CH_3MgBr. This compound was first made in these laboratories by A. H. Klahn by the reaction of [Cp*Re(CO)(MeCN)(*p*-$N_2C_6H_4OMe$)][BF_4] with MeLi, but was not fully characterized at that time.[5] The methyl complex **3** exhibits singlet resonances for the CH_3, OMe, and Cp* methyls in the 400 MHz ^1H NMR spectrum at 291 K in acetone-d_6. The methyl resonance is noticeably broad, and the aromatic C_6H_4 protons occur as two broad resonances. However, at 231 K there are two sharp singlet resonances at δ 0.93 and 1.13 in a 1:1 ratio for the methyl ligand and two singlet resonances at δ 3.78 and 3.81 for the methoxy protons. The Cp* signal remains unsplit, but there is a significant change in the resonances for the aromatic C_6H_4 protons to well-resolved overlapping AA′BB′ patterns.

Complexes Cp*ReCl(PMe_3)(*p*-$N_2C_6H_4OMe$) (**4**), Cp*-ReCl{$P(OMe)_3$}(*p*-$N_2C_6H_4OMe$) (**5**), Cp*Re(CO){$PO(OMe)_2$}(*p*-$N_2C_6H_4OMe$) (**6**), and Cp*ReCl(PPh_3)(*p*-$N_2C_6H_4OMe$) (**7**) were prepared by treating the corresponding cationic complex [Cp*Re(CO)(L)(*p*-$N_2C_6H_4$-OMe)][BF_4] (L = PMe_3, $P(OMe)_3$, or PPh_3) with ethanolic NaOH and a large excess of KCl in chloroform. No reaction was observed in chloroform alone, possibly because of the low solubility of KCl. Compounds **4**, **5**, and **7** were obtained as brown solids after extraction into hexane and crystallization. The phosphonate complex **6** was obtained as a byproduct of the synthesis of **5** and was synthesized separately by the reaction of chloride or (better) iodide with [Cp*Re(CO){$P(OMe)_3$}-(*p*-$N_2C_6H_4OMe$)] [BF_4] in THF directly (see the following). The formation of the halide complexes Cp*ReX-(CO)(N_2Ar) from reactions of the dicarbonyl complex with X^- in THF−H_2O was considered to result from nucleophilic displacement of the CO ligand.[4] It is possible that this mechanism operates in the present reactions, but the success of the reactions was critically dependent on the concentration of ethanolic NaOH. Therefore, it is also possible that base attack on the CO ligand occurs and that a carboxylate or hydride intermediate is also involved, like that known to be formed with [Cp*Re(CO)$_2$(*p*-$N_2C_6H_4OMe$)][BF_4] in basic conditions.[3]

The ^1H, ^{13}C, and $^{31}P\{^1H\}$ NMR spectra of **4** unambiguously show the presence of coordinated PMe_3, and the distinctive isotope pattern for the chlorine and rhenium isotope contributions to the parent peak in the mass spectrum matches that simulated by computer for **4**. In the synthesis of **5**, spectroscopy on the initial product showed it to be a mixture of two compounds, **5** and **6**. In particular, the ^1H NMR spectrum showed two Cp* resonances, and in the IR spectrum in CH_2Cl_2 a ν(CO) absorption at 1940 cm^{-1} was present that was not due to the starting carbonyl complex, which has ν-(CO) at 1964 cm^{-1} in the same solvent. In addition, two ν(NN) absorptions were evident at 1609 and 1641 cm^{-1} for the aryldiazenido ligand. Compounds **5** and **6** were subsequently isolated by careful chromatography in 43% and 51% yields, respectively. The phosphonate compound **6** was obtained as a yellow oil that could be crystallized from hexane (in which it is not very soluble) at −78 °C, but it melted on attempted isolation. The relative yields of **5** and **6** were critically dependent on the concentration of KCl and the order of addition of the KCl and NaOH. The phosphonate undoubtedly results from an Arbuzov-like reaction[6] of the phosphite ligand in the cation [Cp*Re(CO){$P(OMe)_3$}(*p*-$N_2C_6H_4$-OMe)]$^+$ with a nucleophile, which in this case can be either Cl^- or OH^-. In agreement, **6** was synthesized separately in good yield by nucleophilic attack of KI on [Cp*Re(CO){$P(OMe)_3$}(*p*-$N_2C_6H_4OMe$)][BF_4] in THF and was spectroscopically characterized. The 400 MHz ^1H NMR spectrum of **6** exhibits two doublets at δ 3.56 and 3.59 for the diastereotopic phosphonate OMe protons, with J_{PH} = 11.8 Hz. Similarly, the 100.6 MHz ^{13}C NMR spectrum of **6** shows the two expected carbon resonances at δ 50.33 and 50.39. While these resonances are rather close, this interpretation is consistent with the ^1H NMR results and therefore is more reasonable than the alternative possibility that the resonances represent a phosphorus-coupled doublet (with J_{PC} = 6 Hz) for equivalent methoxy groups. The phosphorus resonance of **6** at δ 68.7 is in a position upfield of that of the

