1,3,7,9-decatetraene (90%), 6-vinyl-1,3,7-octatriene (10%), and THF-insoluble, black cluster compounds. The addition of a small excess of $CuBr\cdot Me_2S$ and a large excess of tributylphosphine with respect to **1a** is essential for a successful selective addition reaction with carbonyl compounds as described in the text. Acetone, isobutanal, or 4-methyl-3-penten-2-one (3 mmol) then was added to the solution at −78 °C, and the mixture was stirred at 10 °C for 2 h. After the mixture was quenched with aqueous HCl, the product was distilled.

**Registry No.** **1a**, 75150-96-8; **1b**, 83573-32-4; **2a**, 93531-53-4; **2b**, 75135-87-4; **2c**, 93531-54-5; **2d**, 93531-55-6; **2f**, 93531-56-7; **2g**, 93531-57-8; **3a**, 93531-58-9; **3b**, 75135-84-1; **3c**, 93531-59-0; **3d**, 93531-60-3; **3e**, 93531-61-4; **3f**, 93531-62-5; **3g**, 93531-63-6; **4**, 83573-33-5; **5a**, 93531-64-7; **5b**, 93531-65-8; **5c**, 93531-67-0; **5d**, 93531-68-1; **6**, 93531-66-9; **7**, 34865-75-3; **8**, 93531-69-2; **10a**, 93531-70-5; **10b**, 93531-71-6; **10c**, 93564-62-6; **10d**, 93531-72-7; **10e**, 93531-73-8; **11**, 93531-91-0; **12**, 93531-92-1; **15a**, 93531-74-9; **15b**, 93531-75-0; **15c**, 93531-76-1; **15d**, 93531-77-2; **15e**, 93531-78-3; **15f**, 93531-79-4; **15g**, 93531-80-7; **16a**, 93531-81-8; **16b**, 93531-82-9; **16c**, 93531-83-0; **16d**, 93531-84-1; **16e**, 93531-85-2; **16f**, 93531-86-3; **17**, 93531-97-6; **18**, 93531-94-3; **19**, 93531-96-5; **20**, 93531-87-4; **21**, 93531-88-5; **22**, 93531-50-1; **23**, 93531-90-9; **24**, 93531-52-3; $C_5H_7CuPBu_3$, 93531-51-2; $(C_2H_5)_2CO$, 96-22-0; $(i\text{-}C_3H_7)_2CO$, 565-80-0; $t\text{-}C_4H_9(CH_3)CO$, 75-97-8; $CH_3CHO$, 75-07-0; $i\text{-}C_3H_7CHO$, 78-84-2; $(CH_3)_2C{=}CHCOCH_3$, 141-79-7; $(CH_3)_2C{=}CHCOOC_2H_5$, 638-10-8; $C_5H_8MgBr$, 93531-89-6; $(CH_3)_2CO$, 67-64-1; HCl, 7647-01-0; cyclohexanone, 108-94-1; cyclohex-2-enone, 930-68-7; 1,3,7,9-decatetraene, 32509-35-6; 2,4,6,8-decatetraenyl potassium, 93531-93-2; 2,4,6,8-decatraen-1,10-diyldipotassium, 93531-95-4; 6-vinyl-1,3,7-octatriene, 33629-84-4; acetic acid, 64-19-7; (*E*,*E*)-1,3-pentadien-1,5-diylbis(trimethylsilane), 83573-51-7.

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# Reactions of the Cationic Rhenium Aryldiazenido Complexes $[(\eta\text{-}C_5H_5)Re(CO)_2(N_2Ar)]^+$ and $[(\eta\text{-}C_5Me_5)Re(CO)_2(N_2Ar)]^+$. Monocarbonyl Derivatives with Halide, Isocyanate, Carbamoyl (Carboxamido), and Alkoxycarbonyl Ligands

Carlos F. Barrientos-Penna, A. Hugo Klahn-Oliva, and Derek Sutton*

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

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Reactions of the dicarbonylrhenium aryldiazenido cations $[CpRe(CO)_2(N_2Ar)]^+$ (1) and $[Cp^*Re(CO)_2(N_2Ar)]^+$ (2) ($Cp = \eta\text{-}C_5H_5$, $Cp^* = \eta\text{-}C_5Me_5$, Ar = aryl) with some nucleophiles are described, leading to monocarbonyl aryldiazenido complexes of the general type $CpReX(CO)(N_2Ar)$ and $Cp^*ReX(CO)(N_2Ar)$, with X = Cl, Br, I, NCO, $CO_2R$ (R = alkyl), $CONH_2$, CONHMe, and $CONMe_2$. Some examples of analogous reactions of the manganese complex $[MeCpMn(CO)_2(N_2Ar)]^+$ ($MeCp = \eta\text{-}C_5H_4Me$) are also included. Solid-state or solution reactions of 1 or 2 with alkali halides are quite dependent on the experimental conditions, the halide, and the $\eta^5$-arene. Under appropriate conditions all examples of $CpReX(CO)(N_2Ar)$ and $Cp^*ReX(CO)(N_2Ar)$ with X = Cl, Br, or I can be isolated, but $CpRe(CO)_2(N_2)$, $CpRe(CO)_2X_2$ (X = Br, I), and $Cp^*Re(CO)_2X_2$ (X = Br, I) may also be formed. The isocyanate complexes $CpRe(NCO)(CO)(N_2Ar)$ and $Cp^*Re(NCO)(CO)(N_2Ar)$ are formed from 1 or 2 with $NCO^-$, $N_3^-$, or $N_2H_4$. Alkoxycarbonyl complexes $CpRe(CO_2R)(CO)(N_2Ar)$ and $Cp^*Re(CO_2R)(CO)(N_2Ar)$ are formed by using $OMe^-$ or $[HB(OCHMe_2)_3]^-$ and carbamoyl complexes $CpRe(CONR_2)(CO)(N_2Ar)$ or $Cp^*Re(CONR_2)(CO)(N_2Ar)$ ($R_2 = H_2$, HMe, $Me_2$) by using $NH_3$, $MeNH_2$, or $Me_2NH$. Where similar manganese complexes form, they are generally much less stable than the rhenium ones, and the tendency to form the dinitrogen complex $MeCpMn(CO)_2(N_2)$ in the manganese reactions is much greater.

## Introduction

In previous publications we described the synthesis of the cyclopentadienyl[1] ($Cp = \eta\text{-}C_5H_5$) and pentamethylcyclopentadienyl[2] ($Cp^* = \eta\text{-}C_5Me_5$), rhenium aryldiazenido complexes $[CpRe(CO)_2(N_2Ar)][BF_4]$ (**1**) and $[Cp^*Re(CO)_2(N_2Ar)][BF_4]$ (**2**) (Ar = aryl). These cations display a rich chemistry, and thus far we have concentrated on reactions by which the aryldiazenido ligand in **1** is transformed into aryldiazene, arylhydrazido(2−), arylhydrazido(1−), and dinitrogen analogues[1,3] and on the remarkably stable hydroxycarbonyl and carboxylate complexes of the type $CpRe(CO)(N_2Ar)(COOH)$ and $[CpRe(CO)(N_2Ar)(CO_2)]^-$ (Cp = Cp or Cp*) formed by $OH^-$ attack at a CO group in compounds **1** and **2**.[2,4] The latter are examples of a wider range of monocarbonyl derivatives of the type $CpReX(CO)(N_2Ar)$ and $Cp^*ReX(CO)(N_2Ar)$ that may be accessed from the dicarbonyl cations **1** and **2**. Some of these are now described in this paper for X = Cl, Br, I, NCO, COOR (R = alkyl), $CONMe_2$, CONHMe, and $CONH_2$. The hydrides $CpReH(CO)(N_2Ar)$ and $Cp^*ReH(CO)(N_2Ar)$ have been discussed elsewhere.[2,4] Some examples of corresponding compounds synthesized from the (methylcyclopentadienyl)manganese complex $[MeCpMn(CO)_2(N_2Ar)][BF_4]$ (**3**) ($MeCp = \eta\text{-}C_5H_4Me$)[5] are also included here. The reaction of **3** with alkali halides to give the dinitrogen complex $MeCpMn(CO)_2(N_2)$ has been described previously.[5]

## Results

**(a) Halides.** A remarkable solid-state reaction was observed to occur when $[Cp^*Re(CO)_2(N_2Ar)][BF_4]$ (**2**, Ar

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(1) Barrientos-Penna, C. F.; Einstein, F. W. B.; Jones, T.; Sutton, D. *Inorg. Chem.* **1982**, *21*, 2578.

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(3) Barrientos-Penna, C. F.; Campana, C. F.; Einstein, F. W. B.; Jones, T.; Tracey, A. S.; Sutton, D. *Inorg. Chem.* **1984**, *23*, 363.

