4a$^+$, 117340-51-9; **4a**$^{2+}$, 117340-38-2; **4b**, 117340-61-1; **4b**$^+$, 117340-52-0; **4b**$^{2+}$, 117340-40-6; **5**, 117340-62-2; **5**$^+$, 117340-53-1; **5**$^{2+}$, 117340-42-8; **6**, 97732-08-6; **6**$^+$, 97732-09-7; **6**$^{2+}$, 12715-84-3; **7**, 117340-57-5; **7**$^+$, 117340-54-2; **7**$^{2+}$, 117340-44-0; **8**, 117340-63-3; **8**$^+$, 117340-55-3; **8**$^{2+}$, 117340-46-2.

Supplementary Material Available: Tables of bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates and isotropic thermal parameters for **6** (4 pages); a listing of structure factors (11 pages). Ordering information is given on a current masthead.

Rhenium Carbonyl Phosphine Dinitrogen Complexes $(\eta^5\text{-}C_5Me_5)Re(CO)(PR_3)(N_2)$

A. Hugo Klahn and Derek Sutton*

Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

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The new rhenium dinitrogen complexes $(\eta^5\text{-}C_5Me_5)Re(CO)(PR_3)(N_2)$ (**3a–f**) have been synthesized for PR_3 = (**a**) PMe_3, (**b**) $P(n\text{-}Bu)_3$, (**c**) PCy_3 (Cy = cyclohexyl), (**d**) PPh_3, (**e**) $P(OMe)_3$, and (**f**) $P(OCH_2)_3CMe$ by treatment of the corresponding *p*-methoxyphenyldiazenido complexes $[(\eta^5\text{-}C_5Me_5)Re(CO)(PR_3)(p\text{-}N_2C_6H_4OMe)][BF_4]$ (**2a–f**) with *t*-BuLi. These cationic phosphine complexes **2a–f** were synthesized from the cationic acetonitrile complex $[(\eta^5\text{-}C_5Me_5)Re(CO)(NCMe)(p\text{-}N_2C_6H_4OMe)][BF_4]$ (**1a**) and the appropriate phosphine. The compounds have been characterized spectroscopically, including unambiguous ^{15}N and ^{14}N NMR assignments of the N_α and N_β resonances of the aryldiazenide and dinitrogen ligands. Comparisons are made with the properties of the related known dicarbonyl compounds $[(\eta^5\text{-}C_5Me_5)Re(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ and $(\eta^5\text{-}C_5Me_5)Re(CO)_2(N_2)$. It is shown that the ^{15}N label in $^{15}N_\alpha$-labeled **2a** and **2e** is retained exclusively at the N_α position in the dinitrogen complexes **3a** and **3e**; however, an equimolar mixture of $^{15}N_\alpha$- and $^{15}N_\beta$-labeled $(\eta^5\text{-}C_5Me_5)Re(CO)_2(^{15}N^{14}N)$ results when this dinitrogen complex is synthesized from exclusively $^{15}N_\alpha$-labeled $[(\eta^5\text{-}C_5Me_5)Re(CO)_2(p\text{-}^{15}N^{14}NC_6H_4OMe)][BF_4]$. Hexane or cyclohexane solution IR spectra of **3d** (PR_3 = PPh_3) and **3e** (PR_3 = $P(OMe)_3$), but not of the remainder, show two ν(NN) absorption bands. This is attributed to the existence of more than one possible conformation of the PR_3 ligand in these complexes. The N_2 ligand in **3a** (PR_3 = PMe_3) is remarkably inert, as it is not displaced by PPh_3 at room temperature in diethyl ether solution and shows no exchange with nitrogen gas when pressurized.

Introduction

Previous publications from this laboratory have described the syntheses of the dinitrogen compounds $CpRe(CO)_2(N_2)$[1] and $Cp^*Re(CO)_2(N_2)$[2] (Cp = η^5-C_5H_5, Cp* = η^5-C_5Me_5) by the treatment of the corresponding cationic aryldiazenido (N_2Ar) complexes $[CpRe(CO)_2(N_2Ar)]^+$ or $[Cp^*Re(CO)_2(N_2Ar)]^+$ with a variety of reagents including I^-, BH_4^-, MeLi, and *t*-BuLi. Elsewhere,[3] we have described the synthesis of the cationic acetonitrile-substituted aryldiazenido complexes $[Cp'Re(CO)(NCMe)(N_2Ar)]^+$ (where Cp' = Cp or Cp*) by means of eq 1.

$$[Cp'Re(CO)_2(N_2Ar)]^+ \xrightarrow[MeCN]{PhIO} [Cp'Re(CO)(NCMe)(N_2Ar)]^+ \quad (1)$$

These acetonitrile complexes readily undergo substitution of the acetonitrile by a variety of ligands. In this paper we describe a series of phosphine complexes of the type $[Cp^*Re(CO)(PR_3)(N_2Ar)]^+$ synthesized in this way. We have found that these carbonyl phosphine complexes, just like the dicarbonyls mentioned above, also undergo the transformation of the N_2Ar ligand into N_2 when treated with *t*-BuLi. This has allowed us to synthesize the series of carbonyl phosphine dinitrogen complexes $Cp^*Re(CO)(PR_3)(N_2)$ that is unobtainable from $Cp^*Re(CO)_2(N_2)$ and PR_3 because of preferential substitution of N_2 by PR_3. Some properties of the PMe_3 complex $Cp^*Re(CO)(PMe_3)(N_2)$, particularly the photodissociation of N_2 and subsequent C–H activation chemistry of the intermediate, have been communicated already.[4] Here, we provide details of the characterization of these complexes and make some comparisons with the dicarbonyl compound $Cp^*Re(CO)_2(N_2)$.

Experimental Section

All reactions were carried out under dry N_2 in Schlenk apparatus connected to a double manifold providing low vacuum or nitrogen. Solvents were purified and dried by conventional methods, distilled under nitrogen, and used immediately. Infrared spectra were measured by using a Perkin-Elmer Model 983-G instrument, usually as solutions in CaF_2 cells. Variable-temperature IR spectra were run on a Bruker IFS-85 FT-IR instrument by using a Specac variable-temperature IR cell. ^1H, ^{13}C, ^{31}P (referenced to external 85% H_3PO_4), ^{15}N, and ^{14}N (referenced to external $MeNO_2$) NMR spectra were measured by using a Bruker WM-400 instrument. The ^{15}N NMR spectra were obtained for 96% ^{15}N isotopically enriched samples. Mass spectra were obtained with a Hewlett-Packard Model 5985 mass spectrometer with electron-impact (EI) or fast atom bombardment (FAB; Phrasor Scientific Inc. accessory) sources. Masses are quoted for the ^{187}Re isotope. Microanalyses were performed by the Simon Fraser University Microanalytical Laboratory.

* To whom correspondence should be addressed.

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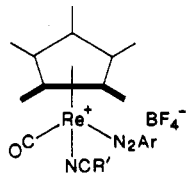
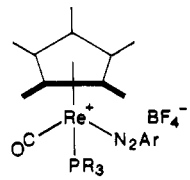
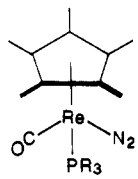


1: Ar = *p*-$MeOC_6H_4$; R' = (a) Me, (b), *n*-Pr, (c) *i*-Pr



2: Ar = *p*-$MeOC_6H_4$; R = (a) PMe_3, (b), $P(n\text{-}Bu)_3$, (c) PCy_3, (d) PPh_3, (e) $P(OMe)_3$, (f) $P(OCH_2)_3CMe$



3a-f: R as above for 2a-f

Trimethyl-, tri-*n*-butyl-, tricyclohexyl-, and triphenylphosphine (Strem Chemical Co.) and trimethyl phosphite (Alfa Chemical Co.) were used as purchased and were stored under N_2 and in the dark ($P(OMe)_3$). The caged phosphite $P(OCH_2)_3CMe$ was kindly synthesized by Dr. R. Alex by the published method.[5] Acetonitrile, *n*-butyronitrile, and isobutyronitrile (Aldrich) were distilled from P_4O_{10}. Iodosobenzene (PhIO) was purchased from Pfaltz and Bauer or was prepared from iodosobenzene diacetate (Aldrich) by the published method[6] and was stored in the refrigerator. Methyllithium (2.4 M in diethyl ether) and *tert*-butyllithium (1.95 M in pentane) were purchased from Aldrich and were used as received. $(\eta\text{-}C_5Me_5)Re(CO)_3$ was synthesized from $Re_2(CO)_{10}$ (Strem) by reaction with pentamethylcyclopentadiene[7] either directly[8a] or with decane as solvent. *p*-Methoxybenzenediazonium tetrafluoroborate was synthesized by diazotization of *p*-methoxyaniline with $NaNO_2$[9] or with $Na^{15}NO_2$ (96% ^{15}N; Stohler Isotopes Inc.) and was recrystallized from acetone–diethyl ether.