(3) Barrientos-Penna, C. F.; Gilchrist, A. B.; Klahn-Oliva, A. H.; Hanlan, A. J. L.; Sutton, D. *Organometallics* **1985**, *4*, 478.
(4) Barrientos-Penna, C. F.; Klahn-Oliva, A. H.; Sutton, D. *Organometallics* **1985**, *4*, 367.
(5) Klahn, A. H. Ph.D. Dissertation, Simon Fraser University, 1986.
(6) Leiva, C.; Mossert, K.; Klahn, A. H.; Sutton, D. *J. Organomet. Chem.* **1994**, *469*, 69.

Table 1. Rate Constants (k_1) Derived from NMR Line Shape Analysis

complex	temp (K)[a]	k_1 (s^{-1})[b]
1[c]	235	3.5 ± 0.5
	251	35 ± 5
	254	40 ± 5
	258	70 ± 5
	293	2000 ± 50
3[d]	241	2.0 ± 0.5
	261	20 ± 2.5
	271	70 ± 5
	273	90 ± 5
	275	100 ± 10
	281	200 ± 10
	291	500 ± 10
4[e]	223	80 ± 5
	233	290 ± 10
	236	600 ± 50
	243	900 ± 50
	273	15000 ± 100
	293	90000 ± 100
5[e]	213	6.0 ± 0.5
	225	30 ± 2
	230	60 ± 5
	253	820 ± 20
	273	5700 ± 100
	293	30000 ± 1000

[a] All errors in temperature are ±1 K. [b] Determined for the isomerization process from the more populated to the less populated conformer. For **3** the populations are equal within experimental error. [c] Measured by using the hydride resonance. [d] Measured by using the methyl ligand resonance. [e] Measured by using the phosphorus resonance.

phosphite complex **5**, in agreement with the general trend for these ligands reported in the literature.[6]

The $^{31}P\{^1H\}$ NMR spectrum of **4** at 293 K in acetone-d_6 has a single sharp resonance at δ −29.0. At 213 K there are two resonances at δ −25.8 and −32.0 in a ratio of 82:18. As the temperature is raised, these resonances broaden, coalesce at about 243 K, and subsequently sharpen to a single resonance. Similarly, the $^{31}P\{^1H\}$ NMR spectrum of **5** at 203 K exhibited two sharp resonances at δ 122.2 and 121.2 in a ratio of 78:22. These signals broadened with increasing temperature and coalesced at 233 K into a broad signal at δ 121.5, which further sharpened to a signal at δ 119.7 at 293 K. Thus, the spectrum showed a marked temperature dependence of chemical shift. The triphenylphosphine complex **7** exhibited a single $^{31}P\{^1H\}$ resonance at all temperatures in the range 213−293 K.

The temperature-dependent ^1H NMR line shapes for the hydride resonance of **1** and the methyl and methoxy protons of **3** and the $^{31}P\{^1H\}$ NMR line shapes of **4** and **5** were simulated by using a slightly modified version of the DNMR3 program.[7] Values of the resulting rate constants from the line shape analyses (Table 1) were then used to obtain the activation parameters for the exchange in essentially the same way that was used previously.[1] These are presented in Table 2.