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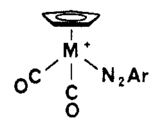
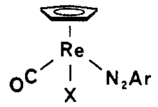
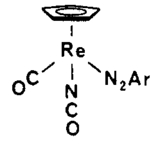
0276-7333/85/2304-0367$01.50/0



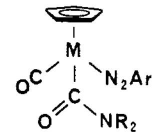
| | M | Ring |
|---|---|---|
| 1 | Re | Cp |
| 2 | Re | Cp* |
| 3 | Mn | $C_5H_4Me$ |



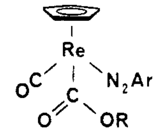
| | X | Ring |
|---|---|---|
| 4 | Cl,Br,I | Cp |
| 5 | Cl,Br,I | Cp* |



| | Ring |
|---|---|
| 6 | Cp |
| 7 | Cp* |



| | M | Ring | $R_2$ |
|---|---|---|---|
| 8 | Re | Cp | $H_2$, $Me_2$, MeH |
| 9 | Re | Cp* | $H_2$, $Me_2$, MeH |
| 10 | Mn | $C_5H_4Me$ | $H_2$, $Me_2$ |



| | R | Ring |
|---|---|---|
| 11 | Me, *i*-Pr | Cp |
| 12 | Me, *i*-Pr | Cp* |

= *p*-$C_6H_4OMe$) was ground up with solid KCl, KBr, or KI and heated at about 95 °C. In each instance, the new monocarbonyl halocomplex Cp*ReX(CO)($N_2Ar$) (**5**) was produced (where X = Cl, Br, I). In the case of the latter two halides, some of the dicarbonyl dihalide Cp*Re-$(CO)_2Br_2$ or Cp*Re$(CO)_2I_2$ was also formed. The diiodide has been synthesized previously,[6] but we are not aware of any report of the dibromide prior to this work. The dichloride is evidently still unreported.[7a] No formation of the dinitrogen complex[8] Cp*Re$(CO)_2(N_2)$ was observed in these reactions. Subsequently, we found reaction in THF–water to be a convenient solution procedure for the synthesis and isolation of these monocarbonyl halides.

The reactions of [CpRe$(CO)_2(N_2Ar)$][$BF_4$] (**1**, Ar = *p*-$C_6H_4OMe$) with solid KCl and KBr at 95 °C likewise gave the corresponding monocarbonyl complexes CpReCl-(CO)($N_2Ar$) and CpReBr(CO)($N_2Ar$). Reactions carried out in acetone were slightly different in that KBr furnished *cis*- and *trans*-CpRe$(CO)_2Br_2$ and CpRe$(CO)_2(N_2)$ in addition to CpReBr(CO)($N_2Ar$), but KCl once again afforded solely CpReCl(CO)($N_2Ar$).[7b] Reactions of KI in either acetone or the solid state afforded *trans*-CpRe$(CO)_2I_2$ and CpRe$(CO)_2(N_2)$ but no CpReI(CO)($N_2Ar$). The latter compound was, however, isolated and characterized along with the diiodide from a reaction carried out in water–THF.

These new monocarbonyl halides CpReX(CO)($N_2Ar$) (**4**) and Cp*ReX(CO)($N_2Ar$) (**5**) are orange-red or red solids with spectroscopic properties fully expected for the monomeric 18-electron structures illustrated, in which the $N_2Ar$ ligand is singly bent and is a three-electron donor. In the IR, $\nu$(CO) and $\nu$(NN) occur near 1950 and 1645 $cm^{-1}$ for **4** and near 1925 and 1630 $cm^{-1}$ for the more electron-rich Cp* analogues **5**. The mass spectra show them to be mononuclear in the vapor phase and to fragment by the loss of a single CO group and/or the aryldiazenide ligand at an early stage. In addition to the synthesis described here, we have found these monohalides to occur during some of our other investigations of rhenium aryldiazenide chemistry. In particular, the carboxylate [Cp*Re-(CO)($N_2Ar$)($CO_2$)]$^-$ (Ar = *p*-$C_6H_4OMe$) was found[2] to yield **5** (X = Cl or Br) when extracted with $CHCl_3$ or $CHBr_3$, in about 50% yield. Similarly, the hydride in Cp*ReH-(CO)($N_2Ar$) is replaced by halogen in these solvents.[2]

The stereochemistry of the dicarbonyl dihalides observed in this work is assigned on the basis of their IR spectra. The $\nu$(CO) positions and relative intensities observed for CpRe$(CO)_2Br_2$ and CpRe$(CO)_2I_2$ indicate the presence of both cis and trans isomers[9] in the former but only the trans isomer in the latter.[10] The compounds Cp*Re$(CO)_2Br_2$ and Cp*Re$(CO)_2I_2$ have IR spectra with the higher wavenumber band ($\nu_{sym}$(CO)) more intense than the lower one ($\nu_{as}$(CO)) and appear, therefore, to be the cis isomers.[11] No isomerization occurred on refluxing these in acetone.

**(b) Isocyanate Complexes.** The monocarbonyl isocyanate complexes CpRe(NCO)(CO)($N_2Ar$) (**6**) and Cp*Re(NCO)CO($N_2Ar$) (**7**) were synthesized from the dicarbonyl cations **1** and **2**, respectively, using either KNCO, $NaN_3$, or $N_2H_4$. The direct reaction with cyanate ion in acetone at room temperature gave the product in excellent yield in the case of **2**, but the corresponding reaction for the Cp analogue [CpRe$(CO)_2$(*p*-$N_2C_6H_4OMe$)]$^+$ was rather less efficient. Here, the use of azide ion is the preferred method. We presume that the mechanisms of these reactions are analogous to those that have been proposed[12] for the very similar reactions of [CpFe$(CO)_3$]$^+$ with $NCO^-$, $N_3^-$, and $N_2H_4$ leading to CpFe(NCO)$(CO)_2$, namely, that in the case of $N_3^-$ and $N_2H_4$, at least, they likely involve initial attack of the nucleophile at a coordinated carbonyl carbon atom. In the $N_2H_4$ reaction with [CpRe$(CO)_2$(*p*-$N_2C_6H_4OMe$)]$^+$ we observed spectroscopic evidence for an intermediate that we assume to be the carbazoyl complex CpRe($CONHNH_2$)-(CO)(*p*-$N_2C_6H_4OMe$). Spectroscopic evidence for a similar carbazoyl intermediate was also observed[12] for [CpFe-$(CO)_3$]$^+$.

**(c) Carbamoyl Complexes.** The cations [CpRe-$(CO)_2(N_2Ar)$]$^+$ (**1**) and [Cp*Re$(CO)_2(N_2Ar)$]$^+$ (**2**) react with liquid ammonia and with the neat amines $MeNH_2$ or $Me_2NH$ at low temperature to produce the corresponding carbamoyl complexes CpRe($CONR_2$)(CO)($N_2Ar$) (**8**) and Cp*Re($CONR_2$)(CO)($N_2Ar$) (**9**) where $R_2$ = $H_2$, MeH, or $Me_2$. No reaction occurs with pure tertiary amines $NMe_3$ or $NEt_3$. Similar, but less stable manganese carbamoyls **10** were obtained from [MeCpMn$(CO)_2$(*o*-$N_2C_6H_4CF_3$)]-[$BF_4$] (**3**) by using $NH_3$ or $Me_2NH$. All these compounds have the expected analytical, spectroscopic and chemical properties[13] and are analogous to the known nitrosyls CpM($CONR_2$)(CO)(NO) for M = Mn and Re.[14] In particular, the parent dicarbonyl cation is regenerated by

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[6] Hoyano, J. K.; Graham, W. A. G. *J. Chem. Soc., Chem. Commun.* **1982**, 27.

[7] (a) Cp*Re$(CO)_2X_2$ (X = Cl, Br) have been synthesized recently in our laboratory from the reaction of Cp*Re$(CO)_2N_2$ with HCl and HBr and their full characterization will be described in a subsequent paper.[8] (b) CpRe$(CO)_2Cl_2$ is currently unknown. The reaction of CpRe$(CO)_3$ with $Cl_2$ has been described to give [CpRe$(CO)_3$Cl]Cl and [CpRe(CO)$Cl_2$]-[Re$(CO)_4Cl_2$] (see ref 10).

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[11] Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; pp 1074–1076.

[12] Angelici, R. J.; Busetto, L. *J. Am. Chem. Soc.* **1969**, *91*, 3197.

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reaction with 2 equiv of mineral acid (e.g., HCl) as in eq 1. The carbamoyl $CpRe(CONH_2)(CO)(N_2Ar)$ was also produced from 1 and $NaNH_2$ in acetone at room temperature.

$$CpRe(CONR_2)(CO)(N_2Ar) + 2HCl \rightarrow [CpRe(CO)_2N_2Ar]^+ + R_2NH_2^+ + 2Cl^- \quad (1)$$

In the case of manganese complex 3, the corresponding reaction with $NaNH_2$ produced $MeCpMn(CONH_2)(CO)(o\text{-}N_2C_6H_4CF_3)$ only if carried out at low temperature (−30 °C). No dinitrogen complex was then formed, unless the solution was warmed to room temperature. A corresponding reaction at room temperature was rapid and produced only $MeCpMn(CO)_2(N_2)$. In keeping with these results, acetone solutions of the carbamoyls are unstable (especially so for manganese). The rhenium carbamoyl complexes generate the dinitrogen complexes $CpRe(CO)_2(N_2)$ and $Cp^*Re(CO)_2(N_2)$ only slowly at room temperature, but the manganese complex rapidly produces $MeCpMn(CO)_2(N_2)$, along with paramagnetic products which render the $^1H$ NMR unobtainable (peaks are extremely broadened). Room-temperature ESR spectra of the solid carbamoyl or its acetone solution gave a broad, six-line spectrum of Mn(II).