Preparation of [Cp*Re(CO)(NCMe)(*p*-$N_2C_6H_4OMe$)][BF_4] (1a) and 1a-$^{15}N_\alpha$. An approximate 20% stoichiometric excess of iodosobenzene was added as a solid to a stirred solution of [Cp*Re(CO)$_2$(*p*-$N_2C_6H_4OMe$)][BF_4][3] or the $^{15}N_\alpha$ analogue (500 mg) in MeCN (40 mL). After 1 h, all of the dicarbonyl cation had reacted (by IR) and no further change occurred. Removal of solvent under vacuum gave a red oily solid which was dissolved in acetone and filtered through Celite. Recrystallization from acetone–ether gave the acetonitrile complex as an orange microcrystalline solid in 91% yield; mp 65–67 °C. IR (CH_2Cl_2): 1962 (vs, ν(CO)), 1659 (s, ν(NN)) (1638 cm^{-1} in 1a-$^{15}N_\alpha$) cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.14 (s, 15 H, Cp*), 3.10 (s, 3 H, MeCN), 3.85 (s, 3 H, OMe), 7.05 (d, 2 H, C_6H_4), 7.24 (d, 2 H, C_6H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 5.00 (*Me*CN), 10.03 (C_5Me_5), 55.80 (O*Me*), 106.31 (C_5Me_5), 115.68, 121.95, 123.95, 161.79 (C_6H_4), 142.77 (Me*C*N), 195.94 (CO) (all resonances singlets). ^{14}N NMR (acetone/acetone-d_6): δ −256.4 (br, s, *N*CMe), −135 (br, s, N_β), −6.9 (br, s, N_α). ^{15}N NMR for 1a-$^{15}N_\alpha$ (acetone/acetone-d_6): δ −6.09 (s, $^{15}N_\alpha$). MS (FAB, xenon, sulfolane): m/z 526 (527 in 1a-$^{15}N_\alpha$) (M^+ of cation), 485 (486 in 1a-$^{15}N_\alpha$) ((M − NCMe)$^+$). Anal. Calcd for 1a: C, 39.21; H, 4.08; N, 6.86. Found: C, 38.77; H, 4.18; N, 6.63.

Photochemical Reaction of [Cp*Re(CO)$_2$(*p*-$N_2C_6H_4OMe$)][BF_4] in Acetonitrile. [Cp*Re(CO)$_2$(*p*-$N_2C_6H_4OMe$)][BF_4] (20 mg) was dissolved in 20 mL of freshly distilled acetonitrile and irradiated through a quartz tube at room temperature for 30 min. During the photolysis a slow flux of N_2 was maintained. After this time, the IR spectrum of the solution showed a 25% conversion into the acetonitrile complex 1a. Solvent was removed in a vacuum, and the residual brown solid was dissolved in CH_2Cl_2. Slow addition of ether precipitated a dark red solid which showed in the IR spectrum (in CH_2Cl_2) the same conversion ratio observed in acetonitrile. Crystallization from acetone–ether (5:1) at −78 °C or extraction with THF also showed (by IR) the same ratio of products. Irradiation for an additional 2 h under the same conditions gave a dark brown solution which showed in the IR spectrum only weak absorptions for 1a.

Preparation of [Cp*Re(CO)(NC-*n*-Pr)(*p*-$N_2C_6H_4OMe$)][BF_4] (1b). This compound was synthesized analogously to 1a using *n*-butyronitrile (*n*-PrCN) as a solvent. [Cp*Re(CO)$_2$(*p*-$N_2C_6H_4OMe$)][BF_4] (100 mg in 8 mL of *n*-PrCN) yielded 73 mg of 1b (68%) as a red-orange solid which decomposed above 98 °C. IR (CH_2Cl_2): 1962 (vs, ν(CO)), 1660 (s, ν(NN)) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.11 (t, 3 H, $NC(CH_2)_2Me$), 1.76 (m, 2 H, $NCCH_2CH_2Me$), 2.15 (s, 15 H, Cp*), 3.46 (t, 2 H, $NCCH_2CH_2Me$), 3.85 (s, 3 H, OMe), 7.05 (d, 2 H, C_6H_4), 7.27 (d, 2 H, C_6H_4). MS (FAB, xenon, sulfolane): m/z 554 (M^+ of cation), 485 ((M − *n*-PrCN)$^+$). Anal. Calcd for 1b: C, 41.75; H, 4.53; N, 6.56. Found: C, 42.03; H, 4.88; N, 6.54.

Preparation of [Cp*Re(CO)(NC-*i*-Pr)(*p*-$N_2C_6H_4OMe$)][BF_4] (1c). This complex was prepared in a similar manner to 1a using *iso*butyronitrile (*i*-PrCN) as a solvent. From 100 mg of [Cp*Re(CO)$_2$(*p*-$N_2C_6H_4OMe$)][BF_4], 65 mg (62%) of 1c was obtained as a dark red solid, mp slow decomposition above 80 °C. IR (CH_2Cl_2): 1959 (vs, ν(CO)), 1658 (s, ν(NN)) cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.10 (s, 15 H, Cp*), 2.19 (d, 6 H, $CHMe_2$), 3.60 (br mult, 1 H, $CHMe_2$), 3.82 (s, 3 H, OMe), 6.98 (d, 2 H, C_6H_4), 7.22 (d, 2 H, C_6H_4). MS (FAB, xenon, sulfolane): m/z 554 (M^+ of cation), 485 ((M − *i*-PrCN)$^+$). Anal. Calcd for 1c: C, 41.25; H, 4.53; N, 6.56. Found: C, 41.48; H, 4.43; N, 6.64.

Preparation of [Cp*Re(CO)(PMe_3)(*p*-$N_2C_6H_4OMe$)][BF_4] (2a) and 2a-$^{15}N_\alpha$. The acetonitrile complex 1a or 1a-$^{15}N_\alpha$ (500 mg) in acetone (40 mL) was stirred with an excess of PMe_3 (0.1 mL). The reaction was followed by IR spectroscopy until all the acetonitrile complex reacted (ca. 4 h). Solvent was pumped off, and the orange oily solid obtained was then solidified by washing three times with diethyl ether (30 mL) and dried under vacuum for 2 days to give 2a or 2a-$^{15}N_\alpha$ as an orange solid: yield 475 mg (90%); mp 169–171 °C. IR (CH_2Cl_2): 1949 (vs, ν(CO)), 1677 (s, ν(NN)) (1642 cm^{-1} in 2a-$^{15}N_\alpha$) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.88 (d, J = 10.69 Hz, 9 H, PMe_3), 2.19 (d, J = 0.52 Hz, 15 H, Cp*), 3.86 (s, 3 H, OMe), 7.02 (d, 2 H, C_6H_4), 7.16 (d, 2 H, C_6H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 10.72 (s, C_5Me_5), 18.45 (d, J = 39.14 Hz, PMe_3), 55.81 (s, O*Me*), 106.24 (s, C_5Me_5), 115.86 (s), 119.50 (s), 122.63 (s), 162.10 (s, C_6H_4), 201.24 (d, J = 12.16 Hz, CO). ^{14}N NMR (acetone–acetone-d_6): δ −126.0 (br, s, N_β), −1.9 (br, s, N_α). ^{15}N NMR for 2a-$^{15}N_\alpha$ (acetone–acetone-d_6): δ −0.64 (d, J_{PN} = 3.5 Hz, $^{15}N_\alpha$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −30.39 (s, PMe_3). MS (FAB, xenon, sulfolane): m/z 561 (562 in 2a-$^{15}N_\alpha$) (M^+ of cation). Anal. Calcd for 2a: C, 38.95; H, 4.79; N, 4.32. Found: C, 38.37; H, 4.82; N, 4.30.

Preparation of [Cp*Re(CO){$P(n\text{-}Bu)_3$}(*p*-$N_2C_6H_4OMe$)][BF_4] (2b). A procedure similar to that for the preparation of the PMe_3 complex 2a gave the tri-*n*-butylphosphine complex 2b in 81% yield as an orange solid which melted at 125 °C. IR (CH_2Cl_2): 1949 (vs, ν(CO)), 1679 (s, ν(NN)) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.95 (t, 9 H, $P(CH_2\{CH_2\}_2Me)_3$), 1.46 (m, 12 H, $P(CH_2\{CH_2\}_2Me)_3$), 1.97 (m, 6 H, $P(CH_2\{CH_2\}_2Me)_3$), 2.17 (s, 15 H, Cp*), 3.88 (s, 3 H, OMe), 7.03 (d, 2 H, C_6H_4), 7.19 (d, 2 H, C_6H_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −2.52 (s, $P(n\text{-}Bu)_3$). MS (FAB, xenon, sulfolane): m/z 687 (M^+ of cation). Anal. Calcd for 2b: C, 46.57; H, 6.34; N, 3.62. Found: C, 46.35; H, 6.47; N, 3.63.

Preparation of [Cp*Re(CO)(PCy_3)(*p*-$N_2C_6H_4OMe$)][BF_4] (2c). This complex was synthesized analogously to 2a as an orange-red solid in 83% yield; mp 102–104 °C. IR (CH_2Cl_2): 1940 (vs, ν(CO)), 1677 (s, ν(NN)) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.30 and 1.80 (both multiplets, ~30 H, PCy_3), 2.15 (s, 15 H, Cp*), 3.88 (s, 3 H, OMe), 7.04 (d, 2 H, C_6H_4), 7.17 (d, 2 H, C_6H_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 22.03 (s, PCy_3). Anal. Calcd for 2c: C, 50.10; H, 6.45;

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N, 3.29. Found: C, 49.70; H, 6.20; N, 3.60.

Preparation of [Cp*Re(CO)(PPh$_3$)(*p*-N$_2$C$_6$H$_4$OMe)][BF$_4$] (2d). This complex was prepared similarly to those previously described. After recrystallization from CH_2Cl_2–ether **2d** was obtained in 70% yield as orange microcrystals which melted at 230 °C. IR (CH_2Cl_2): 1954 (vs, ν(CO)), 1685 (s, ν(NN)) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.12 (s, 15 H, Cp*), 3.89 (s, 3 H, OMe), 7.08 (d, 2 H, C_6H_4), 7.30–7.51 (m, 17 H, PPh_3 + C_6H_4). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 13.1 (s, PPh_3). MS (FAB, xenon, sulfolane): *m/z* 747 (M^+ of cation). Anal. Calcd for **2d**: C, 51.86; H, 4.44; N, 3.36. Found: C, 51.79; H, 4.74; N, 3.31.