Discussion

The variable temperature ^1H or $^{31}P\{^1H\}$ NMR spectra of Cp*ReH(CO)(*p*-$N_2C_6H_4OMe$) (**1**), Cp*Re(CH_3)(CO)(*p*-$N_2C_6H_4OMe$) (**3**), Cp*ReCl(PMe_3)(*p*-$N_2C_6H_4OMe$) (**4**), and Cp*ReCl{$P(OMe)_3$}(*p*-$N_2C_6H_4OMe$) (**5**) are consistent with the presence of two isomers in solution that

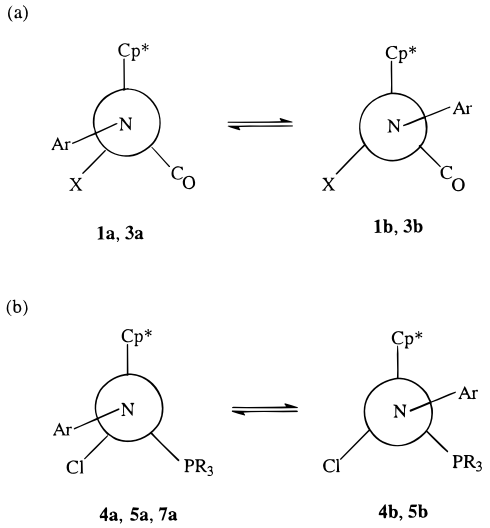
(7) Kleier, D. A.; Binsch, G. A Computer Program for the Calculation of Complex Exchange-Broadened NMR Spectra. Quantum Chemistry Program Exchange, Program 165, Indiana University, 1970.

Table 2. Activation Parameters for Isomerization of the Aryldiazenido Ligand

complex	$\Delta G^‡$ (kJ/mol)[a]	$\Delta H^‡$ (kJ/mol)	$\Delta S^‡$ (J/mol.K)
1[b]	52.9 ± 0.4	60.0 ± 2.2	23.6 ± 8.4
1[c]	52.5 ± 0.4	60.0 ± 2.1	25.0 ± 8.3
3	56.0 ± 0.2	62.8 ± 1.2	22.7 ± 4.5
4[b]	44.0 ± 0.5	51.0 ± 2.0	23.6 ± 8.0
4[c]	40.2 ± 0.5	51.0 ± 2.0	36.2 ± 8.0
5[b]	46.5 ± 0.1	53.3 ± 0.2	22.9 ± 0.8
5[c]	43.3 ± 0.1	53.4 ± 0.2	33.6 ± 0.8

[a] For a temperature of 298 K. [b] Determined for the isomerization process from the more populated to the less populated isomer. [c] Determined for the isomerization process from the less populated to the more populated isomer, assuming no significant change in equilibrium constant in the temperature range of the line shape measurements.

Scheme 2. Newman Projections Showing Interconverting Conformers of Complexes 1, 3−5, and 7[a]



[a] Substituents are X = H (**1**), CH_3 (**3**); R = Me (**4**), OMe (**5**), Ph (**7**). Ar = *p*-$N_2C_6H_4OMe$.

are in dynamic equilibrium on the NMR time scale (Scheme 2). However, for the triphenylphosphine complex Cp*ReCl(PPh_3)(*p*-$N_2C_6H_4OMe$) (**7**), there is no indication of more than one isomer present in solution.

These results are similar to those reported earlier[1] where the isomers of the complexes $[Cp^*ReL_1L_2(N_2Ar)]^+$ (where Cp* = η^5-C_5Me_5, L_1 = CO, L_2 = phosphine, and Ar = *p*-C_6H_4OMe) were assigned as the structural isomers illustrated in Scheme 1, which interconvert by some kind of flipping of the aryl group. The complex with $L_2 = PPh_3$ did not exhibit observable isomers, and this was considered to result from the steric bulk of the PPh_3 ligand inhibiting the conformer with the aryl group syn to the PPh_3. It is presumed that a similar argument holds for **7**.

The most notable result to emerge from the present study is the observation of isomers of **1** and **3** by ^1H NMR. In the previous study, distinguishable NMR resonances for isomers were evident in $^{31}P\{^1H\}$ but not ^1H NMR spectra. The same is true for compounds **4** and **5** here. The distinguishable resonances for the isomers of **1** and **2** are seen best in the low temperature hydride and methyl ligand signals, respectively, but for **2,** in particular, there are even clear separations of the aromatic and methoxy substituent proton resonances at low temperature, though not the Cp* methyls.