The IR spectra of $CpRe(CONH_2)(CO)(N_2Ar)$ and $Cp^*Re(CONH_2)(CO)(N_2Ar)$ in THF show only the expected single $\nu$(CO) absorption. However, replacing the THF by $CH_2Cl_2$ produces spectra with weak additional $\nu$(CO) absorptions in the positions associated with the cations $[CpRe(CO)_2(N_2Ar)]^+$ and $[Cp^*Re(CO)_2(N_2Ar)]^+$. This sequence is reversible. There is no evidence for any contamination with starting compounds 1 or 2 used in the syntheses. The IR spectra thus suggest that in $CH_2Cl_2$ the carbamoyls partly undergo autodissociation according to eq 2. This is directly analogous to the weak autodissociation previously observed and discussed[2] for the corresponding hydroxycarbonyls $CpRe(CO)(N_2Ar)(COOH)$ and $Cp^*Re(CO)(N_2Ar)(COOH)$. The N-substituted and N,N-disubstituted carbamoyls show similar behavior.

$$CpRe(CONH_2)(CO)(N_2Ar) \rightleftarrows [CpRe(CO)_2(N_2Ar)]^+[NH_2]^- \quad (2)$$

The $^1H$ NMR of the *N*-methylcarbamoyl complexes $CpRe(CONHMe)(CO)(N_2Ar)$ and $Cp^*Re(CONHMe)(CO)(N_2Ar)$ show NH resonances at $\delta$ 5.57 and 5.35, respectively, in $CDCl_3$, and the methyl resonance remains unchanged as a sharp doublet in each ($J_{HNCH}$ = 4.8 Hz for the Cp and Cp* compounds over the temperature range −40 to +50 °C). These chemical shifts and coupling constants [$\delta$; $J$] agree well with previously reported values for *N*-methylcarbamoyls $CpW(CO)_3(CONHMe)$ [6.0; 5 Hz],[15] $Re(CO)_5(CONHMe)$ [5.45; 5.4 Hz],[16] $Mn(CO)_3(PPh_3)_2(CONHMe)$ [4.85; 4.2 Hz],[17] and $Re(CO)_3(PPh_3)_2(CONHMe)$ [4.40; 4.2 Hz].[17]

The ambient temperature $^1H$ NMR spectrum ($CDCl_3$) of each of the *N,N*-dimethylcarbamoyls $CpRe(CONMe_2)(CO)(N_2Ar)$ and $Cp^*Re(CONMe_2)(CO)(N_2Ar)$ shows a single broad resonance for the methyl groups, but on cooling to −20 and 0 °C, respectively, this splits into two equal intensity singlets from magnetically distinct methyls. Nonequivalent methyl groups have been observed in other *N,N*-dimethylcarbamoyl complexes of Mo, W, Pt, and Pd and rationalized by restricted rotation about the CN bond.[13,15] Since the rhenium complexes here possess a chiral center at the metal, equivalence of the methyl groups implies that CN bond rotation must be accompanied by inversion at the nitrogen atom or else that the $CNMe_2$ skeleton must be coplanar. $^1H$ NMR spectra of the (*N,N*-dimethylcarbamoyl)manganese complex were unobtainable as a result of decomposition to paramagnetic Mn(II) products in organic solvents.

**(d) Alkoxycarbonyl Complexes.** The rhenium cations $[CpRe(CO)_2(N_2Ar)]^+$ (1, Ar = $p\text{-}C_6H_4Me$, $p\text{-}C_6H_4OMe$, or $p\text{-}C_6H_4NEt_2$) and $[Cp^*Re(CO)_2(N_2Ar)]^+$ (2, Ar = $p\text{-}C_6H_4OMe$) reacted with 1 equiv of NaOMe in methanol to produce the neutral methoxycarbonyl derivatives $CpRe(COOR)(N_2Ar)$ (11, R = Me) and $Cp^*Re(COOR)(CO)(N_2Ar)$ (12, R = Me). The IR spectra of 11 and 12 exhibit the expected single terminal $\nu$(CO) band in the 1900 cm$^{-1}$ region and a series of overlapping strong broad bands in the region 1550–1650 cm$^{-1}$ that contain the $\nu$(NN) and $\nu$(C=O) vibrational modes. Isotopic $^{15}N$ substitution at the metal-bound nitrogen in 11 caused a change in the pattern but only small shifts of most of these bands to lower wavenumber, indicating that $\nu$(NN) is strongly coupled to other vibrational modes in this region, and an unambiguous assignment is not possible on present data. The $^1H$ NMR data are as expected, the resonance from the COOMe group appearing near $\delta$ 3.5. These complexes react in the expected manner with HCl or $HBF_4$ to regenerate the parent dicarbonyl cations.

Alkoxycarbonyl compounds were also isolated in good yield from reactions of the cations 2 with tris(isopropoxy)borohydride that were carried out initially with the intention of delivering a hydride. In methanol, a near quantitative yield of the methoxycarbonyl complex was recovered. More interestingly, in THF this borohydride delivered an isopropoxide group to the cation with the production of the isopropoxycarbonyl complex $Cp^*Re(COOCHMe_2)(CO)(N_2Ar)$, easily recognized by the diastereotopic methyl groups in the $^1H$ NMR.

No alkoxycarbonyl compounds have so far been observed in reactions of the manganese complex 3 with alkoxides such as NaOMe. Instead, the dinitrogen complex $MeCpMn(CO)_2(N_2)$ is formed.[5]

## Discussion

The reactions of the cations 1 and 2 with the nucleophiles $Cl^-$, $Br^-$, $I^-$, $CNO^-$, $N_3^-$, $N_2H_4$, $NH_3$, $NH_2Me$, $NHMe_2$, and $OMe^-$ that are reported here all have a superficial similarity in that the products 4–12 are neutral monocarbonyl complexes of general formula Cp(or Cp*)$ReX(CO)(N_2Ar)$. However, they are of two types and involve either the substitution of a CO group in 1 and 2 (as in the case of X = halide) or the transformation of a CO group into the ligand X (e.g., where X = COOMe, $CONH_2$, etc.). The mechanism of these reactions are not known with equal certainty, and especially in the case of the halides the complexity suggests that more than one is probably involved.

The production of the monocarbonyl carbamoyl (8 and 9) or alkoxycarbonyl (11 and 12) complexes from the dicarbonyl cations $[CpRe(CO)_2(N_2Ar)]^+$ (1) and $[Cp^*Re(CO)_2(N_2Ar)]^+$ (2) evidently results from straightforward attack of the nucleophile on the relatively electrophilic carbonyl carbon atoms in these cations.[12] The manner in which the carbamoyls $CpRe(CONH_2)(CO)(N_2Ar)$ and $Cp^*Re(CONH_2)(CO)(N_2Ar)$ are then able to generate the dinitrogen complexes $CpRe(CO)_2(N_2)$ and $Cp^*Re(CO)_2(N_2)$ when they decompose is a matter of some interest but one about which presently we have no mechanistic information. Conversion of the corresponding manganese carbamoyl complex $MeCpMn(CONH_2)(CO)(o\text{-}N_2C_6H_4CF_3)$ to $MeCpMn(CO)_2(N_2)$ occurs even more readily, and here we

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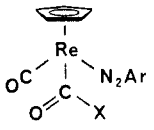
(17) Angelici, R. J.; Brink, R. W. *Inorg. Chem.* **1973**, *12*, 1067.

can observe a close correspondence with the reaction of $[MeCpMn(CO)_2(o\text{-}N_2C_6H_4CF_3)]^+$ with $NaNH_2$, which gives the carbamoyl at low temperature but gives the dinitrogen complex at room temperature. Both the manganese and rhenium carbamoyl complexes show increased stability when N-substituted or N,N-disubstituted carbamoyl ligands are present, and these tend not to give the dinitrogen complexes.

Alkoxycarbonyl ligands are stable in the rhenium complexes **11** and **12**, and these complexes do not readily decompose to the dinitrogen complexes. But in the reaction of methoxide with the manganese cation **3**, no evidence for a methoxycarbonyl analogue was observed; instead, only the dinitrogen complex resulted.

At this point it is worth noting that possible products which were *not* observed in these reactions were the monocarbonyl amides or alkoxides Cp(or Cp*)MX(CO)($N_2Ar$) (where X or OR or $NR_2$) resulting from CO substitution. These could have arisen either from direct displacement of a CO group in **1**, **2**, or **3** by the alkoxide or amine nucleophile or from a rearrangement of the carbamoyls or alkoxycarbonyls **8–12**, whereby the adjacent CO group is labilized and the OR or $NR_2$ group migrates intramolecularly to the metal. This point is made because such compounds are analogous to the products Cp(or Cp*)ReX(CO)($N_2Ar$) (**4** and **5**) that *are* observed when the nucleophile is a halide. Conversely, the halocarbonyl analogues of **8**, **9**, **11**, and **12**, namely, Cp(or Cp*)Re(COX)(CO)($N_2Ar$) of structure I, which might equally have been formed by attack of halide on a CO group, are *not* observed as stable products. It nevertheless seems to us that the intermediacy of I must be considered[18] when proposing possible mechanisms for the formation of **4** or **5**.



I ; X = Cl, Br, I

Whatever may be the route to complexes **4** and **5**, the reactions of the rhenium dicarbonyl cations **1** and **2** with alkali halides in total are clearly much more complex than this, and the major dependence of the products on the solvent, the oxidizability of the halide, and the nature of the $\eta^5$-arene group is an important factor yet to be determined.

## Experimental Section

All reactions were carried out under dry $N_2$ in Schlenk apparatus connected to a switchable double manifold providing low vacuum or nitrogen. Solvents were dried by conventional methods, distilled under nitrogen, and used immediately. Infrared spectra were measured by using Perkin-Elmer Model 983 or 599B instruments, usually in $CaF_2$ cells (solutions). $^1H$ NMR spectra were measured by using Varian XL-100 (100-MHz) or Bruker WM-400 (400-MHz) Fourier transform spectrometers. Mass spectra and GC mass spectra were obtained by using a Hewlett-Packard Model 5985 mass spectrometer, capable of providing both electron-impact (EI) and fast-atom bombardment (FAB; Phrasor Scientific Inc. accessory) ionizing methods. GC separations were obtained on SE-30 or OV-1 capillary or packed columns using a Hewlett-Packard 5880A gas chromatograph. Microanalyses were performed by M. K. Yang and J. Hewitt of the S.F.U. Microanalytical Laboratory.