Preparation of [Cp*Re(CO){P(OMe)$_3$}(*p*-N$_2$C$_6$H$_4$OMe)][BF$_4$] (2e) and 2e-$^{15}N_\alpha$. This complex was prepared following the same procedure used for **2a** and **2a**-$^{15}N_\alpha$ in 75% yield as an orange solid, mp 108 °C. IR (CH_2Cl_2): 1965 (vs, ν(CO)), 1689 (s, ν(NN)) 1650 cm^{-1} in **2e**-$^{15}N_\alpha$) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.17 (d, J = 0.69 Hz, 15 H, Cp*), 3.78 (d, J = 12.18 Hz, 9 H, $P(OMe)_3$), 3.86 (s, 3 H, OMe), 7.04 (d, 2 H, C_6H_4), 7.20 (d, 2 H, C_6H_4). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 10.32 (s, C_5Me_5), 54.68 (d, J = 6.76 Hz, $P(OMe)_3$), 55.90 (s, *OMe*), 106.91 (s, C_5Me_5), 115.85 (s), 118.64 (s), 123.31 (s), 162.52 (s, C_6H_4), 199.01 (d, J = 19.63 Hz, CO). ^{15}N NMR for **2e**-$^{15}N_\alpha$ (acetone–acetone-d_6): δ −1.97 (d, J_{NP} = 3.0 Hz, $^{15}N_\alpha$). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 108.79 (s, $P(OMe)_3$). MS (FAB, xenon, sulfolane): *m/z* 609 (610 in **2e**-$^{15}N_\alpha$) (M^+ of cation). Anal. Calcd for **2e**: C, 36.26; H, 4.46; N, 4.03. Found: C, 36.39; H, 4.38; N, 4.26.

Preparation of [Cp*Re(CO){P(OCH$_2$)$_3$CMe}(*p*-N$_2$C$_6$H$_4$OMe)][BF$_4$] (2f). This orange complex was prepared analogously to **2a** in 70% yield. The phosphite $P(OCH_2)_3CMe$ was sublimed twice at room temperature immediately before use. Anal. Calcd for **2f**: C, 38.40; H, 4.34; N, 3.89. Found: C, 37.29; H, 4.29; N, 3.58. IR (CH_2Cl_2): 1985 (vs, ν(CO)), 1699 (s, ν(NN)) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.94 (s, 3 H, CCH_3), 2.19 (d, J = 0.9 Hz, 15 H, Cp*), 3.90 (s, 3 H, OMe), 4.50 (d, J = 5.1 Hz, 6 H, OCH_2), 7.07 (d, 2 H, C_6H_4), 7.26 (d, 2 H, C_6H_4). MS (FAB, xenon, sulfolane): *m/z* 633 (M^+ of cation).

Preparation of Cp*Re(CO)(PMe$_3$)(N$_2$) (3a) and 3a-$^{15}N_\alpha$. The trimethylphosphine cationic complex **2a** or **2a**-$^{15}N_\alpha$ (150 mg) was dissolved in freshly distilled THF (50 mL) and heated at 60 °C; then an excess of *t*-butyllithium (0.5 mL) was added by syringe. A fast reaction took place, and the color of the solution changed from orange-red to light brown. The IR spectrum of this mixture showed the total disappearance of the cationic complex and the presence of absorptions due to the dinitrogen complex. In addition, a third medium-intensity absorption was observed at 1850 cm^{-1} believed to be the ν(CO) of the hydrazido(2–) complex Cp*Re(CO)(PMe_3)[*p*-NN(*t*-Bu)C_6H_4OMe]. After 15 min of stirring at room temperature, the volume was reduced to one-tenth under vacuum. One drop of water was added to hydrolyze the unreacted *tert*-butyllithium and the mixture stirred for 5 min. Diethyl ether (50 mL) was added and stirred for 30 min and the solution filtered through a short column of Celite–neutral alumina. Evaporation of the solvent under reduced pressure gave a pale brown oily solid which was chromatographed on a neutral alumina column (prepared in hexane). Hexane elution moved the dinitrogen complex **3a** and organic side products. Recrystallization from pentane at −78 °C gave the product as pale yellow microcrystals in 51% yield (54 mg); mp 99–100 °C with decomposition. IR (hexane): 2043 (s, ν(NN)) (2010 cm^{-1} in **3a**-$^{15}N_\alpha$) 1864 (vs, ν(CO)) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.56 (d, J = 8.76 Hz, 9 H, PMe_3), 1.99 (d, J = 0.68 Hz, 15 H, Cp*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 10.74 (s, C_5Me_5), 20.64 (d, J = 33.16 Hz, PMe_3), 93.26 (s, (C_5Me_5)), 207.16 (d, J = 7.04 Hz, *CO*). ^{14}N NMR (acetone–acetone-d_6): δ −90.2 (br, s, N_α), −29.4 (br, s, N_β). ^{15}N NMR for **3a**-$^{15}N_\alpha$ (acetone–acetone-d_6): δ −90.7 (s, $^{15}N_\alpha$). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −29.81 (s, PMe_3). MS (EI): *m/z* 454 (455 in **3a**-$^{15}N_\alpha$) (M^+), 426 ((M − $^{14}N_2$)$^+$ in **3a** or (M − $^{15}N^{14}N$)$^+$ in **3a**-$^{15}N_\alpha$). Anal. Calcd for **3a**: C, 37.08; H, 5.30; N, 6.16. Found: C, 37.38; H, 5.50; N, 5.95.

Preparation of Cp*Re(CO){P(*n*-Bu)$_3$}(N$_2$) (3b). A procedure similar to that described for the preparation of **3a** was used and gave **3b** in 44.5% yield as a pale yellow microcrystalline solid; mp 73 °C. IR (hexane): 2040 (s, ν(NN)), 1863 (vs, ν(CO)) cm^{-1}. ^{1}H NMR (CDCl)$_3$): δ 0.93 (t, 9 H, P{$CH_2(CH_2)_2CH_3$}$_3$), 1.38 (m, 12 H, P{$CH_2(CH_2)_2CH_3$}$_3$), 1.71 (m, 6 H, P{$CH_2(CH_2)_2CH_3$}$_3$)), 1.95 (s, 15 H, Cp*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 10.60 (s, C_5Me_5), 13.86 (s, P{$(CH_2)_3CH_3$}$_3$), 24.33 (d, J = 13.1 Hz, P{$CH_2CH_2CH_2CH_3$}$_3$), 25.97 (s, P{$CH_2CH_2CH_2CH_3$}$_3$), 29.06 (d, J = 29.9 Hz, P{$CH_2CH_2CH_2CH_3$}$_3$), 92.72 (s, C_5Me_5), 208.24 (d, J = 7.7 Hz, CO). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −0.21. MS (EI): *m/z* 580 (M^+), 552 ((M − N_2)$^+$). Anal. Calcd for **3b**: C, 46.57; H, 6.34; N, 3.62. Found: C, 46.35; H, 6.47; N, 3.63.

Preparation of Cp*Re(CO)(PCy$_3$)(N$_2$) (3c). This complex was synthesized analogously to **3a** as a pale yellow solid in 38% yield; mp 129 °C with decomposition. IR (hexane): 2030 (s, ν(NN)), 1856 (vs, ν(CO)) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.25, 1.70 (m, 33 H, $P(C_6H_{11})_3$), 1.93 (s, 15 H, Cp*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 10.75 (s, C_5Me_5), 26.67 (s), 27.74 (d, J = 7.05 Hz), 30.09 (d, J = 37.07 Hz), 38.74 (d, J = 24.40 Hz) (all $P(C_6H_{11})_3$), 92.63 (s, C_5Me_5), 209.81 (d, J = 8.47 Hz, *CO*). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 27.48 (s). MS (EI): *m/z* 658 (M^+), 630 ((M − N_2)$^+$). Anal. Calcd for **3c**: C, 53.00; H, 7.31; N, 4.26. Found: C, 53.90; H, 7.77; N, 4.15.

Preparation of Cp*Re(CO)(PPh$_3$)(N$_2$) (3d). This complex was synthesized analogously to **3a** as a pale yellow microcrystalline solid in 39% yield; mp 133 °C with decomposition. IR (hexane): 2058 (s), 2045 (m) (ν(NN)), 1866 ((unsymmetrical) vs, ν(CO)) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.73 (s, 15 H, Cp*), 7.37 (m, 15 H, PPh_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 9.94 (s, C_5Me_5), 93.22 (s, C_5Me_5), 127.84 (d, J = 9.79 Hz), 129.19 (s), 133.53 (d, J = 11.83 Hz), 137.84 (d, J = 47.20 Hz) (all PPh_3), 207.41 (d, J = 8.76 Hz, *CO*). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 32.20 (s). MS (EI): *m/z* 640 (M^+), 612 ((M − N_2)$^+$). Anal. Calcd for **3d**: C, 54.45; H, 4.70; N, 4.38. Found: C, 54.63; H, 4.81; N, 4.60.

Preparation of Cp*Re(CO){P(OMe)$_3$}(N$_2$) (3e) and 3e-$^{15}N_\alpha$. This complex was prepared following the same procedure used for the synthesis of **3a** and **3a**-$^{15}N_\alpha$ in 48% yield as a pale yellow microcrystalline solid, mp 54 °C. IR (hexane): 2078 (m), 2066 (s) (ν(NN)), 1887 ((unsymmetrical) vs, ν(CO)) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.99 (d, J = 0.79 Hz, 15 H, Cp*), 3.50 (d, J = 12.10 Hz, 9 H, $P(OMe)_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 10.28 (s, C_5Me_5), 51.22 (s, $P(OMe)_3$), 94.12 (d, J = 1.50 Hz, C_5Me_5), 204.94 (d, J = 12.40 Hz, *CO*). ^{14}N NMR (acetone–acetone-d_6): δ −98.3 (br, s, N_α), −30.5 (br, s, N_β). ^{15}N NMR (acetone–acetone-d_6): δ −98.2 (s, $^{15}N_\alpha$). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 139.0 (s). MS (EI): *m/z* 502 (503 in **3e**-$^{15}N_\alpha$) (M^+), 474 ((M − $^{14}N_2$)$^+$ in **3e** or (M − $^{15}N^{14}N$)$^+$ in **3e**-$^{15}N_\alpha$). Anal. Calcd for **3e**: C, 33.46; H, 4.78; N, 5.57. Found: C, 33.60; H, 4.83; N, 5.66.

