15 reveal some of the structural constraints that control this coordination.

Acknowledgment. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation.

Supplementary Material Available: Tables of anisotropic thermal parameters for **22** and analytical data for compounds **1**–**21** (3 pages); a listing of observed and calculated structure factor amplitudes for the X-ray structure of **22** (11 pages). Ordering information is given on any current masthead page.

Cycloaddition of Imines and $\mathrm{Bu^tN{=}O}$ with the Carbyne Complexes $[\mathrm{Cp(CO)_2M{\equiv}CTol}]^+$ (M = Mn, Re)

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The cationic carbyne complex $[\mathrm{Cp(CO)_2Re{\equiv}CTol}]^+$ (**2**) reacts with the imines $\mathrm{PhCH{=}NCH_3}$ and $\mathrm{PhCH{=}N{-}N{=}CHPh}$ to give a net [2 + 2] cycloaddition of the imine across the metal–carbyne linkage and form the metallacycles $[\mathrm{Cp(CO)_2Re(\eta^2(}C,C\mathrm{)\text{-}C\{Tol\}N\{R\}CH\{Ph\})}]^+$ (**3**, R = $\mathrm{CH_3}$; **4**, R = $\mathrm{N{=}CHPh}$). Complex **3** is hydrolytically unstable and reacts with water to form benzaldehyde and the carbene complex $\mathrm{Cp(CO)_2Re{=}C(NHMe)Tol}$. Trimethylphosphine adds to the tolyl-substituted carbon of complex **3** to form the new metallacycle $[\mathrm{Cp(CO)_2Re(\eta^2(}C,C\mathrm{)\text{-}CH\{Ph\}N\{Me\}C\{Tol\}\{PMe_3\}}]^+$. Upon photolysis, the $\mathrm{BCl_4^-}$ salt of complex **3** loses CO and abstracts $\mathrm{Cl^-}$ from the $\mathrm{BCl_4^-}$ anion to form $\mathrm{Cp(CO)ClRe(\eta^2(}C,C\mathrm{)\text{-}C\{Tol\}N\{Me\}CH\{Ph\})}$. A similar chloride abstraction occurs when the $\mathrm{BCl_4^-}$ salt of $[\mathrm{Cp(CO)_2Re{\equiv}CTol}]^+$ reacts with $\mathrm{Bu^tN{=}O}$ to give $\mathrm{Cp(CO)(Cl)Re\{\eta^2(}C,O\mathrm{)\text{-}C(O)C(Tol)N(Bu^t)O\}}$, **15**, in which a CO ligand has also inserted between the Re atom and the carbyne carbon. In contrast, the $\mathrm{BPh_4^-}$ salt of $[\mathrm{Cp(CO)_2Re{\equiv}CTol}]^+$ reacts with $\mathrm{Bu^tN{=}O}$ by a net [2 + 2] cycloaddition reaction to form $[\mathrm{Cp(CO)_2Re\{\eta^2(}C,O\mathrm{)\text{-}C(Tol)N(Bu^t)O\}]BPh_4}$, **16**. The metallacycle **15** can be converted into **16** by abstraction of chloride with $\mathrm{Ag^+}$, and complex **16** reacts with excess $\mathrm{PMe_3}$ to form $\mathrm{(CO)_2(PMe_3)_2Re\{\eta^2(}C,O\mathrm{)\text{-}C(Tol)N(Bu^t)O\}}$, **18**, in which the metallacycle has been retained but the Cp ligand has been displaced. Reaction of the $\mathrm{BCl_4^-}$ salt of $[\mathrm{Cp(CO)_2Re{\equiv}CTol}]^+$ with the dimer $[\mathrm{Bu^tN{=}O}]_2$ leads to the formation of the five-membered metallacycle $[\mathrm{Cp(CO)_2Re\{\eta^2\text{-}(}C,O\mathrm{)\text{-}C(O)C(Tol)N(Bu^t)O\}]BCl_4}$. In contrast to the reactions of **2**, the manganese carbyne complex $[\mathrm{Cp(CO)_2Mn{\equiv}CPh}]^+$ reacts with $\mathrm{PhCH{=}NCH_3}$ and $\mathrm{PhCH{=}N{-}N{=}CHPh}$ to give new carbene complexes which result from insertion of the imine between the carbyne carbon and a carbon atom of the Cp ligand. The complex $[\mathrm{Cp^*(CO)_2Mn{\equiv}CTol}]\mathrm{BCl_4}$ (**12**) reacts with $\mathrm{PhCH{=}NCH_3}$ to give an analogous product formed by an unprecedented substitution of a Cp* methyl group by the imine carbon. Complexes **3**, **15**, **16**, and **18** were crystallographically characterized: **3**, triclinic, $P\bar{1}$, $a = 10.367$ (2), $b = 11.306$ (2), $c = 11.858$ (2) Å, $\alpha = 83.96$ (2), $\beta = 83.04$ (2), $\gamma = 67.78$ (2)°, $V = 1274.6$ (5) Å^3, $Z = 2$, $R(F) = 3.56\%$, $R(\mathrm{w}F) = 4.53\%$ for 4804 reflections with $F_o > 5\sigma(F_o)$; **15**, orthorhombic, $Fdd2$, $a = 21.700$ (4), $b = 38.016$ (7), $c = 11.120$ (2) Å, $V = 9173.4$ (22) Å^3, $Z = 16$, $R(F) = 5.22\%$, $R(\mathrm{w}F) = 5.76\%$ for 4144 reflections with $F_o \geq 5\sigma(F_o)$; **16**, monoclinic, $P2_1/c$, $a = 9.007$ (2), $b = 15.003$ (4), $c = 27.839$ (6) Å, $\beta = 95.67$ (2)°, $V = 3743$ (2) Å^3, $Z = 4$, $R(F) = 4.73\%$, $R(\mathrm{w}F) = 4.72\%$ for 5084 reflections with $F_o > 5\sigma(F_o)$; **18**, triclinic, $P\bar{1}$, $a = 10.026$ (2), $b = 11.075$ (2), $c = 11.201$ (2) Å, $\alpha = 85.76$ (2), $\beta = 86.99$ (2), $\gamma = 85.59$ (2)°, $V = 1235.3$ (4) Å^3, $Z = 2$, $R(F) = 3.88\%$, $R(\mathrm{w}F) = 4.21\%$ for 3724 reflections with $F_o > 5\sigma(F_o)$.