Rhenium aryldiazenido complexes $[CpRe(CO)_2(N_2Ar)][BF_4]$ (**1**, Ar = $p\text{-}C_6H_4OMe$, $p\text{-}C_6H_4Me$, $p\text{-}C_6H_4NEt_2$, $o\text{-}C_6H_4CF_3$, or $2,6C_6H_3Me_2$)[1] and $[Cp^*Re(CO)_2(N_2Ar)][BF_4]$ (**2**, Ar = $p\text{-}C_6H_4OMe$)[2] were synthesized as described previously, as was the similar manganese complex $[MeCpMn(CO)_2(N_2Ar)][BF_4]$ (**3**, Ar = $o\text{-}C_6H_4CF_3$).[5] Anhydrous $MeNH_2$, $Me_2NH$ (Linde Specialty Gases), and hydrazine (Matheson, Coleman and Bell) were used as received.

**Halogen Complexes. Reaction of $[CpRe(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ with KBr. (i) In Acetone.** To a solution of the rhenium complex (40 mg, 0.076 mmol) in acetone (10 mL) was added a stoichiometric amount of solid KBr (9.1 mg), and the mixture was stirred at room temperature. An IR spectrum of this solution after 1 h showed very little reaction, probably due to the insolubility of KBr in acetone, but after addition of excess of finely ground solid KBr and stirring a further 12 h the reaction was completed. GC–MS analysis of this reaction mixture revealed the presence of $BrC_6H_4OCH_3$ (*m/e* 188), $C_6H_5OCH_3$ (*m/e* 108), and $CpRe(CO)_2(N_2)$ (*m/e* 336, 334). The IR spectrum of this solution in the $\nu$(CO) region was complicated, indicating the presence of several metal carbonyl compounds. Evaporation of the acetone under vacuum yielded a red brownish residue that was extracted with hexane. The IR spectrum of the yellow hexane extract showed only the presence of the dinitrogen complex ($\nu$(CO) 1974 (vs), 1920 (vs), $\nu$(NN) 2145 (vs) $cm^{-1}$).[5] The remaining residue was dissolved in $CH_2Cl_2$ (deep red color), and its IR spectrum showed that this solution was essentially a mixture of *cis*- and *trans*-$CpRe(CO)_2Br_2$[9] and $CpReBr(CO)(p\text{-}N_2C_6H_4OMe)$ ($\nu$(CO) 1956 (vs), $\nu$(NN) 1644 (vs) $cm^{-1}$). The mass spectrum of this residue showed peaks for $CpRe(CO)_2Br_2$ ($M^+$, $(M - CO)^+$, $(M - 2CO)^+$, $(M - Br)^+$, $(M - CO - Br)^+$, $(M - 2CO - Br)^+$) that agreed perfectly with the spectrum previously reported[19] and peaks for $CpReBr(CO)(p\text{-}N_2C_6H_4OMe)$ (vide infra).

Similar reactions were conducted by using other rhenium aryldiazenide complexes **1**, with Ar = $p\text{-}C_6H_4Me$, $p\text{-}C_6H_4NEt_2$, $o\text{-}C_6H_4CF_3$, or $2,6\text{-}C_6H_4Me_2$ with corresponding results. In each case, the arene and bromoarene were identified to be formed.

**(ii) Solid State.** The solid rhenium compound (50 mg, 0.095 mmol) was fully ground with excess solid KBr. This mixture was heated at 95 °C in an oven. The reaction was much slower compared with the KI one (see below), and it required 24 h for completion. Following the reaction by IR in a KBr pellet showed the formation of $CpReBr(CO)(p\text{-}N_2C_6H_4OMe)$ as the major product, but $CpRe(CO)_2(N_2)$ was not formed under these conditions.

$CpReBr(CO)(p\text{-}N_2C_6H_4OMe)$ was extracted from the solid reaction mixture by $CH_2Cl_2$ and chromatographed on a silica gel column prepared in hexane and eluted with $CH_2Cl_2$–hexane (7:3). Evaporation of the solvent afforded it as an analytically pure red-orange microcrystalline air-stable solid in ca. 80% yield: IR (KBr) $\nu$(CO) 1939 (vs), $\nu$(NN) 1642 (vs), $cm^{-1}$, ($CH_2Cl_2$) $\nu$(CO) 1956 (vs), $\nu$(NN) 1644 (vs) $cm^{-1}$; $^1H$ NMR (acetone-$d_6$) $\delta$ 7.26 (d), 7.04 (d, 4 H, $C_6H_4$), 6.05 (s, 5 H, $C_5H_5$), 3.84 (s, 3 H, $OCH_3$); MS, $M^+$, $(M - CO)^+$, $(M - N_2Ar)^+$, $(M - CO - N_2Ar)^+$, $(M - CO - N_2Ar - Br)^+$. Anal. Calcd for $CpReBr(CO)(p\text{-}N_2C_6H_4OMe)$: C, 31.58, H, 2.43; N, 5.67. Found: C, 31.60; H, 2.46; N, 5.61.

A similar procedure was used also for $[CpRe(CO)_2(p\text{-}N_2C_6H_4Me)][BF_4]$ and the monobromo complex $CpReBr(CO)(p\text{-}N_2C_6H_4Me)$ was obtained as a red-orange microcrystalline air-stable solid in ca. 80% yield: IR (KBr) $\nu$(CO) 1945 (vs), $\nu$(NN) 1643 (vs) $cm^{-1}$, (hexane) $\nu$(CO) 1967 (vs), $\nu$(NN) 1644 (vs) $cm^{-1}$; MS, $M^+$, $(M - CO)^+$, $(M - N_2Ar)^+$, $(M - CO - N_2Ar)^+$, $(M - CO - N_2Ar - Br)^+$. Anal. Calcd for $CpReBr(CO)(p\text{-}N_2C_6H_4Me)$: C, 32.64; H, 2.51; N, 5.86. Found: C, 32.66; H, 2.53, N, 5.81.

**Reaction of $[CpRe(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ with Iodide. (i) In THF–Water.** The rhenium complex (50 mg, 0.095 mmol) was stirred with excess KI in THF–water (1:1; 15 mL) for 5 days. THF was removed under vacuum, and residual water was decanted from the insoluble red solid. The latter was dissolved in THF and chromatographed on a silica column by using THF–hexane (1:3). This did not efficiently separate the products and was followed by TLC on silica gel; eluting with $CH_2Cl_2$–hexane

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[18] This suggestion has a precedent, see, for example: Busetto, L.; Angelici, R. J. *Inorg. Chim. Acta* **1968**, *2*, 391.

[19] Sizoi, V. F.; Nekrasov, Y. S.; Makarov, Y. V.; Kolobova, N. E. *J. Organomet. Chem.* **1975**, *94*, 425.

(1:3) separated a red band of CpReI(CO)(*p*-N$_2$C$_6$H$_4$OMe) in 60% yield and a yellow band of CpRe(CO)$_2$I$_2$ that was identified by comparison of its IR and mass spectra with those previously reported:[6] IR (acetone) 2041 (s), 1980 (vs) cm$^{-1}$, (CH$_2$Cl$_2$) 2046 (s), 1986 (vs) cm$^{-1}$ ($\nu$(CO)); MS, M$^+$, (M − CO)$^+$, (M − 2CO)$^+$, (M − I)$^+$, (M − CO − I)$^+$, (M − 2CO − I)$^+$. GC–MS of the THF volatiles showed predominantly the presence of anisole. For CpReI(CO)(*p*-N$_2$C$_6$H$_4$OMe): mp 134 °C; IR (CH$_2$Cl$_2$, cm$^{-1}$) 1948 (vs) ($\nu$(CO)), 1643 ($\nu$(NN)); $^1$H NMR (CDCl$_3$) $\delta$ 3.83 (s, 3 H, OMe), 5.82 (s, 5 H, Cp), 6.94 (d), 7.28 (d) (4 H, C$_6$H$_4$); MS (EI; based on $^{187}$Re), *m/e* 542 (M$^+$), 514 (M − CO$^+$), 484 (CpReI(N$_2$C$_6$H$_5$)$^+$), 407 (CpReI(CO)$^+$), 379 (CpReI$^+$). Anal. Calcd for CpReI(CO)(*p*-N$_2$C$_6$H$_4$OMe): C, 28.78; H, 2.21; N, 5.16. Found: C, 28.79; H, 2.26; N, 4.98.

**(ii) In Acetone.** The rhenium complex (50 mg, 0.095 mmol) dissolved in acetone (10 mL) was treated with excess of solid NaI, and the mixture was stirred at room temperature for 20 min. The IR spectrum of this solution indicated that reaction was complete and showed the presence of CpRe(CO)$_2$(N$_2$) ($\nu$(CO) 1960 (vs), 1898 (vs), cm$^{-1}$, $\nu$(NN) 2142 (s) cm$^{-1}$) and CpRe(CO)$_2$I$_2$ ($\nu$(CO) 2041 (s), 1980 (vs) cm$^{-1}$). GC–MS analysis of this solution showed the presence of three compounds, anisole *p*-iodoanisole, and CpRe(CO)$_2$(N$_2$); the involatile CpRe(CO)$_2$I$_2$ was not detected in this analysis. Hexane was added to the reaction mixture to precipitate the excess of NaI, which was separated by filtration. The acetone–hexane solution was pumped down just to dryness under vacuum and a dark brown-red solid residue was obtained. Sublimation of this residue under vacuum at room temperature afforded *p*-iodoanisole as a white solid that was identified by $^1$H NMR and MS: $^1$H NMR (CDCl$_3$) $\delta$ 7.56 (d) 6.68 (d, 4 H, C$_6$H$_4$), 3.77 (s, 3 H, OCH$_3$); MS, *m/e* 234 (M$^+$). By increasing the vacuum ($\sim 10^{-6}$ mmHg), a second solid (yellow) was obtained that was identified as CpRe(CO)$_2$(N$_2$): $^1$H NMR (CDCl$_3$) $\delta$ 5.23 (5 H, C$_5$H$_5$); MS, *m/e* 336, 334 (M$^+$); IR as above. Finally, the dark red-brown residue (which did not sublime under these conditions) was identified to contain CpRe(CO)$_2$I$_2$ by IR and MS. (See above.)