Preparation of Cp*Re(CO){P(OCH$_2$)$_3$CMe}(N$_2$) (3f). This complex was prepared following the same procedure as above, but on a small scale sufficient to enable the characteristic IR spectrum to be obtained following chromatographic purification. Low-temperature crystallization was not achieved, and no other data were obtained on this complex. IR (hexane): 2091 (m, ν(NN)), 1900 (s, ν(CO)) cm^{-1}.

Reaction of [Cp*Re(CO)$_2$(*p*-N$_2$C$_6$H$_4$OMe)][BF$_4$] with MeLi. A suspension of red-brown [Cp*Re(CO)$_2$(*p*-$N_2C_6H_4OMe$)][BF_4] (50 mg) in hexane (10 mL) was stirred with an excess of MeLi (0.2 mL) at room temperature. The solution slowly turned red and after 4 h was separated from unreacted solid. Solvent was evaporated in vacuo to give a dark red solid which was recrystallized from diethyl ether–hexane (1:1) at −78 °C: yield 18 mg (38%) of Cp*Re(CO)$_2$[*p*-NN(Me)C_6H_4OMe]; mp decomposed above 160 °C. IR (hexane): 1936 (s), 1862 (s) (ν(CO)) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.13 (s, 15 H, Cp*), 3.69 (s, 3 H, *Me*), 3.80 (s, 3 H, *OMe*), 6.82 (d, 2 H, C_6H_4), 7.34 (d, 2 H, C_6H_4). MS (EI): *m/z* 528 (M^+), 500 ((M − CO)$^+$), 472 ((M − 2CO)$^+$). Cp*Re(CO)$_2$(N$_2$) (4 mg) was recovered from the supernatant.

By using *t*-BuLi instead of MeLi under identical conditions, the hydrazido(2–) complex Cp*Re(CO)$_2$[*p*-NN(*t*-Bu)C_6H_4OMe] and the dinitrogen complex were formed in approximate 5:1 ratio (by IR). The hydrazido(2–) complex exhibited two strong ν(CO) absorptions at 1935 and 1861 cm^{-1} in hexane solution.

Reaction of [Cp*Re(CO)(PR$_3$)(*p*-N$_2$C$_6$H$_4$OMe)][BF$_4$] (R = Me (2a) and Ph (2d)) with Methyllithium in THF. (a) At Room Temperature. Addition of an excess of MeLi (0.1 mL) to a THF solution of **2d** (20 mg) resulted in a dark red solution which showed in the IR spectrum an intense absorption at 1805 cm^{-1} (in THF). This absorption occurred at 1795 cm^{-1} in the PMe_3 complex. In both cases about 20% (by IR) of the respective dinitrogen complex was also formed. Attempts to isolate these monocarbonyl species, which we believe are the arylmethylhydrazido(2–) complexes Cp*Re(CO)(PR$_3$)[*p*-NN(Me)C_6H_4OMe],

were unsuccessful due to their low stability to silica gel column. A partially purified sample derived from **2d** (by extraction with hexane at 0–5 °C) gave unsatisfactory ^{1}H NMR and mass spectra. In $CDCl_3$ or hexane solutions these hydrazido(2–) complexes decomposed after about 3 h at room temperature to give green solutions which showed no ν(CO) absorption for the hydrazido(2–) complexes. In both cases the intensities of ν(NN) and ν(CO) absorptions of the dinitrogen complex initially present were not increased.

(b) At 60 °C. These reactions were carried out under identical conditions to those described using *t*-BuLi. In both cases, the dinitrogen complexes were the major products: **3b** (39% isolated yield) and **3e** (29% isolated yield). The respective putative arylbutylhydrazido(2–) complexes were also present in small amounts (by IR).

Reaction of [Cp*Re(CO)$_2$(*p*-N$_2$C$_6$H$_4$OMe)][BF$_4$] with *t*-BuLi at 60 °C. [Cp*Re(CO)$_2$(*p*-N$_2$C$_6$H$_4$OMe)][BF$_4$] (100 mg) was dissolved in THF (20 mL), heated at 60 °C, and treated with 0.1 mL of *t*-BuLi. Following the same purification procedure as that used for the PMe_3 complex **2a**, the dinitrogen complex Cp*Re(CO)$_2$(N$_2$) was obtained in 31% yield (21 mg). A small amount of the putative hydrazido(2–) complex Cp*Re(CO)$_2$[*p*-NN(*t*-Bu)C$_6$H$_4$OMe] was also formed. (IR (hexane): 1935, 1861 cm^{-1} (ν(CO))).

Reaction of [Cp*Re(CO)(PR$_3$)(*p*-N$_2$C$_6$H$_4$OMe)][BF$_4$] (R = Me (2a) or Ph (2d)) with NaBH$_4$. The phosphine aryldiazenido complex **2a** or **2d** (50 mg) was dissolved in 5 mL of acetone at room temperature. An excess of solid $NaBH_4$ (ca. 5 mg) was added and the solution was stirred for 1 h. The color changed from orange-red to yellow. Evaporation of the solvent under vacuum at room temperature gave an orange-red solid which was extracted with hexane and characterized as the hydrido complex Cp*Re(CO)(H)(*p*-N$_2$C$_6$H$_4$OMe) by comparison with an authentic sample.[3] In both cases yields were over 70%.

Preparation of Cp*Re(CO)(Me)(*p*-N$_2$C$_6$H$_4$OMe). The acetonitrile complex **1a** (50 mg) was dissolved in THF (15 mL) at room temperature. MeLi (0.1 mL) was added by syringe, and the solution was stirred for 3 h. Evaporation of the solvent under vacuum gave a red oily solid which was extracted with hexane and chromatographed on a neutral alumina column. Elution with ether–hexane (2:1) followed by evaporation gave the product Cp*Re(CO)(Me)(*p*-N$_2$C$_6$H$_4$OMe) (13 mg, 32% yield) as a red solid, mp 138–140 °C. This complex was characterized by IR and ^{1}H NMR. IR (hexane): 1941 (vs, ν(CO)), 1629 (s, ν(NN)) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.06 (s, 3 H, ReMe), 2.06 (s, 15 H, Cp*), 3.81 (s, 3 H, OMe), 6.90 (d, 2 H, C$_6$H$_4$), 7.27 (d, 2 H, C$_6$H$_4$).

Investigation of ^{15}N Exchange for Cp*Re(CO)$_2$(^{15}N^{14}N) by Magnetization Transfer. A sample of Cp*Re(CO)$_2$(^{15}N^{14}N) in acetone–acetone-d_6 exhibited equal intensity signals in the ^{15}N NMR spectrum arising from the presence of an equimolar proportion of Cp*Re(CO)$_2$(^{15}N^{14}N) [δ(N$_\alpha$) – 110.97] and Cp*Re(CO)$_2$(^{14}N^{15}N) [δ(N$_\beta$) –28.13]. The relaxation times T_1 for these two signals were measured to be 9.8 and 9.7 s, respectively, by the inversion-recovery procedure. This consisted of the application of a nonselective π pulse and spectrum acquisition following delay times varying between 0.01 and 20 s. A relaxation delay of 20 s was applied to all spectra. To examine for magnetization transfer, an attenuator was coupled into the rf transmitter line and adjusted to give a π pulse of 220 μs. A sequence of 50 4.4 μs pulses was therefore equivalent to a single π pulse. A delay of 200 μs between each 4.4 μs pulse thus provided a selective π pulse of 0.01 s. The transmitter frequency was adjusted to coincide with one of the ^{15}N signals (N$_\alpha$) in the sample. The above DANTE sequence was followed by a fixed delay of 5 s, and then a nonselective $\pi/2$ pulse in order to acquire the spectrum. This procedure was repeated 32 times with a 10-s relaxation delay between each sequence. A second spectrum consisting of an additional 32 runs was acquired in the normal way by using a delay equal to the 5-s fixed delay time plus the time required for the DANTE sequence (0.01 s) and was subtracted from the first spectrum. The complete sequence was repeated a sufficient number of times to provide an adequate signal-to-noise ratio. The fixed 5-s delay time following the π pulse in the first spectrum would allow magnetization to transfer from the inverted (N$_\alpha$) signal to the second (N$_\beta$) signal if the ^{15}N label were exchanging on this time scale between the N$_\alpha$ and N$_\beta$ positions. This would result in a residual signal in the N$_\beta$ position after subtraction of the second spectrum. None was observed.

Results and Discussion

(a) Nitrile Complexes. One of the CO groups in [Cp*Re(CO)$_2$(*p*-N$_2$C$_6$H$_4$OMe)]$^+$ can be oxidatively removed by reaction with iodosobenzene in the presence of a nitrile solvent to give reasonable yields of the nitrile complexes [Cp*Re(CO)(NCR′)(*p*-N$_2$C$_6$H$_4$OMe)]$^+$ (**1**, R′ = (**a**) Me, (**b**) *n*-Pr, (**c**) *i*-Pr) (eq 1). This follows closely the corresponding chemistry of the nitrosyls [Cp′Re(CO)$_2$(NO)]$^+$ (Cp′ = Cp or Cp*) reported by Gladysz.[8] No success was achieved with Me_3NO replacing PhIO. The reaction works equally well with the corresponding Cp complex.[3] The nitrile complex **1a** was also formed by the UV photolysis of [Cp*Re(CO)$_2$(*p*-N$_2$C$_6$H$_4$OMe)][BF$_4$] in acetonitrile, but it was not easily separated from residual starting material and appeared to decrease in concentration on prolonged irradiation. The orange or red complexes **1a–c** are insoluble in hexane, benzene, and diethyl ether but dissolve in CH_2Cl_2 and acetone. In the IR spectra (CH_2Cl_2), ν(CO) appeared as a broad and very strong absorption near 1960 cm^{-1}, and a broad and strong absorption near 1660 cm^{-1} was observed for ν(NN). The latter assignment was confirmed by ^{15}N isotopic substitution at N$_\alpha$ of the diazenido ligand in the acetonitrile complex [Cp*Re(CO)(NCMe)(*p*-^{15}NNC$_6$H$_4$OMe)]$^+$ (**1a**-$^{15}N_\alpha$). A shift to lower wavenumber by 20 cm^{-1} was then observed. Notably, ν(CN) for the nitrile ligand, usually expected to occur quite strongly near 2300 cm^{-1} in the IR spectrum of η^1-bonded nitrile complexes, could not be observed, either in CH_2Cl_2 solution or Nujol emulsion for either complex (see below).[10]

In addition to the typical resonances for the Cp* and aryldiazenido groups, the presence of the nitrile ligands was clearly indicated in the ^{1}H NMR spectra of these compounds. The FAB mass spectra showed the unfragmented cations as molecular ions M$^+$, and fragments corresponding to the loss of the nitrile ligand (M – NCR)$^+$. No fragments corresponding to the loss of CO or the loss of CO and nitrile were observed.