In compound **1** or **3** the steric interactions between the aryl group of the N_2Ar ligand and the hydride or

methyl ligands are probably small and comparable with the interaction with the carbonyl ligand. For this reason, the populations of the two conformers **a** and **b** (Scheme 2a) are roughly the same. We do not know whether **a** or **b** corresponds to the slightly more populated conformer in reality. For the phosphorus complexes **4** and **5**, we consider that the phosphine and phosphite ligands are sterically more bulky than the chloride ligand and that the preferred conformer is **a** in each case (Scheme 2b). Finally, for the bulky PPh_3 ligand complex, the only observed conformer is expected to be **7a**.

Activation parameters for the isomerization of compounds **1** and **3**−**5** are in Table 2 and may be compared with those of the compounds studied previously.[1] Entropy of activation values are small and positive as observed before.[1] The greatest values of $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$ are those for the hydride and methyl complexes **1** and **3**, which have $\Delta G^{\ddagger}$ values in the range 53−56 kJ mol^{-1} and $\Delta H^{\ddagger}$ values of 60−63 kJ mol^{-1}. By comparison, the corresponding cationic complexes [Cp*Re(CO)(PR_3)(*p*-$N_2C_6H_4OMe$)][BF_4] obtained when H or CH_3 in **1** and **3** is replaced by PR_3 = PMe_3, $P(OMe)_3$, or $P(OCH_2)_3CH_3$ were observed to have $\Delta G^{\ddagger}$ values in the region 38−43 kJ mol^{-1} and $\Delta H^{\ddagger}$ values of 41−47 kJ mol^{-1}.[1] Since steric effects are the least for the H and CH_3 ligands, this seems to point to an electronically-driven increase in the activation free energy and enthalpy in going from the ground state conformers **a** or **b** to the transition state in which the NNC skeleton is linear (if inversion alone is the mechanism) or the plane of the NNAr group has been rotated by 90° (if rotation alone is the mechanism). This is understandable when it is considered that good σ donor ligands like H or Me are expected to stabilize the ground state conformations **a** or **b** relative to the transition state in these neutral complexes by increasing the electron density on Re and, thus, the degree of back-bonding from the rhenium fragment to the singly-bent N_2Ar^+ fragment. In the frontier orbital analysis this interaction has maximum overlap when the filled Re d_π orbital and in-plane empty p orbital on the N_2Ar group are coplanar (cf. Scheme 1b), and this corresponds to the conformations **a** or **b** when L_1 and L_2 differ substantially in π donor−acceptor ability, as here. However, upon rotation to the perpendicular conformation, this overlap is lost as the orbitals are now orthogonal; in a different manner, linearization of the NNC skeleton also decreases the π acceptor propensity of the N_2Ar ligand.[1, 2] Of course, a synchronous combination of these processes is also possible. The neutral compounds **4** and **5** are also related to the cationic complexes [Cp*Re(CO)(PR_3)(*p*-$N_2C_6H_4OMe$)][BF_4] (where R = Me or OMe) in the sense that the Cl ligand in **4** or **5** has been replaced by CO. The $\Delta G^{\ddagger}$ values for **4** and **5** are 40−47 kJ mol^{-1}, which are quite close to those of the cationic complexes, but the $\Delta H^{\ddagger}$ values of 51−53 kJ mol^{-1} are higher than those of the cationic complexes (41−47 kJ mol^{-1}). A consistent interpretation would be that the presence of the π electron-withdrawing CO ligand and the positive charge deplete the π electron density in the rhenium d_π orbital in the cationic complexes by comparison with neutral **4** and **5**. This makes the π bond to the aryldiazenido ligand (Scheme 1b) less effective and raises the ground state conformation enthalpies relative to the transition state in the cationic complexes by comparison with the neutral chloro compounds.

Because the complexes used in this study are neutral, and as a result complexes **1** and **3** are soluble in alkanes and therefore, in principle, could give quite well-resolved IR solution spectra in hexane, it was anticipated that the conformers **a** and **b** might be observable by individual ν(NN) or ν(CO) absorptions in IR spectroscopy in view of its shorter time scale. This is not the case. The N═N stretch is typically broad as is usual for aryldiazenido complexes. The ν(CO) mode gives a very sharp absorption band, which on close inspection is somewhat asymmetric but certainly is not resolved into separate bands.