Similar reactions were conducted by using other rhenium aryldiazenide complexes 1 with Ar = *p*-C$_6$H$_4$CH$_3$, *p*-C$_6$H$_4$NEt$_2$, *o*-C$_6$H$_4$CF$_3$, and 2,6-C$_6$H$_3$Me$_2$. Results were similar to those just described, and in each case, the arenes and iodoarenes were observed to be formed.

**(iii) Solid State.** A solid sample of the rhenium complex was finely ground with solid KI and then heated in the oven (95 °C) for 5 min. A strong odor of iodoanisole was produced. An IR spectrum of a KI pellet of this heated mixture showed the presence of a large amount of CpRe(CO)$_2$(N$_2$) and a small amount of CpRe(CO)$_2$I$_2$.

The reaction was completed in 15 min. No production of the monocarbonyl [CpReI(CO)(*p*-N$_2$C$_6$H$_4$OCH$_3$)] was observed.

**Reaction of CpRe(CO)$_2$(*p*-N$_2$C$_6$H$_4$OMe)][BF$_4$] with KCl. (i) In Acetone.** To a solution of the rhenium complex (50 mg, 0.095 mmol) in acetone (10 mL) was added excess finely ground solid KCl and the mixture stirred at room temperature for 48 h. An IR spectrum of this solution showed clearly the formation of CpReCl(CO)(*p*-N$_2$C$_6$H$_4$OMe) (which was isolated and characterized as described in reaction ii below), plus a small amount of the tricarbonyl complex CpRe(CO)$_3$. A large amount of unreacted material was also observed. Neither CpRe(CO)$_2$(N$_2$) nor CpRe(CO)$_2$Cl$_2$ were formed under these conditions.

**(ii) Solid State.** A similar procedure to that described for KBr and KI was used. This reaction was even slower compared with KBr. After 24 h heating at 95 °C, a significant amount of the original rhenium complex remained. Again CpReCl(CO)(*p*-N$_2$C$_6$H$_4$OMe) was the major product; no formation of CpRe(CO)$_2$(N$_2$) was observed. The reaction mixture was extracted with CH$_2$Cl$_2$ and this solution chromatographed on a silica gel column prepared in hexane. Elution with CH$_2$Cl$_2$–hexane (7:3) moved an orange band of CpReCl(CO)(*p*-N$_2$C$_6$H$_4$OMe) that was isolated by evaporation of the solvent as a red-orange microcrystalline air-stable solid in ca. 30% yield. Red crystals were obtained from a hexane solution at −12 °C: mp 107–109 °C; IR (KBr) $\nu$(CO) 1936 (vs), $\nu$(NN) 1642 (vs) cm$^{-1}$, (CH$_2$Cl$_2$) $\nu$(CO) 1949 (vs), $\nu$(NN) 1643 (vs) cm$^{-1}$, (hexane) $\nu$(CO) 1963 (vs), $\nu$(NN) 1642 (vs) cm$^{-1}$; $^1$H NMR (acetone-$d_6$): $\delta$ 7.27 (d), 7.07 (d, 4 H, C$_6$H$_4$), 6.07 (s, 5 H, C$_5$H$_5$), 3.88 (s, 3 H, OMe); MS, M$^+$, (M − CO)$^+$, (M − N$_2$Ar)$^+$, (M − CO − N$_2$Ar)$^+$, (M − CO − N$_2$Ar − Cl)$^+$. Anal. Calcd for CpReCl(CO)(*p*-*p*N$_2$C$_6$H$_4$OMe): C, 34.71; H, 2.67; N, 6.23. Found: C, 34.69; H, 2.64; N, 6.22.

**Reaction of [Cp*Re(CO)$_2$(*p*-N$_2$C$_6$H$_4$OMe)][BF$_4$] with KBr. (i) In THF–Water.** The rhenium complex (50 mg, 0.083 mmol) was stirred with excess KBr in THF–H$_2$O (1:1; 15 mL) for 36 h. THF was removed under vacuum, and the slightly yellow water that remained was decanted from the insoluble red solid. The latter was dissolved in THF and placed on a Florisil column (prepared in hexane) and a red fraction eluted with THF–hexane (1:4) to yield Cp*ReBr(CO)(*p*-N$_2$C$_6$H$_4$OMe) (40 mg, 80%; mp 149–151 °C) after evaporation. Next, a yellow fraction was eluted with THF–hexane (2:1) to yield after precipitation with hexane at low temperature, 5–8 mg of Cp*ReO$_3$:[20] IR (CH$_2$Cl$_2$, cm$^{-1}$) 1927 (vs) ($\nu$(CO)), 1628 (s) ($\nu$(NN)), 1592 (m); MS (EI) *m/e* 562, 564, 566 (M$^+$), 534, 536, 538 (M − CO$^+$); $^1$H NMR (CDCl$_3$) $\delta$ 2.06 (s, 15 H, C$_5$Me$_5$), 3.81 (s, 3 H, OMe), 6.90 (d), 7.27 (d, 4 H, C$_6$H$_4$). Anal. Calcd for (C$_5$Me$_5$)ReBr(CO)(*p*-N$_2$C$_6$H$_4$OMe): C, 38.29; H, 3.90; N, 4.96. Found: C, 38.44; H, 3.89; N, 4.71.

**(ii) Solid State.** The rhenium complex (130 mg, 0.22 mmol) was finely ground with solid KBr and the mixture heated at 95 °C for 4 h, by which time all the starting material has reacted (by IR) and strong absorption occurred at 1919 and 1628 cm$^{-1}$ from Cp*ReBr(CO)(*p*-N$_2$C$_6$H$_4$OMe). Extraction with CH$_2$Cl$_2$ then chromatography on silica gel with CH$_2$Cl$_2$–hexane (7:3) moved an orange-red band of Cp*ReBr(CO)(*p*-N$_2$C$_6$H$_4$OMe) (IR 1944, 1631 cm$^{-1}$ in CH$_2$Cl$_2$–hexane). Elution with CH$_2$Cl$_2$ removed a further red-orange fraction containing Cp*ReBr(CO)(*p*-N$_2$C$_6$H$_4$OMe) and Cp*Re(CO)$_2$Br$_2$, which was identified spectroscopically by comparison with an authentic sample:[7a] IR (CH$_2$Cl$_2$, cm$^{-1}$) for Cp*Re(CO)$_2$Br$_2$ 2033 (vs), 1958 (s) ($\nu$(CO)); MS (M$^+$), (M − CO$^+$), (M − 2CO$^+$), (M − Br$^+$), (M − 2CO − Br$^+$).

**Reaction of [Cp*Re(CO)$_2$(*p*-N$_2$C$_6$H$_4$OMe)][BF$_4$] with KCl. (i) In THF–Water.** This was carried out as described for KBr (above). From 50 mg (0.083 mmol) of the rhenium complex, 38 mg of the red solid Cp*ReCl(CO)(*p*-N$_2$C$_6$H$_4$OMe) was obtained (87%); mp 125–127 °C. Only a very small amount of Cp*ReO$_3$[20] was observed to be formed: IR (CH$_2$Cl$_2$, cm$^{-1}$) 1924 (vs) ($\nu$(CO)) 1624 (s) ($\nu$(NN)); MS, *m/e* 518, 520, 522 (M$^+$), 490, 492, 494 (M − CO$^+$); $^1$H NMR (CDCl$_3$) $\delta$ 2.00 (s, 15 H, C$_5$Me$_5$), 3.81 (s, 3 H, OMe), 6.92 (d), 7.29 (d, 4 H, C$_6$H$_4$). Anal. Calcd for (C$_5$Me$_5$)ReCl(CO)(*p*-N$_2$C$_6$H$_4$OMe): C, 41.54; H, 4.23; N, 5.38. Found: C, 41.41; H, 4.15; N, 5.19.

**(ii) Solid State.** This was carried out as described for KBr, but the reaction was much slower and complete disappearance of starting compound was only observed after 12 h at 95 °C; IR bands at 1919 (vs) and 1627 (s) cm$^{-1}$ from Cp*ReCl(CO)(*p*-N$_2$C$_6$H$_4$OMe) were produced.

**Reaction of [Cp*Re(CO)$_2$(*p*-N$_2$C$_6$H$_4$OMe)][BF$_4$] with KI. (i) In THF–Water.** This reaction was carried out as described for KBr (above) using 50 mg (0.083 mmol) of the rhenium complex, to yield Cp*ReI(CO)(*p*-N$_2$C$_6$H$_4$OMe) as a red solid in 80% yield. Elution with THF–hexane (7:3) then removed a small amount (ca. 5 mg) of Cp*Re(CO)$_2$I$_2$ as a yellow band. Then a second yellow compound eluted by using THF and was identified as Cp*ReO$_3$[20] (5 mg). The Cp*Re(CO)$_2$I$_2$ was characterized to be cis by spectroscopy: For Cp*Re(CO)$_2$I$_2$: IR (CH$_2$Cl$_2$, cm$^{-1}$) 2022 (vs) ($\nu_s$(CO)), 1953 (s) ($\nu_{as}$(CO)); MS (EI; based on $^{187}$Re), *m/e* 632 (M$^+$), 604 (M − CO$^+$), 576 (M − 2CO$^+$), 505 (M − I$^+$), 477 (M − CO − I), 449 (M − 2CO − I$^+$); $^1$H NMR (CDCl$_3$) $\delta$ 2.23 (C$_5$Me$_5$). For (C$_5$Me$_5$)ReI(CO)(*p*-N$_2$C$_6$H$_4$OMe): IR (CH$_2$Cl$_2$, cm$^{-1}$) 1928 (vs) ($\nu$(CO)), 1630 (s) ($\nu$(NN)); MS (based on $^{187}$Re), *m/e* 610 (M$^+$), 582 (M − CO$^+$); $^1$H NMR (CDCl$_3$) $\delta$ 2.13 (s, 15 H, C$_5$Me$_5$), 3.81 (s, 3 H, OMe), 6.90 (d), 7.28 (d, 4 H, C$_6$H$_4$). Anal. Calcd for (C$_5$Me$_5$)ReI(CO)(*p*-N$_2$C$_6$H$_4$OMe): C, 35.35; H, 3.60; N, 4.58. Found: C, 35.37; H, 3.73; N, 4.64.