The acetonitrile complex **1a** was studied by nitrogen NMR spectroscopy. The ^{15}N NMR spectrum of **1a**-$^{15}N_\alpha$ exhibited a single resonance for ^{15}N$_\alpha$ at δ –6.09. Interestingly, three broad ^{14}N resonances were observed for **1a** at δ –6.9, –135.0, and –256.4, assignable to the three distinct nitrogen atoms. The one at δ –6.9 was immediately assigned to N$_\alpha$, in good agreement with the ^{15}N NMR spectrum of **1a**-$^{15}N_\alpha$. The resonance at δ –135.0 was assigned to N$_\beta$. These N$_\alpha$ and N$_\beta$ resonances are typically at positions expected for N$_\alpha$ and N$_\beta$ of a singly bent aryldiazenido ligand by comparison with previous examples.[11,12] The third resonance at much higher field (δ –256.4) is assigned to the nitrogen of the coordinated MeCN. This is shifted by about 120 ppm upfield by comparison with free MeCN (δ –138.4).[13] This large coordination shift contrasts with the expected magnitude discussed by Mason[14] and the small shift observed in

(10) It should be noted, however, that examples of η^1-bonded nitrile complexes with weak or unobserved ν(CN) absorptions have been documented. See, for example: (a) Rouschias, G.; Wilkinson, G. *J. Chem. Soc. A* **1967**, 993. (b) Butcher, A. V.; Chatt, J.; Leigh, G. J.; Richards, P. L. *J. Chem. Soc., Dalton Trans.* **1972**, 1064.

(11) (a) Dilworth, J. R.; Kan, C.-T.; Richards, R. L.; Mason, J.; Stenhouse, I. A. *J. Organomet. Chem.* **1980**, *20*, C24. (b) Dilworth, J. R.; Donovan-Mtunzi, S.; Kan, C.-T.; Richards, R. L.; Mason, J. *Inorg. Chim. Acta* **1981**, *53*, L161.

(12) Barrientos-Penna, C. F.; Klahn-Oliva, A. H.; Sutton, D., unpublished results.

(13) Martin, G. P.; Martin, M. L.; Govesnard, J. P. *^{15}N-NMR Spectroscopy*; Springer-Verlag: Berlin, 1981; p 158.

$Cr(CO)_5(NCMe)$ (δ −146.0).[15]

There are two other possibly anomalous features of **1a**: (i) the lack of an observable ν(CN) absorption near 2300 cm^{-1} has been mentioned; (ii) in addition, the ^{13}C chemical shift for the nitrile carbon of **1a** occurred at δ 142.77 (in the same region as the value reported for $[Cp^*Re(CO)(NCMe)(NO)]^+$ (δ 139.30)),[8] both some 10 ppm downfield from the resonances for comparable cationic MeCN complexes such as $[Re(CO)_5(NCMe)]^+$[16] and $[CpFe(CO)(NCMe)_2]^+$[17,18] which have IR spectra with ν(CN) ~2300 cm^{-1} in accordance with η^1-NCMe groups. It is possible that these anomalies are an indication that the MeCN ligand in **1a** may not be typically η^1-bonded, and a crystal structure determination would be worthwhile on this complex. It should be noted that a side-bonded nitrile in a pentamethylcyclopentadienyl complex of iridium, i.e., $Cp^*Ir(CO)(\eta^2\text{-}p\text{-}NCC_6H_4Cl)$, has been characterized by its X-ray structure and ν(CN) absorption at ca. 1780 cm^{-1}, but no ^{13}C or N NMR parameters for the nitrile ligand have been published.[19] Compounds **1a–c** did not, however, exhibit any IR absorption band between 1600 and 2500 cm^{-1} that we can assign to ν(CN) of a side-bonded ligand.

(b) Cationic Carbonyl Phosphine Complexes $[Cp^*Re(CO)(PR_3)(N_2Ar)]^+$. The nitrile complexes **1** are valuable for the synthesis of derivatives in which the nitrile is substituted by another ligand. As an example, MeLi reacts with **1a** to give the neutral methyl complex $Cp^*Re(CO)(Me)(p\text{-}N_2C_6H_4OMe)$. Thus, good yields of the cationic phosphine complexes $[Cp^*Re(CO)(PR_3)(p\text{-}N_2C_6H_4OMe)]^+$ (**2a–f**) were obtained by reaction of the acetonitrile complex **1a** with the respective phosphine in acetone at room temperature (eq 2). In all the cases, the

$$[Cp^*Re(CO)(NCMe)(p\text{-}N_2C_6H_4OMe)][BF_4] \xrightarrow{PR_3} \underset{\mathbf{2a\text{-}f}}{[Cp^*Re(CO)(PR_3)(p\text{-}N_2C_6H_4OMe)][BF_4]} \quad (2)$$

compounds were isolated as orange-red solids, soluble in the majority of polar organic solvents and insoluble in hexane and ether. For comparison, an attempt to synthesize the triphenylphosphine complex **2d** by direct reaction of $[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ with an excess of PPh_3 in acetone failed. The only organometallic product isolated was the dicarbonyl triphenylphosphine complex $Cp^*Re(CO)_2(PPh_3)$.[20,21] A similar reaction was observed in the case of $[CpRe(CO)_2(N_2Ar)]^+$ with PPh_3, where $CpRe(CO)_2(PPh_3)$ and $[Ph_3PNNAr][BF_4]$ were identified.[12]

All **2a–f** exhibited in the IR spectrum in CH_2Cl_2 a very strong terminal ν(CO) band in the 1965–1940 cm^{-1} region and one strong and broad band at about 1680 cm^{-1} assigned to ν(NN). The ν(NN) absorption showed the expected isotopic shift to lower wavenumber in going from **2a** to **2a**-$^{15}N_\alpha$ [$\Delta\nu$(NN) = 35 cm^{-1}] and from **2e** to **2e**-$^{15}N_\alpha$ [$\Delta\nu$(NN) = 39 cm^{-1}] in CH_2Cl_2 solution. The relative electronic properties of the phosphine ligands are revealed more strongly by changes in ν(CO) than in ν(NN), and the values of ν(CO) follow the order $P(OCH_2)_3CMe > PPh_3 > P(n\text{-}Bu)_3 \approx PMe_3 > PCy_3$. The ^1H NMR spectra were exactly those expected; similarly, the ^{31}P NMR spectra showed a single resonance in the normal region for a coordinated phosphine. The ^{13}C and ^{15}N NMR spectra were recorded for $PR_3 = PMe_3$ (**2a**) and $P(OMe)_3$ (**2e**). The ^{13}C NMR shows that the replacement of one carbonyl in the parent dicarbonyl cation $[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)]^+$ by a phosphorus ligand leads to a deshielding of the carbonyl carbon resonance for the remaining CO ligand. Within the phosphorus containing complexes a small downfield shift of $\delta(^{13}CO)$ occurs in the PMe_3 complex **2a** (δ 201.24) compared with the trimethyl phosphite complex **2e** (δ 199.01). A comparable shift has been observed in several other systems containing carbonyl and phosphorus ligands L in, e.g., $Ni(CO)_3L$[22] and $CpMn(CO)_2L$.[23]

This above trend also occurs in the $^{15}N_\alpha$ resonance of the diazenido ligand in the ^{15}N NMR spectra, where $\delta(N_\alpha)$ occurs at −7.32 in $[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)]^+$, at δ −1.97 in the $P(OMe)_3$ complex, and at δ −0.64 in the PMe_3 complex. The values of the coupling constants to phosphorus ($^2J_{PN}$) of 3.5 and 3.0 Hz for **2a**-$^{15}N_\alpha$ and **2e**-$^{15}N_\alpha$, respectively, are comparable with those observed in other phosphine complexes with dinitrogen and related ligands, i.e., *cis*-$Mo(PMe_2Ph)_4(^{15}N_2)_2$ ($^2J_{PN}$ = 5.2 Hz),[24] *trans*-$W(^{15}N_2)(dppe)_2$ ($^2J_{PN}$ = 2.0 Hz),[24] and *trans*-$[WBr\{^{15}N_2(Et)H\}(dppe)_2]Br$ ($^2J_{PN}$ = 5.0 Hz).[25] The ^{14}N NMR spectrum of the trimethylphosphine complex **2a** exhibited a broad resonance at δ −1.9 assigned to N_α, which agrees well with the ^{15}N NMR spectrum of **2a**-$^{15}N_\alpha$. A second ^{14}N resonance observed at δ −126 is assigned to N_β. FAB mass spectra showed the unfragmented cation as the molecular peak except for the cyclohexylphosphine complex **2c** for which the FAB MS could not be observed. No fragments corresponding to loss of CO and PR_3 were observed.