Introduction

Transition metal–carbene complexes have found numerous applications in synthetic organic chemistry through a variety of carbene transfer and cycloaddition reactions.[1] In contrast, carbyne complexes have far fewer applications, in part because their overall chemistry is significantly less developed.[2] Particularly scarce have been well-defined cycloaddition reactions of metal carbynes. The only well-documented reactions of this class are those involving the formation of metallacyclobutadiene complexes from metal carbynes and alkynes,[3] e.g., eq 1,[3a] mainly because of the relevance of this reaction to alkyne metathesis.[4]

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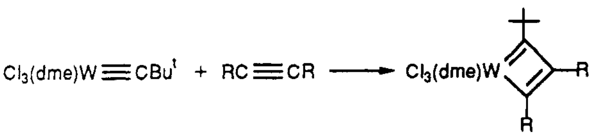
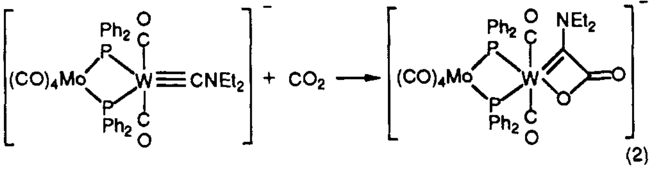
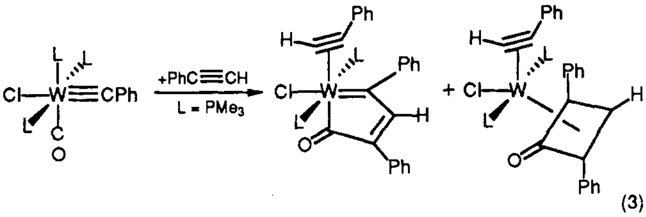