**(ii) Solid State.** This was carried out as described for KBr and KCl, but the reaction was faster then either, and all starting material reacted within 40 min at 95 °C. IR showed the presence of Cp*ReI(CO)(*p*-N$_2$C$_6$H$_4$OMe) (1925 (vs), 1928 (s) cm$^{-1}$) as major product, and some Cp*Re(CO)$_2$I$_2$ ($\nu_{sym}$(CO)) 2013 cm$^{-1}$, $\nu_{asym}$ obsd). Chromatography on silica gel eluting with CH$_2$Cl$_2$–hexane (7:3) eluted first Cp*Re(CO)$_2$I$_2$ and then Cp*ReI(CO)(*p*-N$_2$C$_6$H$_4$OMe), characterized as above.

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[20] Klahn-Oliva, A. H.; Sutton, D. *Organometallics* **1984**, *3*, 1313.

**Preparation of $CpRe(NCO)(CO)(p\text{-}N_2C_6H_4OMe)$. (i) From $[CpRe(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ and KNCO.** The rhenium complex (50 mg, 0.095 mmol) in acetone (10 mL) was stirred for 1 h with KNCO (10 mg, 0.12 mmol) in which time all starting material reacted. The solvent was pumped off and the residue extracted with $CH_2Cl_2$. Chromatography on neutral alumina eluting with $CH_2Cl_2$–hexane (1:3) removed a small amount of the isocyanate complex as a yellow band but most eluted as an orange fraction with $CH_2Cl_2$–acetone (1:1). Recrystallization from ether–pentane gave $CpRe(NCO)(CO)(p\text{-}N_2C_6H_4OMe)$ as orange microcrystals in 30% yield: mp 127 °C; IR ($CH_2Cl_2$, $cm^{-1}$) 2246 (vs) ($\nu$(NCO)), 1948 (vs ($\nu$(CO)), 1642 (s) ($\nu$(NN)); $^1H$ NMR ($CDCl_3$) $\delta$ 3.84 (s, 3 H, OMe), 5.82 (s, 5 H, $C_5H_5$), 6.95 (d), 7.20 (d, 4 H, $C_6H_4$); MS (EI, based on $^{187}Re$), $m/e$ ($M^+$), 429 ($M - CO^+$). Anal. Calcd for $CpRe(NCO)(CO)(p\text{-}N_2C_6H_4OMe)$: C, 36.84; H, 2.63; N, 9.21. Found: C, 36.55; H, 2.64; N, 9.17.

**(ii) From $[CpRe(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ and $NaN_3$.** The rhenium complex (50 mg, 0.095 mmol) was stirred with excess (ca. 15 mg, 0.23 mmol) $NaN_3$ in acetone. In 15 min all had reacted. Acetone was pumped off of the residue extracted with diethyl ether to give a red solution from which the isocyanate complex was obtained by evaporation; yield 40 mg (92%).

**(iii) From $[CpRe(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ and $N_2H_4$.** The rhenium complex (50 mg, 0.095 mmol) was dissolved in $CH_2Cl_2$ and cooled to −70 °C, and $N_2H_4$ was added. No reaction occurred at −70 °C. At room temperature the color changed from yellow to red in 5 min. The IR showed bands at 1941 (vs), 1640 (vs) and 1574 (br, m) $cm^{-1}$ but none for the isocyanate complex. Evaporation of the $CH_2Cl_2$ under vacuum gave a yellow-orange solid insoluble in hexanes. When redissolved in $CH_2Cl_2$, the IR of this solution now exhibited additional bands for the isocyanate complex that grew at the expense of the above spectrum. In 4 days the transformation of the solid was about 90% complete. The intermediate spectrum is probably that of $CpRe(CONHNH_2)(CO)(p\text{-}N_2C_6H_4OMe)$.

**Preparation of $Cp^*Re(NCO)(CO)(p\text{-}N_2C_6H_4OMe)$. (i) From $[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ and KNCO.** The rhenium complex (40 mg, 0.067 mmol) was stirred in acetone with excess KNCO (10 mg, 0.12 mmol) for 30 h. Acetone was pumped off and the residue dissolved in $CH_2Cl_2$. The filtered red solution was chromatographed on silica gel, and the product eluted with $CH_2Cl_2$–hexane (1:1) as an orange fraction. Removal of solvent gave a red solid (32 mg, 0.061 mmol), mp 40 °C, in about 90% yield, characterized as in (iii) below.

**(ii) From $[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ and $NaN_3$.** The rhenium complex (50 mg, 0.083 mmol) in acetone (15 mL) was stirred with excess solid $NaN_3$ (15 mg, 0.23 mmol) for 1 h. The color changed quickly from maroon to brown. Acetone was removed by pumping and the residue dissolved in $CH_2Cl_2$. The filtered solution was chromatographed as above to yield the product as a red solid in 90% yield (40 mg, 0.075 mmol).

**(iii) From $[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ and $N_2H_4$.** Excess $N_2H_4$ was added to a solution of the rhenium complex (50 mg, 0.083 mmol) in $CH_2Cl_2$ (ca. 8 mL) at −78 °C. The color changes from maroon to yellow-orange. The solution was slowly warmed to room temperature, and the product separated by chromatography as above in 95% yield: IR ($CH_2Cl_2$, $cm^{-1}$) 2240 (vs) ($\nu$(NCO)), 1926 (vs) ($\nu$(CO)), 1626 (s) ($\nu$(NN)); IR (hexane, $cm^{-1}$) 2233 (s), 1939 (vs), 1627 (s); MS, $m/e$ 525, 527 ($M^+$), 497, 499 ($M - CO^+$); $^1H$ NMR ($CDCl_3$) $\delta$ 2.08 (s, 15 H, $C_5Me_5$), 3.83 (s, 3 H, OMe), 6.94 (d), 7.25 (d, 4 H, $C_6H_4$). Anal. Calcd for $(C_5Me_5)Re(NCO)(CO),(p\text{-}N_2C_6H_4OMe)$: C, 43.34; H, 4.18; N, 7.98. Found: C, 43.27; H, 4.05; N, 7.80.

**Carbamoyl Complexes. Reaction of $[(MeCp)Mn(CO)_2(o\text{-}N_2C_6H_4CF_3)][BF_4]$ with $NH_3$(l).** Liquid ammonia (ca. 5 mL) was condensed at −50 °C. The solid manganese complex (50 mg, 0.11 mmol) was added and the mixture stirred at this temperature for 15 min. A fast reaction took place, and a brown-orange solid precipitated out of the solution, isolated by decanting the excess of ammonia, and then washed twice with ca. 2 mL of liquid ammonia to remove $NH_4BF_4$. The solid residue was dried, first with a stream of dry nitrogen and then under vacuum. The solid could be handled in air for about 30 min without deterioration, but with longer exposure it decomposed. Solutions in organic solvents were extremely air sensitive: yield 40 mg (0.105 mmol, 96%); IR ($CH_2Cl_2$) 1980 (vs) ($\nu$(CO)), 1665 (vs) ($\nu$(NN)), 1600, 1578, 1558 ($\nu$($CONH_2$)) $cm^{-1}$. Anal. Calcd for $(MeCp)Mn(CONH_2)(CO)(o\text{-}N_2C_6H_4CF_3)$: C, 47.49; H, 3.43; N, 11.08. Found: C, 47.21; H, 3.46; N, 11.25.

**Reaction of $[(MeCp)Mn(CO)_2(o\text{-}N_2C_6H_4CF_3)][BF_4]$ with $HN(CH_3)_2$.** This reaction was carried out in neat $HN(CH_3)_2$; about 5 mL of the secondary amine was condensed at −50 °C. Solid manganese complex (50 mg, 0.11 mmol) was added and the mixture stirred at this temperature for 15 min. A fast reaction took place, and a brown reddish solid precipitated out of the solution. The excess of amine was evaporated under vacuum and the brown-reddish residue was dissolved in $CH_2Cl_2$. Addition of diethyl ether precipitated the ammonium salt $[H_2N(CH_3)_2][BF_4]$, as a white solid which was filtered off. The brown-reddish solution was pumped to dryness affording an oily product, which when washed twice with hexane gave the product as a brown-reddish micro-crystalline solid: yield 95%; IR ($CH_2Cl_2$) 1970 (vs, br) ($\nu$(CO)), 1655 (s, br) ($\nu$(NN)), 1600, 1580 ($\nu$($CONMe_2$)) $cm^{-1}$. Anal. Calcd. for $(MeCp)Mn(CONMe_2)(CO)(o\text{-}N_2C_6H_4CF_3)$: C, 50.12; H, 4.18; N, 10.32. Found: C, 49.89; H, 4.20; N, 10.28%.