(c) Dinitrogen Complexes. The dinitrogen complexes $Cp^*Re(CO)(PR_3)(N_2)$ (**3a–f**) were synthesized by reacting the respective cationic aryldiazenido complex $[Cp^*Re(CO)(PR_3)(p\text{-}N_2C_6H_4OMe)][BF_4]$ (**2a–f**) with an excess of *t*-BuLi (eq 3). In the synthesis of the parent complex

$$\underset{\mathbf{2a\text{-}f}}{[Cp^*Re(CO)(PR_3)(p\text{-}N_2C_6H_4OMe)][BF_4]} \xrightarrow[\text{THF, 60 °C}]{t\text{-BuLi}} \underset{\mathbf{3a\text{-}f}}{Cp^*Re(CO)(PR_3)(N_2)} \quad (3)$$

$Cp^*Re(CO)_2(N_2)$ from the aryldiazenido complex $[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ the *t*-BuLi may be replaced by $NaBH_4$.[2] This is not possible in the case of the phosphine complexes **2**, assuming that the results obtained with **2a** and **2e** are typical, since we observed that reaction instead proceeded cleanly to give the known[3] hydrido complex $Cp^*Re(CO)(H)(p\text{-}N_2C_6H_4OMe)$ by displacement of the phosphine ligand.

The mechanism for the conversion of the coordinated $[N_2Ar]^+$ group to N_2 by *t*-BuLi is not known. When the reaction was followed by IR spectroscopy, no evident intermediate could be detected, but a second product was formed along with the dinitrogen complex which has spectroscopic properties that agree with formulation as the hydrazido(2−) complex (see below). The direct reaction

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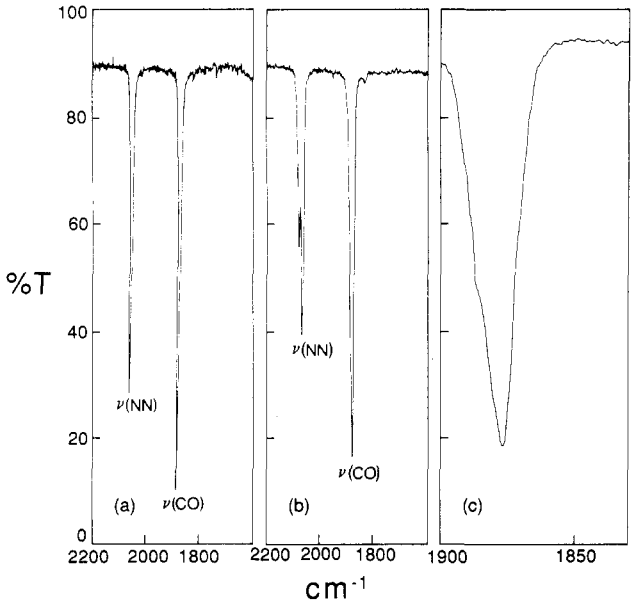

Figure 1. IR spectra (hexane; 1600–2200 cm^{-1} region) of (a) $Cp^*Re(CO)(PMe_3)(N_2)$ (**3a**), (b) $Cp^*Re(CO)\{P(OMe)_3\}(N_2)$ (**3e**), and (c) expanded view of ν(CO) for **3e** showing the asymmetric structure of the absorption band.

of $Cp^*Re(CO)_2(N_2)$ with PR_3, in the case of PPh_3 (and presumably the other phosphines also), does not give $Cp^*Re(CO)(PR_3)(N_2)$. No reaction occurs at room temperature in diethyl ether; upon photolysis in THF, $Cp^*Re(CO)_2(PPh_3)$ results.

The new dinitrogen complexes **3a–f** are very soluble in the majority of organic solvents. As solids, they can be exposed to air for short periods of time without appreciable deterioration and can be stored indefinitely at low temperature (−15 °C) under N_2; solutions are more sensitive to air. In the IR spectra, ν(NN) is observed as a strong absorption in the 2091–2030 cm^{-1} region. The assignment of ν(NN) has been confirmed by ^{15}N isotopic substitution at N_α in **3a** and **3e**. Both ν(NN) and ν(CO) decrease as the phosphine is varied from $P(OCH_2)_3CMe$, $P(OMe)_3$, PPh_3, $P(n\text{-}Bu)_3$, PMe_3 to PCy_3.

The ν(NN) absorption of the triphenylphosphine (**3d**) and trimethyl phosphite (**3e**) dinitrogen complexes occurs as *two* closely spaced bands in nonpolar organic solvents such as hexane and cyclohexane. In **3d** the strong band at 2058 cm^{-1} is accompanied by a medium absorption at *lower* wavenumber, 2045 cm^{-1}. In **3e** the strong band at 2066 cm^{-1} is accompanied by a medium intensity band occurring at higher wavenumber, 2078 cm^{-1} (Figure 1). Exactly the same pattern is observed in **3e**-$^{15}N_\alpha$, but shifted by 34 cm^{-1}. Thus, both absorptions are shifted to lower wavenumber, and on this basis both must be assigned to ν(NN). Variable-temperature IR studies using solutions of **3e** in pentane showed that the relative peak heights of these components decreased from 0.73:1 at 20 °C to 0.5:1 as the temperature was lowered to −100 °C. The relative heights in cyclohexane at room temperature and +60 °C showed no significant change. In the ν(CO) region the complexes show a single, very strong absorption between 1878 and 1856 cm^{-1}. However, on close inspection, the bands for **3d** and **3e** appear to contain a second unresolved ν(CO) absorption which appears as a shoulder. This is illustrated in Figure 1 for **3e**. This shoulder became less distinct in **3e** as the temperature was lowered from +20 to −100 °C in pentane.

The secondary ν(NN) absorptions might be accounted for either as a result of the presence of an impurity having ν(NN) in the same region as the phosphine complex

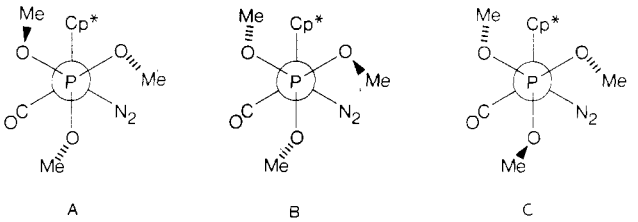

Figure 2. Possible conformational isomers of $Cp^*Re(CO)\{P(OMe)_3\}(N_2)$ (**3e**).

(possibilities might be $Cp^*Re(PR_3)_2(N_2)$ or $Cp^*Re(PR_3)(N_2)_2$) or because of the presence of a second isomer or conformer. The presence of an impurity can be eliminated since repeated crystallization of both complexes did not alter their IR spectra. Furthermore, the ^1H, ^{13}C, and ^{31}P NMR spectra of these complexes show the presence of only a single compound. These results suggest that the secondary ν(NN) and (less distinct) ν(CO) absorptions occur because isomers or conformers are present in solution for these dinitrogen complexes, but not for the others.

The literature on carbonyl phosphine and carbonyl phosphite metal complexes contains several examples of the occurrence of additional ν(CO) absorptions[26–31] that have been attributed to the presence of two conformational isomers in solutions. If we are correct, the complexes **3d** and **3e** appear to provide the first documented examples where conformational effects have been observed in the ν(NN) vibrations of dinitrogen complexes.

The most closely comparable carbonyl phosphine complexes that have been found to display this effect (i.e., examples containing the CpM(CO) fragment with $P(OMe)_3$ or PPh_3 coligands) are $(C_5H_4Me)Fe(CO)\{P(OMe)_3\}I$ and $(C_5H_4Me)Fe(CO)(PPh_3)I$.[29] The former exhibited ν(CO) absorptions at 1978 and 1966 cm^{-1} in *n*-heptane solution with an intensity ratio of 0.49:1, which changed, on cooling to −80 °C, to 0.29:1. For $(C_5H_4Me)Fe(CO)(PPh_3)I$, the ν(CO) values in *n*-heptane solution were 1961 and 1955 cm^{-1} in a ratio 1:0.8.

Considering first the $P(OMe)_3$ ligand, this has been shown by crystallography for a wide range of complexes to adopt a "two down–one up" arrangement of the methyl groups.[26] For $Ru(CO)_4\{P(OMe)_3\}$ it was shown that the asymmetry observed in the solid state is also maintained, on the IR time scale, in solution since the equatorial CO groups give rise to two ν(CO) absorptions.[26]

A similar arrangement of "two down–one up" methyl groups in **3e** would theoretically give rise to three different conformers which are shown in Newman projections in Figure 2. If all three different conformational isomers for complex **3e** were present in significant amounts in solution, ideally three different ν(NN) absorptions (and three ν(CO) absorptions) would be expected. The fact that only two ν(NN) absorptions occur may be understood if the absorption for one of the conformers is obscured, or, more likely, if one conformer (probably C) is disfavored by steric hindrance (in this case, that of two methyls with the bulky Cp* group). The "caged phosphite" complex **3f** was synthesized deliberately to provide further evidence that we are observing a conformational effect. In $P(OCH_2)_3CMe$

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Table I. Nitrogen NMR Parameters for Aryldiazenido and Dinitrogen Ligands[a]

compound	δ(15N)		δ(14N)	
	N_α	N_β	N_α	N_β
$[CpRe(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$[b,c]	−16.99		−16.1	−125.5
$[CpRe(CO)_2(N_2C_6H_5)][BF_4]$[c,d]		−125.1	e	e
$[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$[b]	−7.32		−6.7	−123.0
$[Cp^*Re(CO)_2(N_2C_6H_5)][BF_4]$[d]		−118.50	−8.5	−118.0
$[Cp^*Re(CO)(NCMe)(p\text{-}N_2C_6H_4OMe)][BF_4]$ (**1a**)[b]	−6.09		−6.9	−135.1
$[Cp^*Re(CO)(PMe_3)(p\text{-}N_2C_6H_4OMe)][BF_4]$ (**2a**)[b]	−0.64[f]		−1.9	−126.0
$[Cp^*Re(CO)\{P(OMe)_3\}(p\text{-}N_2C_6H_4OMe)][BF_4]$ (**2e**)[b]	−1.97[g]		e	e
$CpRe(CO)_2(N_2)$[c,h]	−121.12	−58.18	e	e
$Cp^*Re(CO)_2(N_2)$[h]	−110.97	−28.13	−110.9	−26.1
$Cp^*Re(CO)(PMe_3)(N_2)$[b]	−90.70		−90.2	−29.94
$Cp^*Re(CO)\{P(OMe)_3\}(N_2)$[b]	−98.20		−98.3	−30.5

[a] Measured in acetone/acetone-d_6, referenced to external $MeNO_2$; ^{15}N NMR spectra are for ^{15}N-enriched samples (96%). [b] ^{15}N-enriched at N_α only. [c] Supplied by Dr. C. F. Barrientos-Penna. [d] ^{15}N-enriched at N_β only. [e] Not measured. [f] J_{PN} = 3.5 Hz. [g] J_{PN} = 3.0 Hz. [h] Equimolar mixture of $^{15}N_\alpha$ and $^{15}N_\beta$ singly enriched species (see text).