(1)

dme = 1, 2-dimethoxyethane; R = Me, Et



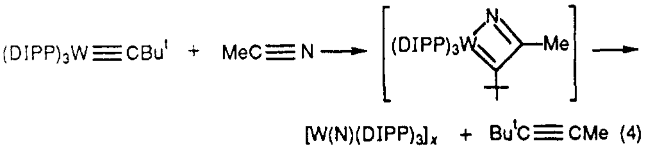
(2)



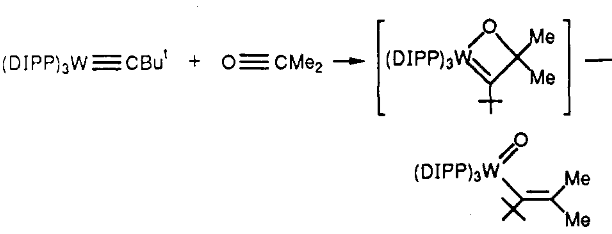
(3)

The only other cycloaddition reactions of metal carbynes that have led to well-defined metallacycles are those illustrated in eqs 2[5] and 3,[6] which respectively involve net [2 + 2] cycloaddition of CO_2 and apparent insertion of CO into an intermediate metallacyclobutadiene to form metallacyclopentadienone and η^3-oxocyclobutenyl complexes.

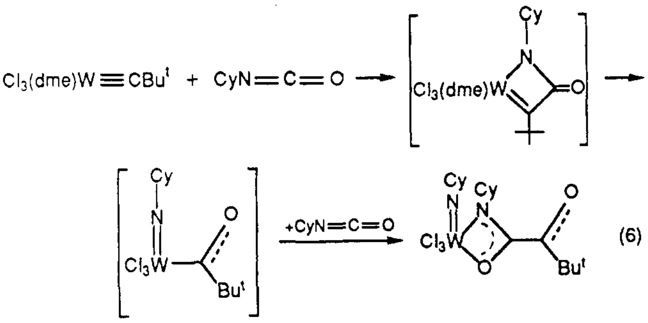
Other reactions of carbyne complexes have been reported to give products that likely derive from transient metallacycles. One example is illustrated in eq 4 in which the carbyne complex $(DIPP)_3W{\equiv}CBu^t$ (DIPP = 2,6-diisopropylphenoxide) reacts with acetonitrile to form $Bu^tC{\equiv}CCH_3$ and $[W(N)(DIPP)_3]_x$, apparently via the intermediacy of an azatungstenacyclobutadiene complex.[7] Analogous Wittig-like reactions occured with benzaldehyde, paraformaldehyde, ethyl formate, and *N*,*N*-dimethylformamide.[7] Acetone was also shown to react rapidly with this carbyne complex to give an oxo vinyl species via a proposed oxotungstenacyclobutene intermediate, eq 5.[7] Cycloaddition of cyclohexyl isocyanate with $Cl_3(dme)W{\equiv}CBu^t$ (dme = 1,2-dimethoxyethane) has also been proposed as the first step in the reaction shown in eq 6[8] and a 1-phospha-3-molybdacyclobutadiene complex was recently proposed as a key intermediate in the transformation shown in eq 7.[9]



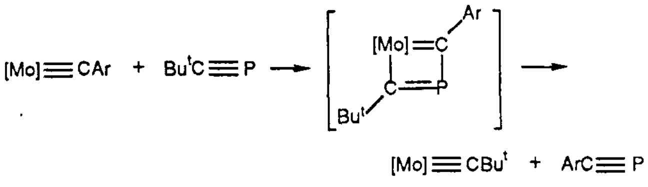
(4)



(5)



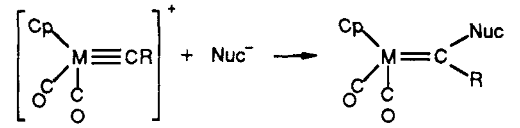
(6)



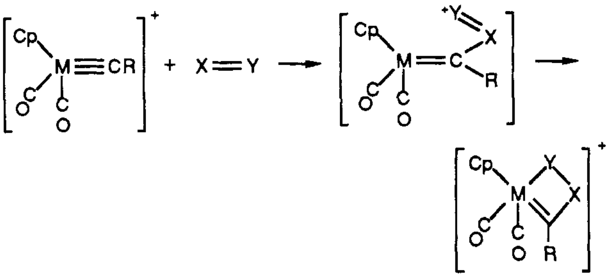
(7)