**Reaction of $[(MeCp)Mn(CO)_2(o\text{-}N_2C_6H_4CF_3)][BF_4]$ with $NaNH_2$.** To a solution of the manganese complex (50 mg, 0.11 mmol) in acetone (10 mL) was added to stoichiometric amount of solid $NaNH_2$, and the mixture was stirred at room temperature for 15 min. The IR spectrum of the red solution showed the presence of $(MeCp)Mn(CO)_2(N_2)$[5] as the only carbonyl-containing product. When the reaction was carried out at −30 °C, the carbamoyl complex $(MeCp)Mn(CONH_2)(CO)(o\text{-}N_2C_6H_4CF_3)$ was obtained instead and characterized by IR (see above).

**Reaction of $[CpRe(CO)_2(o\text{-}N_2C_6H_4CF_3)][BF_4]$ with $NH_3$(l).** A procedure similar to that described above for the corresponding manganese compound gave the rhenium carbamoyl complex $CpRe(CONH_2)(CO)(o\text{-}N_2C_6H_4CF_3)$ as a golden yellow microcrystalline solid in 97% yield: IR ($CH_2Cl_2$) 1960 (vs) ($\nu$(CO)), 1632 (s) ($\nu$(NN)), 1595, 1574, 1558 ($\nu$($CONH_2$)) $cm^{-1}$. Anal. Calcd for $CpRe(CONH_2)(CO)(o\text{-}N_2C_6H_4CF_3)$: C, 33.87; H, 2.22; N, 8.47. Found: C, 33.92; H, 2.28; N, 8.45.

**Reaction of $[CpRe(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ with $NH_3$(l).** A procedure similar to that above gave the carbamoyl complex $CpRe(CONH_2)(CO)(p\text{-}N_2C_6H_4OMe)$ as a golden yellow microcrystalline solid in 96% yield: IR ($CH_2Cl_2$) 1945 (vs) ($\nu$(CO)), 1641 (s) ($\nu$(NN)), 1586, 1555 ($\nu$($CONMe_2$)) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.19 (d), 6.92 (d, 4 H, $C_6H_4$), 5.78 (s, 5 H, $C_5H_5$), 3.81 (s, 3 H, OMe), $\delta$ ($NH_2$) unobserved. Anal. Calcd for $CpRe(CONH_2)(CO)(p\text{-}N_2C_6H_4OMe)$: C, 36.68; H, 3.06; N, 9.17. Found: C, 36.22; H, 3.11; N, 9.20.

**Reaction of $[CpRe(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ with $H_2NCH_3$.** A procedure similar to that used for the reactions with liquid ammonia gave the carbamoyl complex $CpRe(CONHCH_3)(CO)(p\text{-}N_2C_6H_4OMe)$ as a golden yellow microcrystalline solid in 96% yield and characterized by spectroscopy: IR ($CH_2Cl_2$) 1940 (vs) ($\nu$(CO)), 1640 (s) ($\nu$(NN)) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.22 (d), 6.95 (d, 4 H, $C_6H_4$), 5.79 (s, 5 H, $C_5H_5$), 3.84 (s, 3 H, OMe), 2.84 (d, 3 H, $CH_3$, $J$(HNCH) = 4.8 Hz), 5.57 (s, br, 1 H, NH).

**Reaction of $[CpRe(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ with $HN(CH_3)_2$.** A procedure similar to that used for the reactions with liquid ammonia gave the carbamoyl complex $CpRe(CONMe_2)(CO)(p\text{-}N_2C_6H_4OMe)$ as a golden yellow microcrystalline solid in 98% yield and characterized by spectroscopy: IR ($CH_2Cl_2$) 1942 (vs) ($\nu$(CO)), 1640 (s) ($\nu$(NN)), 1592, 1580 ($\nu$($CONMe_2$)) $cm^{-1}$; $^1H$ NMR (ambient temperature, $CDCl_3$) $\delta$ 7.22 (d), 6.95 (d, 4 H, $C_6H_4$), 5.75 (s, 5 H, $C_5H_5$), 3.84 (s, 3 H, OMe), 3.09 (s, 6 H, $NMe_2$). At −20 °C the $NMe_2$ resonance was split into two similar intensity signals at $\delta$ 3.03 and 3.16.

**Reaction of $[CpRe(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ with $NaNH_2$.** To a solution of the rhenium complex (50 mg, 0.095 mmol) in $CH_2Cl_2$ (10 mL) was added solid $NaNH_2$ (4 mg, 0.11 mmol), and the mixture was stirred at room temperature for 5 min. The color changed from red to yellow-orange. The IR spectrum of this solution showed only the presence of the carbamoyl complex $CpRe(CONH_2)(CO)(p\text{-}N_2C_6H_4OMe)$.

**Preparation of $Cp^*Re(CONH_2)(CO)(p\text{-}N_2C_6H_4OMe)$.** Solid $[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ (50 mg, 0.083 mmol) was added to 5 mL of liquid $NH_3$ at −50 °C. A fast reaction ensued, and the yellow solid that precipitated was washed twice with liquid $NH_3$ to remove $NH_4BF_4$: yield 43 mg (98%); mp 78–80 °C dec. The compound is stable at room temperature under nitrogen but is extremely hygroscopic, and it was difficult to entirely prevent this when performing microanalysis. The best analysis corresponded to the presence of approximately one $H_2O$ per mole: IR ($CH_2Cl_2$) 1929 (s) ($\nu$(CO)), 1624 (s), ($\nu$(NN)), 1584 (m) ($\nu(CONH_2)$) $cm^{-1}$, weak absorptions for $[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)]^+$ at 2053, 1996 and 1738 $cm^{-1}$ are also visible in this solvent; MS (FAB), *m/e* 511, 513 ($M - NH_2^+$); $^1H$ NMR ($CDCl_3$) $\delta$ 2.10 (s, 15 H, $C_5Me_5$), 3.82 (s, 3 H, OMe), 6.93 (d), 7.26 (d, 4 H, $C_6H_4$), weak resonances from $[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)]^+$ were also observed, $\delta$ (NH) was unobserved. Addition of HCl transformed the IR and NMR entirely to that of the parent dicarbonyl cation. Anal. Calcd for $Cp^*Re(CONH_2)(CO)(p\text{-}N_2C_6H_4OMe)\cdot H_2O$: C, 41.75; H, 4.76; N, 7.69. Found: C, 41.63; H, 4.95; N, 7.47.

**Preparation of $Cp^*Re(CONHMe)(CO)(p\text{-}N_2C_6H_4OMe)$.** A solution of $MeNH_2$ in $CH_2Cl_2$ was prepared by extracting aqueous $MeNH_2$ with $CH_2Cl_2$ and drying over $Na_2SO_4$. Addition of $[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ (60 mg, 0.10 mmol) instantaneously resulted in reaction to give, after filtering to remove insoluble $[MeNH_3][BF_4]$ and pumping off solvent, an orange oil, which solidified on further pumping to yield the product as a yellow-orange solid: yield 50 mg (92%); mp 57–59 °C dec; IR ($CH_2Cl_2$), 1925 (br, s) ($\nu$(CO)), 1621 (s) ($\nu$(NN)), 1568 (br, m) ($\nu$(CONHMe)) $cm^{-1}$, weak absorptions from $[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)]^+$ were visible; $^1H$ NMR ($CDCl_3$) $\delta$ 2.09 (s, 15 H, $C_5Me_5$), 2.84 (d, 3 H, NMe), 3.82 (s, 3 H, OMe), 5.35 (vbr, 1 H, NH), 6.93 (d), 7.30 (d, 4 H, $C_6H_4$). Anal. Calcd for $Cp^*Re(CONHMe)(CO)(p\text{-}N_2C_6H_4OMe)$: C, 44.28; H, 4.80; N, 7.75. Found: $C^*Re(CONHMe)(CO)(p\text{-}N_2C_6H_4OMe)$: 44.01; H, 5.01; N, 7.99.

**Preparation of $Cp^*Re(CONMe_2)(CO)(p\text{-}N_2C_6H_4OMe)$.** Liquid $Me_2NH$ was condensed at −50 °C (5 mL), and solid $[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ (60 mg) was added. The reaction mixture was stirred for 1 h and then the orange solution filtered under $N_2$ and pumped until an orange solid formed. The elemental analysis at this stage was correct for a 1:1 mixture of $Cp^*Re(CONMe_2)(CO)(p\text{-}N_2C_6H_4OMe)$ and $[Me_2NH_2][BF_4]$. Anal. Calcd: C, 39.94; H, 5.20; N, 8.10. Found: C, 39.68; H, 5.22; N, 8.00. The mixture was repeatedly extracted with ether and precipitated with pentane to give a yellow-orange solid that gave expected IR and NMR spectra for $Cp^*Re(CONMe_2)(CO)(p\text{-}N_2C_6H_4OMe)$ but unaccountably low carbon analysis: IR ($CH_2Cl_2$, $cm^{-1}$) 1925 (vs) ($\nu$(CO)), 1621 (s) ($\nu$(NN)); $^1H$ NMR ($CDCl_3$, 40 °C) $\delta$ 2.05 (s, 15 H, $C_5Me_5$), 3.08 (s, br, 6 H, $NMe_2$), 3.82 (s, 3 H, OMe), 6.93 (d), 7.35 (d, 4 H, $C_6H_4$). At 0 °C, the $NMe_2$ resonance was split into two peaks of similar intensity at $\delta$ 3.00 and 3.16.