Conclusion

It is clear from these additional examples that in the spectroscopic characterization of aryldiazenido complexes by ^{1}H NMR, as well as by heteronuclear NMR spectroscopy, the possibility of observing broad or multiple signals and temperature-dependent behavior resulting from conformational isomerization of the aryldiazenido ligand can be anticipated in favorable situations. More still needs to be understood regarding the mechanism of isomerization and the factors influencing the size of the barriers and the stereochemical preferences. We are endeavoring to clarify the situation by means of suitable calculations and a continued experimental investigation of appropriate complexes.

Experimental Section

General Methods. The general synthetic procedures and the spectroscopic instrumentation and techniques used in this work were similar to those described previously, except where otherwise noted.[1] Hydride complex **1** was prepared by a minor modification of the published method, as indicated in the Results section, and gave IR and NMR spectroscopic data in agreement with the literature.[3]

Cp*Re(CH_3)(CO)(*p*-$N_2C_6H_4OMe$) (3). An excess of CH_3-MgBr (ca. 3 mL of 3.0 M in ether, Aldrich) was added to a stirred solution of Cp*ReCl(CO)(*p*-$N_2C_6H_4OMe$) (**2**)[4] (50 mg, 0.010 mmol) in freshly distilled ether. The reaction was followed by IR and was complete in 36 h. Two drops of water were added to destroy excess Grignard reagent, and the mixture was extracted with hexane−ether (1:1) and filtered through Celite. The solvent was removed under vacuum to yield an orange-yellow solid that was recrystallized from hexane at −78 °C. Yield: 38.9 mg (0.078 mmol, 81%). IR (CH_2Cl_2, cm^{-1}): ν(CO) 1896, ν(NN) 1613. IR (hexane, cm^{-1}): ν(CO) 1915, ν(NN) 1618. ^{1}H NMR (298 K, 400 MHz, $CDCl_3$): δ 1.16 (s, 3H, CH_3), 1.98 (s, 15H, Cp*), 3.83 (s, 3H, OMe), 6.89 (d, 2H, J = 9 Hz, C_6H_4), 7.19 (d, 2H, J = 9 Hz, C_6H_4). EIMS: m/z 500 (M^+), 472 (M^+ − CO). Anal. Calcd: C, 45.68; H, 5.04; N, 5.61. Found: C, 46.04; H, 5.23; N, 5.47.

Cp*ReCl(PMe_3)(*p*-$N_2C_6H_4OMe$) (4). A large excess of finely ground KCl was added to a stirred solution of [Cp*Re(CO)(PMe_3)(*p*-$N_2C_6H_4OMe$)][BF_4][8] (50 mg, 0.080 mmol) in $CHCl_3$ (5 mL). Then, NaOH in ethanol (4 M, 3 mL) was added slowly. The solution was stirred overnight and excess KCl was removed by filtration through Celite. The solvent was removed under vacuum, and the remaining solid was extracted with hexane; removal of the hexane yielded a yellow oily product. This was recrystallized from hexane to give **4** as a brown solid in 78% yield (38 mg, 0.067 mmol). IR (CH_2Cl_2 or $CHCl_3$, cm^{-1}): ν(NN) 1605. ^{1}H NMR (298 K, 400 MHz, $CDCl_3$): δ 1.54 (d, 9H, PMe_3), 1.93 (s, 15H, Cp*), 3.79 (s, 3H, OMe), 6.87 (d, 2H, J = 9 Hz, C_6H_4), 7.26 (d, 2H, J = 9 Hz, C_6H_4). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): δ 10.96 (s, C_5Me_5), 16.68 (d, PMe_3, J = 34 Hz), 55.52 (s, OMe), 100.76 (s, C_5Me_5), 114.34, 120.85,

(8) Klahn, A. H.; Sutton, D. *Organometallics* **1989**, *8*, 198.

123.61, 156.93 (s, C_6H_4). $^{31}P\{^1H\}$ NMR: δ −29.00 (acetone-d_6), −35.64 ($CDCl_3$). EIMS: m/z 568 (M^+), 492 ($M^+ - PMe_3$). Anal. Calcd: C, 42.28; H, 5.50; N, 4.93. Found: C, 42.44; H, 5.56; N, 5.10.