Ar = o-$C_6H_4OCH_3$
[Mo] = $\{H_2B(pyrazol\text{-}1\text{-}yl)(P(OMe)_3)_2(CO)\}$

The objective of the work reported herein was to extend the cycloaddition reactions of metal carbynes to other substrates with a particular aim of preparing and delineating the reactivity of new types of metallacycles. We have chosen to initially study the cationic carbyne complexes $[Cp(CO)_2M{\equiv}CAr]^+$ (**1**, M = Mn, Ar = Ph; **2**, M = Re, Ar = Tol) since these species have been shown to readily add a variety of nucleophiles (e.g., Cl^-, R^-, CN^-, H^-, RNC, PMe_3) to the carbyne carbon to form carbene complexes, eq 8.[2,10] We reasoned that nucleophilic, unsaturated organic molecules might likewise add to the carbyne carbon and then undergo ring closure to form metallacycles, as illustrated in eq 9. Herein we describe the reactions of complexes **1** and **2** with imines and with $Bu^tN{=}O$, which give a series of previously unknown types of metallacycles. A preliminary account of part of this work has appeared.[11]



(8)



(9)

Results

Reaction of $[Cp(CO)_2Re{\equiv}CTol]BCl_4$ with $PhCH{=}NCH_3$ and $PhCh{=}N{-}N{=}CHPh$. The carbyne complex

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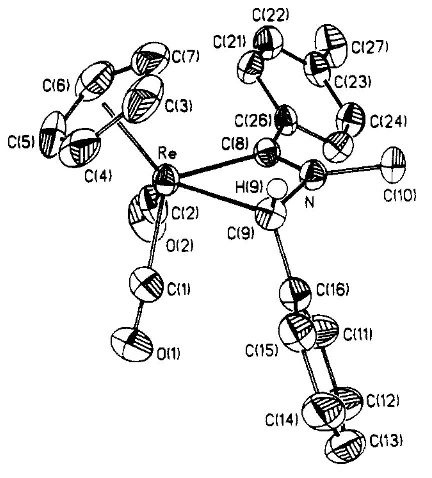
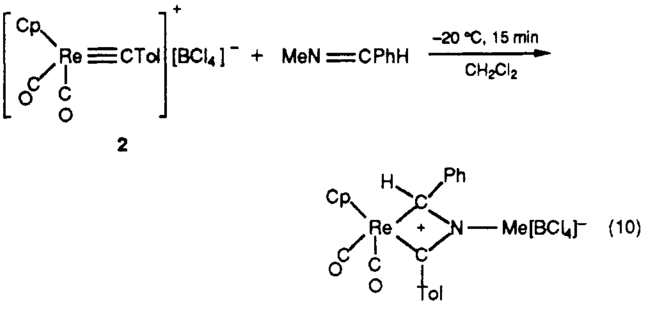


Figure 1. ORTEP diagram of [Cp(CO)$_2$Re(η^2-CH{Ph}N{CH$_3$}C{Tol})]BCl$_4$, 3.

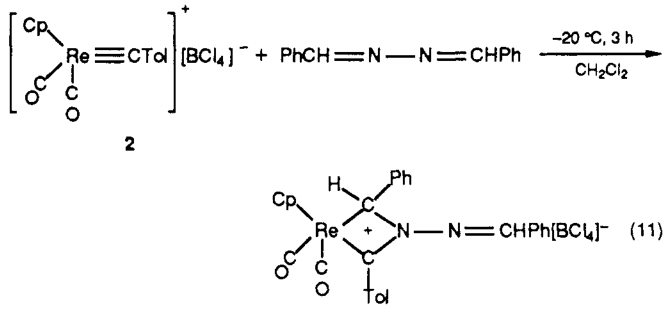
[Cp(CO)$_2$Re≡CTol]$^+$, 2, rapidly reacts with the imines PhCH=NCH$_3$ and PhCH=N—N=CHPh to form the metallacycles 3 and 4 shown in eqs 10 and 11. These



2

(10)