**Alkoxycarbonyl Complexes. Reaction of $[CpRe(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ with $NaOCH_3$.** To a solution of the rhenium complex (50 mg, 0.095 mmol) in methanol (5 mL) was added solid $NaOCH_3$ (6 mg, 0.1 mmol), and the mixture was stirred at room temperature for 15 min. The color changed from red to yellow, and the IR spectrum of this solution showed the presence of the new methoxycarbonyl complex $CpRe(COOCH_3)(CO)(p\text{-}N_2C_6H_4OMe)$. Evaporation of the solvent under vacuum and extraction with $CH_2Cl_2$ afforded it as a microcrystalline orange solid (42 mg, 93%): mp 99–101 °C; IR ($CH_2Cl_2$, $cm^{-1}$) 1948 (vs) ($\nu$(CO)), 1648 (s), 1623, 1592, 1583 ($\nu$(NN) + $\nu(COOCH_3)$); $^1H$ NMR (acetone-$d_6$) $\delta$ 3.54 (s, 3 H, $COOCH_3$), 3.86 (s, 3 H, OMe), 5.97 (s, 5 H, Cp), 7.04 (d), 7.44 (d, 4 H, $C_6H_4$). Anal. Calcd: C, 37.97; H, 3.16; N, 5.90. Found: C, 37.85; H, 3.32; N, 5.94.

**Reaction of $[CpRe(CO)_2(p\text{-}N_2C_6H_4Me)][BF_4]$ with $NaOCH_3$.** A procedure similar to that used above gave the alkoxycarbonyl complex $CpRe(COOCH_3)(CO)(p\text{-}N_2C_6H_4Me)$ as a crystalline yellow solid: IR ($CH_2Cl_2$, $cm^{-1}$) 1952 (vs) ($\nu$(CO)) 1550–1650 (m, cplx) ($\nu$(NN) + $\nu(COOCH_3)$); $^1H$ NMR (acetone-$d_6$) $\delta$ 2.45 (s, 3 H, Me), 3.54 (s, 3 H, $COOCH_3$), 5.99 (s, 5 H, Cp), 7.34 (s, 4 H, $C_6H_4$).

**Reaction of $[CpRe(CO)_2(p\text{-}N_2C_6H_4NEt_2)][BF_4]$ with $NaOCH_3$.** A procedure similar to that used above gave the alkoxycarbonyl complex $CpRe(COOCH_3)(CO)(p\text{-}N_2C_6H_4NEt_2)$ as a microcrystalline red-orange solid: IR ($CH_2Cl_2$, $cm^{-1}$) 1939 (vs) ($\nu$(CO)), 1550–1650 (m, cplx) ($\nu$(NN) + $\nu(COOCH_3)$); $^1H$ NMR (acetone-$d_6$) $\delta$ 1.17 (t, 6 H, $CH_3$), 3.48 (q, 4 H, $CH_2$), 3.52 (s, 3 H, $COOCH_3$), 5.92 (s, 5 H, Cp), 6.78 (d), 7.29 (d, 4 H, $C_6H_4$).

**Preparation of $Cp^*Re(COOCH_3)(CO)(p\text{-}N_2C_6H_4OMe)$.** (a) The rhenium complex $[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ (50 mg, 0.083 mmol) in acetone (10 mL) was treated with $NaOCH_3$ (5 mg, 0.09 mmol) and stirred for 15 min. The color changed quickly from red to yellow. The solvent was removed under vacuum, $CH_2Cl_2$ was added, and the solution was filtered. Addition of hexane gave the product $Cp^*Re(COOCH_3)(CO)(p\text{-}N_2C_6H_4OMe)$ as a golden yellow solid (43 mg) in 95% yield: IR ($cm^{-1}$) 1944 (vs) ($\nu$(CO)), 1643 (m), 1624 (s) ($\nu$(NN) + $\nu(COOCH_3)$ (hexane), 1930 (vs), 1638 (s), 1620 (s) (THF); $^1H$ NMR ($CDCl_3$) $\delta$ 2.08 (s, 15 H, $C_5Me_5$), 3.65 (s, 3 H, $COOCH_3$), 3.81 (s, 3 H, OMe), 6.91 (d), 7.44 (d, 4 H, $C_6H_4$); MS (FAB) *m/e* 511, 513 ($M - OCH_3^+$). Anal. Calcd for $Cp^*Re(COOCH_3)(CO)(p\text{-}N_2C_6H_4OMe)$: C, 44.20; H, 4.60; N, 5.15. Found: C, 43.91; H, 4.64; N, 5.25.

(b) The rhenium complex $[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ (50 mg, 0.083 mmol) in methanol (10 mL) at −78 °C was treated with $K[HB(OCHMe_2)_3]$ (0.08 mL, 1 M in THF) by syringe. IR monitoring showed reaction to be complete in 15 min. The solvent was removed at ambient temperature under vacuum. The orange oily solid residue was extracted with hexane–THF (9:1) and filtered through Celite. Precipitation of a golden yellow solid occurred when the solution was concentrated under vacuum and was completed by cooling to −78 °C; yield 44 mg (98%) of the methoxycarbonyl $Cp^*Re(COOCH_3)(CO)(p\text{-}N_2C_6H_4OMe)$ characterized as above. An analogous synthesis conducted in THF yielded instead the isopropoxycarbonyl complex $Cp^*Re(COOCHMe_2)(CO)(p\text{-}N_2C_6H_4OMe)$ as a yellow solid: mp 107–109 °C dec which was characterized by spectroscopy; IR ($cm^{-1}$) 1944 (vs) ($\nu$(CO)), 1640 (m), 1619 (s) ($\nu$(NN) + $\nu(COOCHMe_2)$) (hexane), 1934 (vs), 1623 (s) ($CHCl_3$), 1930 (vs), 1618 (s) (THF); $^1H$ NMR ($C_6D_6$) $\delta$ 1.29 (d, 3 H), 1.36 (d, 3 H, $CHMe_2$), 1.85 (s, 15 H, $C_5Me_5$), 3.24 (s, 3 H, OMe), 5.52 (app septet, 1 H, $CHMe_2$), 6.83 (d), 7.92 (d, 4 H), $C_6H_4$).

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**Registry No.** 1 (Ar = $p\text{-}C_6H_4OMe$), 81028-27-5; 1 (Ar = $p\text{-}C_6H_4Me$), 81028-25-3; 1 (Ar = $p\text{-}C_6H_4NEt_2$), 81028-31-1; 1 (Ar = $o\text{-}C_6H_4CF_3$), 73838-58-1; 1 (Ar = $2,6\text{-}C_6H_4Me_2$), 81028-33-3; 2 (Ar = $p\text{-}C_6H_4OMe$), 92786-90-8; **3** (Ar = $o\text{-}C_6H_4CF_3$), 73838-50-3; **4** (Ar = $p\text{-}C_6H_4OMe$, X = Br), 92786-91-9; **4** (Ar = $p\text{-}C_6H_4Me$, X = Br), 92786-92-0; **4** (Ar = $p\text{-}C_6H_4OMe$, X = I), 92786-93-1; **4** (Ar = $p\text{-}C_6H_4OMe$, X = Cl), 92786-94-2; **5** (Ar = $p\text{-}C_6H_4OMe$, X = Br), 92786-95-3; **5** (Ar = $p\text{-}C_6H_4OMe$, X = Cl), 92786-96-4; **5** (Ar = $p\text{-}C_6H_4OMe$, X = I), 92786-97-5; 6 (Ar = $p\text{-}C_6H_4OMe$), 92786-98-6; **7** (Ar = $p\text{-}C_6H_4OMe$), 92786-99-7; **8** (Ar = $o\text{-}C_6H_4CF_3$, $R_2$ = $H_2$), 92787-00-3; **8** (Ar = $p\text{-}C_6H_4OMe$, $R_2$ = $H_2$), 92787-01-4; **8** (Ar = $p\text{-}C_6H_4OMe$, $R_2$ = MeH), 92787-02-5; **8** (Ar = $p\text{-}C_6H_4OMe$, $R_2$ = $Me_2$), 92816-64-3; **9** (Ar = $p\text{-}C_6H_4OMe$, $R_2$ = $H_2$), 92787-03-6; **9** (Ar = $p\text{-}C_6H_4OMe$, $R_2$ = MeH), 92787-04-7; **9** (Ar = $p\text{-}C_6H_4OMe$, $R_2$ = $Me_2$), 92787-05-8; **10** (Ar = $o\text{-}C_6H_4CF_3$, $R_2$ = $H_2$), 92787-06-9; **10** (Ar = $o\text{-}C_6H_4CF_3$, $R_2$ = $Me_2$), 92787-07-0; **11** (Ar = $p\text{-}C_6H_4OMe$, R = Me), 92787-08-1; **11** (Ar = $p\text{-}C_6H_4Me$, R = Me), 92787-09-2; **11** (Ar = $p\text{-}C_6H_4NEt_2$, R = Me), 92787-10-5; **12** (Ar = $p\text{-}C_6H_4OMe$, R = Me), 92787-11-6; **12** (Ar = $p\text{-}C_6H_4OMe$, R = *i*-Pr), 92787-12-7; $CpRe(CO)_2(N_2)$, 36543-62-1; *cis*-$CpRe(CO)_2Br_2$, 57195-35-4; *trans*-$CpRe(CO)_2Br_2$, 57194-43-1; $CpRe(CO)_2I_2$, 78295-40-6; $CpRe(CO)_3$, 12079-73-1; $Cp^*Re(CO)_2Br$, 92787-13-8; $Cp^*Re(CO)_2I_2$, 92934-67-3; $CpRe(CONHNH_2)(CO)(p\text{-}N_2C_6H_4OMe)$, 92787-14-9; $(MeCp)Mn(CO)_2(N_2)$, 73838-59-2; $Cp^*Re(CO)_2Cl_2$, 92844-08-1; $Cp^*Re(CO)_2N_2$, 92787-15-0.