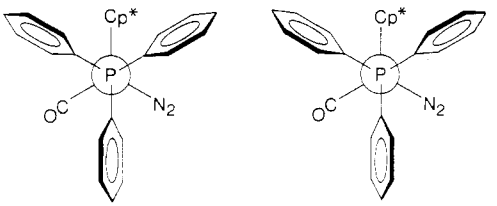

Figure 3. Possible conformational isomers of $Cp^*Re(CO)(PPh_3)(N_2)$ (**3d**).

the methylenes cannot adopt a "two down–one up" arrangement but are necessarily "three-up", and only one conformer of **3f** exists. In agreement ν(NN) and ν(CO) for **3f** occurred as single absorptions.

Turning to the PPh_3 ligand, the conformational effects that have been observed previously have been attributed to restricted rotation of the phenyl groups about the phosphorus–carbon bond.[28-31] The phenyl rings of the PPh_3 ligand can adopt a "propeller-like" conformation which may be right- or left-handed as shown in Figure 3 for $Cp^*Re(CO)(PPh_3)(N_2)$ (**3d**). These two conformers are suggested to be responsible for the observed two ν(NN) absorptions and the asymmetry observed in ν(CO) for **3d**.

The ^1H NMR spectra of these compounds show no unusual features. In general, a single resonance or a doublet with very small coupling to phosphorus ($J_{PH} \approx 0.7$ Hz) is observed for the Cp* groups. In the ^{31}P NMR spectrum a single resonance is observed in all the cases.

In the ^{13}C NMR spectra the replacement of one carbonyl in $Cp^*Re(CO)_2(N_2)$ by a phosphorus ligand PR_3 produces a low-field shift of the carbon resonance of the remaining CO group. This trend is similar to that mentioned above for the aryldiazenido precursors and follows the same order of PR_3 ligands.

Two of the phosphine compounds (**3a** and **3e**) along with $Cp^*Re(CO)_2(N_2)$ were also studied by ^{14}N and ^{15}N NMR. In the ^{14}N NMR spectra the dicarbonyl and the PMe_3 (**3a**) and $P(OMe)_3$ (**3e**) complexes all exhibited two broad resonances at about δ −90 to −110 and δ −28 to −30 assigned to N_α and N_β, respectively (Table I). For the phosphine complexes, the assignment was confirmed by recording the ^{15}N NMR spectra of **3a**-$^{15}N_\alpha$ and **3e**-$^{15}N_\alpha$, and in both cases a sharp line, with no measurable coupling to phosphorus, was observed in almost exactly the same position as one of the ^{14}N resonances allowing it to be assigned unequivocally to N_α. The positions of the N_α and N_β resonances are in the region observed in other studies of dinitrogen complexes by ^{15}N NMR,[11,24,32,33] but it should be pointed out that this is the first time that these assignements of N_α and N_β chemical shifts have been based, unequivocally, on *selective* labeling of the N_α position rather than on the magnitude of coupling constants.

An effect similar to the ^{13}C shift just mentioned is also observed in the N_α resonance of the N_2 ligand in the ^{14}N or ^{15}N NMR spectra. By contrast, the resonance for N_β remains essentially unchanged. Varying the electron density on the metal evidently produces smaller changes in δ(N_β) than those observed in δ(N_α), in agreement with previous results for a wide range of dinitrogen complexes.[32,33]

The IR and combined ^{15}N and ^{14}N NMR spectra obtained for **3a** and **3e** show unequivocally that the dinitrogen ligand is end-on (η^1) coordinated in these complexes. Without the results from the ^{14}N NMR spectrum, the observation of a single signal in the ^{15}N NMR spectrum of each of the singly ^{15}N-labeled compounds **3a**-$^{15}N_\alpha$ and **3e**-$^{15}N_\alpha$ would not be sufficient to distinguish between static coordination $Re\text{–}^{15}N_\alpha\text{–}^{14}N_\beta$ and a rapid exchange of the type

$$Re\text{–}^{15}N_\alpha\text{–}^{14}N_\beta \rightleftarrows Re\text{–}^{14}N_\alpha\text{–}^{15}N_\beta$$

which would result in a ^{15}N signal at the average chemical shift for N_α and N_β. The close correspondence of the N_α resonances in both the ^{15}N and ^{14}N spectra, the large chemical shift separation between the N_α and N_β resonances in the ^{14}N spectrum, and the absence of a signal in the position expected for N_β in the ^{15}N spectrum of the singly labeled compounds show that there is negligible incorporation of ^{15}N at the β-position and negligible exchange under these experimental conditions for these phosphine complexes. In agreement, a hexane solution of **3a**-$^{15}N_\alpha$ showed no observable IR absorptions for $\nu(^{14}N^{14}N)$ when pressurized with $^{14}N_2$ at 2000 psi over 24 h.

In stark contrast to these results, the ^{15}N spectrum of the *singly* ^{15}N-labeled dicarbonyl complex $Cp^*Re(CO)_2(N_2)$ exhibited *two* ^{15}N resonances of equal intensity; these were in the same positions as the two ^{14}N resonances for the N_α and N_β sites in the unlabeled complex (Table I). Thus, for this dicarbonyl complex there is present an equimolar mixture of $Re\text{–}^{15}N_\alpha\text{–}^{14}N_\beta$ and $Re\text{–}^{14}N_\alpha\text{–}^{15}N_\beta$ molecules, which was not the case for **3a** and **3e**, even though the precursor aryldiazenido complexes were all specifically ^{15}N-labeled at N_α only. This could result from (i) a slow-exchange process in the dicarbonyl dinitrogen complex occurring through either dissociation–recombination or an intramolecular process via an η^2-bonded intermediate (eq

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4) or (ii) scrambling of the ^{15}N label at some point in the

$$Re-{}^{15}N\equiv{}^{14}N \rightleftharpoons Re-{}^{15}_{14}\!\!\parallel_{N} \rightleftharpoons Re-{}^{14}N\equiv{}^{15}N \quad (4)$$

synthesis, i.e., during the transformation of the [$^{15}N_\alpha$]-aryldiazenido complex to the dinitrogen complex.[34]

A sample of the equimolar mixture of $Cp^*Re(CO)_2(^{15}N^{14}N)$ and $Cp^*Re(CO)_2(^{14}N^{15}N)$ in hexane was examined for dissociative exchange with atmospheric $^{14}N_2$ by measuring the ν(NN) intensities at 2124 cm^{-1} [$\nu(^{14}N^{14}N)$] and 2091 cm^{-1} [$\nu(^{15}N^{14}N)$ and $\nu(^{14}N^{15}N)$; see below]. After 24 h at 500 psi of N_2 the relative intensity of the 2124 cm^{-1} absorption was 1.1% (corrected for residual ^{14}N isotopic abundance); this increased to 2.7% after a further 24 h at 1500 psi and then to 3.5% after 5 days at 2000 psi. We conclude that slow dissociative exchange of N_2 occurs under pressure. However, the IR spectrum of a sample of the ^{15}N-labeled compound showed negligible incorporation of $^{14}N_2$ when stored as an acetone solution under 1 atm of $^{14}N_2$ for 8 months. These results do not support a dissociation–recombination mechanism for the ^{15}N scrambling. In order to test for an intramolecular rearrangement process (eq 4), a sample of the equimolar mixture of $Cp^*Re(CO)_2(^{15}N^{14}N)$ and $Cp^*Re(CO)_2(^{14}N^{15}N)$ was examined for ^{15}N magnetization transfer from the N_α position to the N_β position in a ^{15}N NMR experiment. No observable magnetization transfer (5% upper limit) was observed during the delay time (5 s) before spectral aquisition. This, of course, does not rule out the possibility that exchange does indeed occur at a much slower rate. We have not yet been able to construct suitable experiments to examine the distribution of the ^{15}N signal in the sample during (or immediately following) the synthesis.

To summarize, in the case of $Cp^*Re(CO)_2(N_2)$ *but not the phosphine complexes* **3a** and **3e** scrambling of the ^{15}N label equally between the N_α and N_β sites occurs (either by intramolecular exchange or via the reaction mechanism) so that equimolar amounts of the $^{15}N_\alpha$- and $^{15}N_\beta$-labeled molecules result. All these complexes were prepared by the same procedure, i.e., by reacting *t*-BuLi with either the cationic dicarbonyl or carbonyl phosphine aryldiazenido complex labeled specifically at N_α. For labeled $Cp^*Re(CO)_2(N_2)$ the synthesis using $NaBH_4$ was also used with identical results. As reported previously,[2] the IR spectrum of singly ^{15}N-labeled $Cp^*Re(CO)_2(N_2)$ exhibits a single sharp absorption at 2091 cm^{-1} (2 cm^{-1} resolution, hexane solution) for ν(NN). At the time of that report, the ^{15}N NMR evidence for scrambling of the label had not been obtained, so with hindsight two absorptions corresponding to ν(NN) for $Re-{}^{15}N\equiv{}^{14}N$ and $Re-{}^{14}N\equiv{}^{15}N$ should have been observed. We conclude that these absorptions are coincident at this resolution. A similar result has been reported for *trans*-$RhCl(N_2)(PEt_3)_2$, where the $^{15}N_\alpha$- and $^{15}N_\beta$-labeled compounds synthesized from $^{15}N^{14}N$ both exhibited ν(NN) at the same position at 2 cm^{-1} resolution.[35] Preliminary results obtained for $CpRe(CO)_2(N_2)$ indicate that scrambling of the ^{15}N label occurs similarly in this compound also, when synthesized[1] from the corresponding [$^{15}N_\alpha$]aryldiazenido complex by reaction with NaI or $NaBH_4$. Further work directed toward determining the extent and origin of nitrogen scrambling in these types of dinitrogen compounds is in progress.