3 (85%)

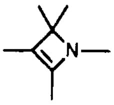


2

(11)

4 (76%)

complexes were isolated in good yields as microcrystalline solids and have been spectroscopically characterized. Complex 3 has been further defined by a crystallographic study, the results of which are shown in Figure 1. To our knowledge, these are the first examples of metallacycles of this type, and they may be termed 3-rhena-2-azetines due to their relationship to the organic ring system 2-azetine.[12] The metallacycle of complex 3 is planar, and the

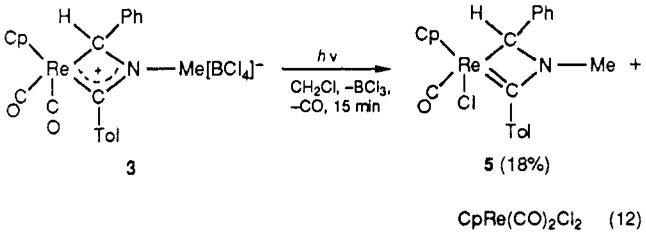


2-azetine

molecule has two chiral centers, C(9) and the Re atom, the latter because of the absence of a mirror plane through this center. Thus 3 and 4 should form as a mixture of diastereomers, and the ^{1}H and ^{13}C NMR data show this to be the case. Although the diastereomers have resisted separation, integration of the ^{1}H NMR spectra show that complex 3 forms as a 1.8:1 mixture of diastereomers whereas a 2:1 mixture results with complex 4. Note that the crystallographically characterized diastereomer of 3 has the cyclopentadienyl and phenyl substituents located on opposite sides of the planar metallacycle, a situation that would be reversed in the other diastereomer.

In addition to Cp, aryl, and *N*-methyl resonances, the ^{1}H NMR spectrum of complex 3 shows benzylic proton resonances at δ 5.48 and 5.61 for the two isomers. A ^{13}C–^{1}H NMR correlation experiment showed these protons to be bound to the ring carbon atoms that gave ^{13}C NMR resonances at δ 20.1 and 16.2, respectively. In addition to these and Cp, aryl, metal carbonyl, and *N*-methyl resonances, the ^{13}C NMR spectrum of 3 also shows a resonance at δ 200.2, which is assigned to a superposition of the resonances of the tolyl-substituted ring carbons of the two isomers. Complex 4 shows spectroscopic features similar to those of 3, indicating similar structures for the two compounds. The lack of imine exchange when complex 3 was stirred for 24 h with excess PhCH=N—N=CHPh or when complex 4 was stirred with excess PhCH=NCH$_3$ indicates that reactions 10 and 11 are irreversible.

Photoinduced Substitution of Chloride for CO in Complex 3. When CH$_2$Cl$_2$ solutions of the BCl$_4^-$ salt of complex 3 were irradiated with near-UV light, loss of CO occurred and a chloride ion was extracted from the BCl$_4^-$ anion to form in low yield complex 5, eq 12. Also isolated from this reaction in low yield was the known complex CpRe(CO)$_2$Cl$_2$.[13] The BCl$_4^-$ anion is proposed to be the chloride source in reaction 12 on the basis of the observation that complex 5 does not form upon photolysis of the BPh$_4^-$ salt of 3. Also, the observation that 5 forms upon irradiation of the BCl$_4^-$ salt of 3 in THF rather than CH$_2$Cl$_2$ solution rules out the possibility of chlorine abstraction from solvent.



3

5 (18%)

(12)

(13%)

Complex 5 has been spectroscopically characterized. It shows a parent ion in its mass spectrum at *m*/*z* 498 and a single ν_{CO} band at 1890 cm^{-1}. Its ^{1}H and ^{13}C NMR spectra show characteristic Cp, Tol, Ph, and N-CH$_3$ resonances in addition to the benzylidene ^{1}H NMR resonance at δ 5.20 and ring carbon ^{13}C NMR resonances at δ 42.1 (Re—CHPh) and 216.7 (Re=CTol). Interestingly, the NMR data show that only one of the two possible diastereomers of 5 is formed in this reaction, although the spectroscopic data are insufficient to indicate which one. It may be that only one of the two diastereomers of complex 3 undergoes clean photosubstitution to give 5, consistent with the low yield of this species.