Cp*ReCl{P(OMe)$_3$}(*p*-N$_2$C$_6$H$_4$OMe) (5). This was synthesized following the procedure used for **4** starting with [Cp*Re(CO){P(OMe)$_3$}(*p*-$N_2C_6H_4OMe$)][BF_4]. The product was obtained in 43% yield following chromatography on a neutral alumina column with hexane as eluant. The phosphonate complex **6** was then eluted with chloroform and purified further by chromatography on neutral alumina with chloroform as eluant. This gave **6** as a yellow oil in 51% yield after removal of the solvent. Data for **5**: IR ($CHCl_3$ or CH_2Cl_2, cm^{-1}): ν(NN) 1609. ^1H NMR ($CDCl_3$): δ 1.93 (s, 15H, Cp*), 3.62 (d, 9H, J = 11.5 Hz, P(OMe)$_3$) 3.79 (s, 3H, OMe), 6.87 (d, 2H, J = 9 Hz, C_6H_4), 7.27 (d, 2H, J = 9 Hz, C_6H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 10.17 (s, C_5Me_5), 52.54 (s, P(OMe)$_3$), 55.48 (s, OMe), 101.86 (s, C_5Me_5), 114.86, 121.99, 157.52 (s, C_6H_4). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 119.75. EIMS: m/z 616 (M^+), 492 ($M^+ - P(OMe)_3$). Anal. Calcd: C, 38.99; H, 5.07; N, 4.55. Found: C, 39.21; H, 5.26; N, 4.45.

Cp*Re(CO){PO(OMe)$_2$}(*p*-N$_2$C$_6$H$_4$OMe) (6). A solution of [Cp*Re(CO){P(OMe)$_3$}(*p*-$N_2C_6H_4OMe$)][BF_4] (50 mg, 0.070 mmol) in THF (5 mL) was heated at 40 °C for 3 h with 20−30% excess KI. The IR spectrum showed the absence of the starting rhenium complex. The solution was filtered through Celite and solvent was removed under vacuum. The oily product was extracted with ether, and the solution was filtered through Celite. The solvent was pumped off and the residue was dissolved in acetone and chromatographed on a short neutral alumina column prepared in hexane. Chloroform eluted **6**, which was obtained as a yellow oil in 97% yield (41 mg, 0.070 mmol). Data for **6**: IR (CH_2Cl_2, cm^{-1}): ν(CO) 1940, ν(NN) 1641. ^1H NMR ($CDCl_3$, 400 MHz): δ 2.15 (s, 15H, Cp*), 3.56 (d, 3H, J = 11.8 Hz, PO(OMe)$_2$), 3.59 (d, 3H, J = 11.8 Hz, PO(OMe)$_2$), 3.82 (s, 3H, OMe), 6.93 (d, 2H, J = 9 Hz, C_6H_4), 7.36 (d, 2H, J = 9 Hz, C_6H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 10.40 (s, C_5Me_5), 50.33 (s, PO(OMe)$_2$), 50.39 (s, PO(OMe)$_2$), 55.60 (s, OMe), 105.00 (s, C_5Me_5), 114.7, 122.8, 124.0, 160.3 (s, C_6H_4), 203.6 (d, CO, J = 19 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 68.7. EIMS: m/z 594 (M^+).

Cp*ReCl(PPh$_3$)(*p*-N$_2$C$_6$H$_4$OMe) (7). This was prepared from [Cp*Re(CO)(PPh_3)(*p*-$N_2C_6H_4OMe$)][BF_4] by following the procedure for **4** given earlier and was obtained as a brown solid in 83% yield after recrystallization from hexane. IR (CH_2Cl_2, cm^{-1}): ν(NN) 1607. ^1H NMR (400 MHz, $CDCl_3$): δ 1.65 (s, 15H, Cp*), 3.80 (s, 3H, OMe), 6.84 (d, 2H, J = 9 Hz, C_6H_4), 7.21 (d, 2H, J = 9 Hz, C_6H_4), 7.30−7.58 (m, 15H, PPh_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 10.00 (s, C_5Me_5), 55.49 (s, OMe), 100.92 (s, C_5Me_5), 114.04 (s, C_6H_4), 121.75−134.34 (PPh_3 and C_6H_4), 167.71 (s, C_6H_4). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 17.11. EIMS: m/z 754 (M^+), 492 ($M^+ - PPh_3$).

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