Further characterization of these dinitrogen complexes was obtained from their mass spectra. In all the cases, the molecular ion was observed as a weak peak and the base peak was the loss of the dinitrogen ligand ($M - 28^+$); this was confirmed by observing the loss of ^{15}NN, i.e., $(M - 29)^+$ from **3a**-$^{15}N_\alpha$ and **3d**-$^{15}N_\alpha$ as well as the parent dicarbonyl $Cp^*Re(CO)_2(^{15}N^{14}N)$.

Triphenylphosphine did not displace the dinitrogen ligand in $Cp^*Re(CO)_2(N_2)$, or in **3a** and **3e**, after stirring for 1 day at room temperature in ether solution; however, for $CpRe(CO)_2(N_2)$ the N_2 ligand was completely displaced by PPh_3 in 6 h under similar conditions.

As stated earlier, *t*-BuLi is effective in converting the aryldiazenide ligand in both the dicarbonyl complex $[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)]^+$ and the carbonyl phosphine complexes $[Cp^*Re(CO)(PR_3)(p\text{-}N_2C_6H_4OMe)]^+$ to the dinitrogen ligand in $Cp^*Re(CO)(L)(N_2)$ (L = CO, PR_3). The same result is obtained for the dicarbonyl complex by using $NaBH_4$, but in the case of the carbonyl phosphine complexes $NaBH_4$ cannot be used because it gives instead the hydrido complex $Cp^*Re(CO)(H)(p\text{-}N_2C_6H_4OMe)$. These are further examples of reagents able to convert specific rhenium or manganese aryldiazenido complexes into dinitrogen complexes that we have discovered since our initial observations with halides.[1,36] In the case of $NaBH_4$, there is evidence that the dinitrogen complex is formed by way of an aryldiazene intermediate.[2,37] Presently available results regarding the *t*-BuLi reactions are not sufficiently detailed to allow a coherent picture of the mechanism to be drawn, but at this point it is possible to make some comparisons with earlier results that we obtained when examining the reactions of organolithium reagents with the related *cyclopentadienyl* rhenium dicarbonyl complexes $[CpRe(CO)_2(N_2Ar)][BF_4]$. Then, it was observed not only that the dinitrogen complex was formed but also that the hydrazido(2–) complexes $CpRe(CO)_2[NN(R')Ar]$ and the acyl complexes $CpRe(CO)(COR')(N_2Ar)$ were obtained competitively, depending on the nature of R′ for R′ = Me, *n*-Bu, and Ph.[37] In the present case, for pentamethylcyclopentadienyl (Cp*) complexes, the acyl derivatives $Cp^*Re(CO)(COR')(N_2Ar)$ or $Cp^*Re(PR_3)(COR')(N_2Ar)$ have never been observed to be formed in reactions with either R′Li = MeLi or *t*-BuLi.

From the reaction of the dicarbonyl $[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ and MeLi in hexane at room temperature the hydrazido(2–) complex $Cp^*Re(CO)_2[NN(Me)(p\text{-}C_6H_4OMe)]$ was isolated in low yield and characterized by IR, ^1H NMR, and MS. IR evidence was obtained for a similar complex formed by using *t*-BuLi under the same conditions. In both cases a small amount of the dinitrogen complex was also formed. When the reaction with *t*-BuLi was carried out in THF at 60 °C, only a small amount of the hydrazido(2–) complex was observed (by IR). The major product was the dinitrogen complex. To demonstrate that the formation of the dinitrogen complex does not occur through decomposition of the hydrazido(2–) complex, the complex $Cp^*Re(CO)_2[NN(Me)(p\text{-}C_6H_4OMe)]$ was boiled in THF in the presence and in the absence of *t*-BuLi; in neither case was the dinitrogen complex observed. This clearly indicates that the formation of the dinitrogen complex and the hydrazido(2–) complexes in the reaction with alkyllithium reagents occurs independently, and the relative amounts of the dinitrogen and hy-

(34) The ^{15}N spectrum of $Cp^*Re(CO)_2(N_2)$ is also possibly accountable if each molecule is instead doubly labeled; i.e., it is $Cp^*Re(CO)_2(^{15}N^{15}N)$. This was disproved by mass spectroscopy and is not in accord with the method of synthesis (from singly labeled aryldiazenido complex) or the absence of $^{15}N^{15}N$ coupling.

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drazido(2–) complexes formed depend on the solvent and temperature.

Reactions of the cationic carbonyl phosphine diazenido complexes **2** with alkyllithium reagents seem to follow the same behavior. For example, with *t*-BuLi at 60 °C in THF solution the corresponding dinitrogen complex $Cp^*Re(CO)(PR_3)(N_2)$ **3** was always the major product.[38] However, the IR spectra of the crude products showed, in addition to ν(NN) and ν(CO) of the dinitrogen complex, a weak or medium absorption at about 1800 cm^{-1} which can be ascribed similarly to ν(CO) of the corresponding hydrazido(2–) complexes $Cp^*Re(CO)(PR_3)[p\text{-}NN(t\text{-}Bu)C_6H_4OMe]$. These species could not be isolated since they decomposed in the process of purification of the dinitrogen complex by column chromatography. Reactions of the trimethyl- or triphenylphosphine diazenido complex **2a** or **2d** with MeLi in THF, but at room temperature, produced a red solution which contained the hydrazido(2–) species in about 80% conversion (by IR), with the rest being the dinitrogen complex. However, these products were too unstable to isolate. Nevertheless, decomposition of these hydrazido(2–) complexes in hexane or $CDCl_3$ solution did not increase the amount of dinitrogen complex initially present. This is similar to the behavior already observed in the dicarbonyl system with alkyllithiums and is independent of the presence of CO or phosphine ligand in the precursor cationic aryldiazenido complex; in neither case is the hydrazido(2–) complex a precursor to the dinitrogen complex. GC and GC–MS analyses of the reaction of the trimethylphosphine complex **2a** with *t*-BuLi in THF at 60 °C indicated the presence of several organic products. Only anisole was positively identified from the analyses. None of the remaining products corresponded to *p-tert*-butylanisole, which is to be the expected product if the dinitrogen complex is formed by direct nucleophilic attack at the ipso carbon of the aromatic ring. Therefore, this pathway seems to be ruled out.

(38) *n*-BuLi in THF at 60 °C works well also.

In summary, the limited evidence presently available seems to suggest that when BH_4^- is used, the reaction with $[Cp^*Re(CO)_2(N_2Ar)]^+$ proceeds with the formation of the diazene complex $Cp^*Re(CO)_2(NHNAr)$ which subsequently decomposes to the dinitrogen complex and ArH.[2,37] Remarkably, the substitution of one CO by a phosphine ligand appears to block this reaction, as none of either the corresponding diazene or dinitrogen complex is observed, and instead the reaction proceeds cleanly to form the hydrido complex $Cp^*Re(CO)(H)(N_2Ar)$ by displacement of the phosphine.

When *t*-BuLi is used, the evidence indicates that a hydrazido(2–) ligand is capable of being formed but that this is not an intermediate in the formation of the dinitrogen complex. The mechanism of this reaction is still far from being understood, but since anisole is observed in the reaction also, it seems likely that a radical mechanism is involved.

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Registry No. **1a**, 94405-88-6; **1a**-$^{15}N_\alpha$, 117119-90-1; **1b**, 117119-86-5; **1c**, 117119-88-7; **2a**, 101835-38-5; **2a**-$^{15}N_\alpha$, 117119-94-5; **2b**, 117119-76-3; **2c**, 117119-78-5; **2d**, 117119-80-9; **2e**, 117119-82-1; **2e**-$^{15}N_\alpha$, 117119-96-7; **2f**, 117119-84-3; **3a**, 101835-36-3; **3a**-$^{15}N_\alpha$, 117119-97-8; **3b**, 117119-70-7; **3c**, 117119-71-8; **3d**, 117119-72-9; **3e**, 117119-73-0; **3e**-$^{15}N_\alpha$, 117119-98-9; **3f**, 117119-74-1; PhIO, 536-80-1; $[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$, 92786-90-8; $[Cp^*Re(CO)_2(p\text{-}^{15}NNC_6H_4OMe)][BF_4]$, 117119-92-3; NC-*n*-Pr, 109-74-0; NC-*i*-Pr, 78-82-0; PMe_3, 594-09-2; $P(n\text{-}Bu)_3$, 998-40-3; PCy_3, 2622-14-2; PPh_3, 603-35-0; $P(OMe)_3$, 121-45-9; $P(OCH_2)_3CMe$, 1449-91-8; $Cp^*Re(CO)_2[p\text{-}NN(Me)C_6H_4OMe]$, 117119-99-0; $Cp^*Re(CO)_2[p\text{-}NN(t\text{-}Bu)C_6H_4OMe]$, 117144-54-4; $Cp^*Re(CO)_2N_2$, 92787-15-0; $Cp^*Re(CO)(H)(p\text{-}N_2C_6H_4OMe)$, 94405-83-1; $Cp^*Re(CO)(Me)(p\text{-}N_2C_6H_4OMe)$, 117120-00-0.