Hydrolysis of Complex 3 To Produce [Cp(CO)$_2$Re=C(NHMe)Tol] and Benzaldehyde. Complex 3 was found to hydrolyze readily upon chromatographic workup but more conveniently by the addition of a 6-fold excess of 0.09 M NaOH(aq). The products of the hy-

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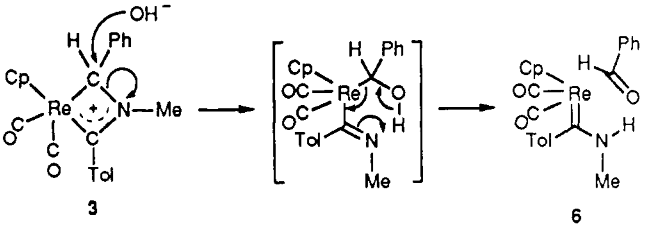
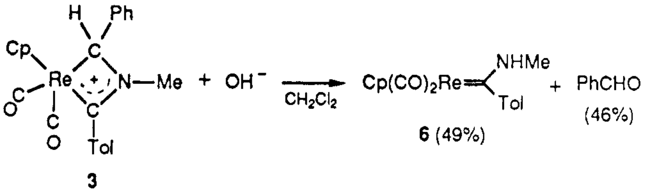
(12) *The Chemistry of Heterocyclic Compounds, Small Ring Heterocycles, Part 2*; Hassner, A., Ed.; Wiley: New York, 1983; Vol. 42, p 4.

(13) Einstein, F. W. B.; Klahn-Oliva, A. H.; Sutton, D.; Tyers, K. G. *Organometallics* **1986**, *5*, 53.

Scheme I

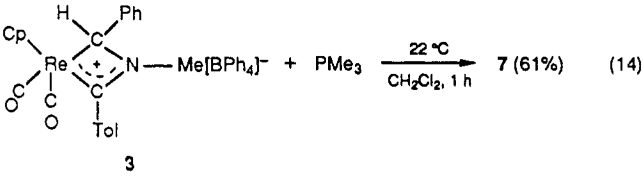


drolysis are the carbene complex Cp(CO)$_2$Re=C(NHMe)Tol, 6, and benzaldehyde, eq 13. Although complex 6 is similar to many other Re–carbene complexes, we have been unable to find evidence that this particular derivative has previously been prepared. Its IR (ν_{CO} 1842 (s), 1919 (s) cm^{-1}), mass spectral (m/z 441 (M$^+$)), and ^{13}C NMR (Re=C δ 245.3) data are consistent with the indicated formulation. The ^{1}H NMR spectrum of complex 6 suggests hindered rotation about the C–N bond as two N–CH$_3$ resonances are apparent at δ 3.36 and 3.37. The formation of benzaldehyde was confirmed by its isolation and spectroscopic identification. This reaction likely proceeds via the mechanism outlined in Scheme I involving initial nucleophilic attack of hydroxide on the benzylic ring carbon followed by a 1,5-hydrogen shift and electrocyclic ring opening to produce the observed products.



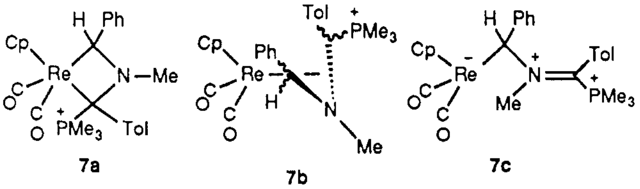
(13)

Reaction of Complex 3 with PMe$_3$. In contrast to the chloride for CO substitution reaction discussed above (eq 12), PMe$_3$ reacts with complex 3 to give a new complex 7, eq 14. Although the exact structure of this product is not known with certainty, its NMR data indicate the presence of a 2:1 mixture of isomers and that the PMe$_3$ group has added to the tolyl-substituted carbon of the metallacycle rather than to the metal. For example, the ^{13}C NMR spectrum of 7 shows two doublets at δ 163.8 (J_{PC} = 48.4 Hz) and 165.1 (J_{PC} = 49.6 Hz) attributed to the ring carbons of the two isomers bearing the PMe$_3$ group with the large J_{PC} coupling indicating that the PMe$_3$ groups is attached to this carbon rather than to the metal. Also present in the ^{13}C NMR spectrum of 7 are two doublets at δ 8.7 and 8.4 assigned to the methyl carbons of the PMe$_3$ groups, two benzylic carbon resonances at δ 70.6 and 72.5, and two Cp ring carbon resonances at δ 89.5 and 89.7, along with the aryl resonances. The ^{31}P and ^{1}H NMR spectral data summarized in the Experimental Section also indicate the presence of a 2:1 isomeric mixture, and the parent ion at m/z 606 observed in the FAB mass spectrum of 7 further supports the proposed formulation. It should be noted that a pure sample of 7 could only be obtained when the [BPh$_4$]$^-$ salt of 3 was allowed to react with PMe$_3$, as the BCl$_4^-$ salt was persistently contaminated with impurities (Me$_3$P–BCl$_3$?).

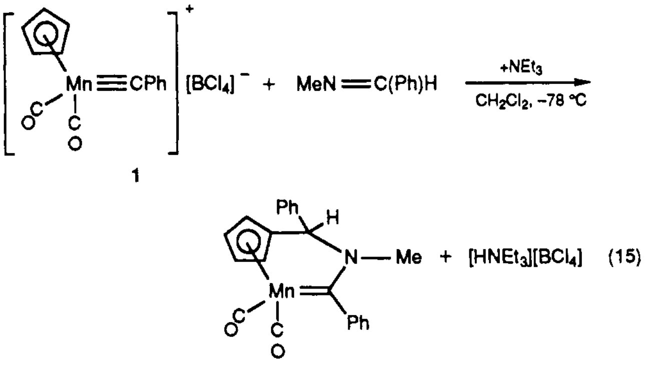


(14)

Possible structures for complex 7 are drawn below. Isomers would be expected for all of the structures 7a–c, consistent with the spectroscopic data. Structure 7a would result from simple addition of PMe$_3$ to the metallacycle. Structures 7b and 7c are η^3-aza-2-allyl and η^1-aza-2-allyl complexes, respectively, which would result from rearrangement of 7a. The downfield positions of the resonances of the carbon atoms of the metallacycle would appear more consistent with the latter two structures. However, complex 7b is a 20-electron species if the azaallyl ligand is assumed to be the usual 4-electron donor and thus seems unlikely. The η^1-2-azaallyl structure 7c cannot be excluded from consideration, although the extensive charge separation makes this structure less attractive. An X-ray crystal structure of 7 thus appears necessary to fully elucidate its structure, although we have thus far been unable to obtain satisfactory crystals.

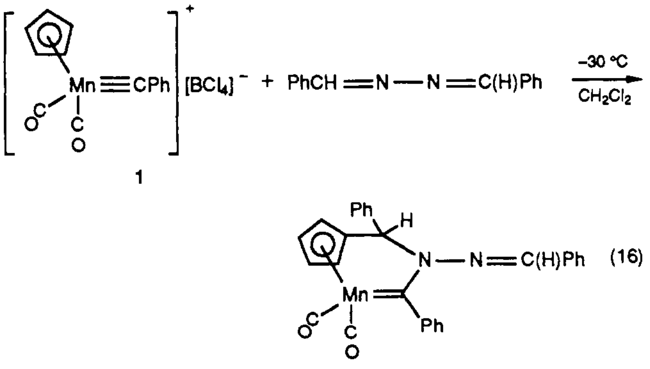


Reaction of [Cp(CO)$_2$Mn$\equiv$CPh]$^+$ and [Cp*(CO)$_2$Mn$\equiv$CTol]$^+$ with Imines. The manganese carbyne complex [Cp(CO)$_2$Mn$\equiv$CPh]$^+$, 1, reacts with the imines PhCH=NCH$_3$ and PhCH=N—N=CHPh to give completely different types of products than those formed with the rhenium analogue described above. The products of these reactions are complexes that result from insertion of the imine between the carbyne carbon and one of the carbon atoms of the cyclopentadienyl ring, eqs 15 and 16.



(15)

8 (45%)

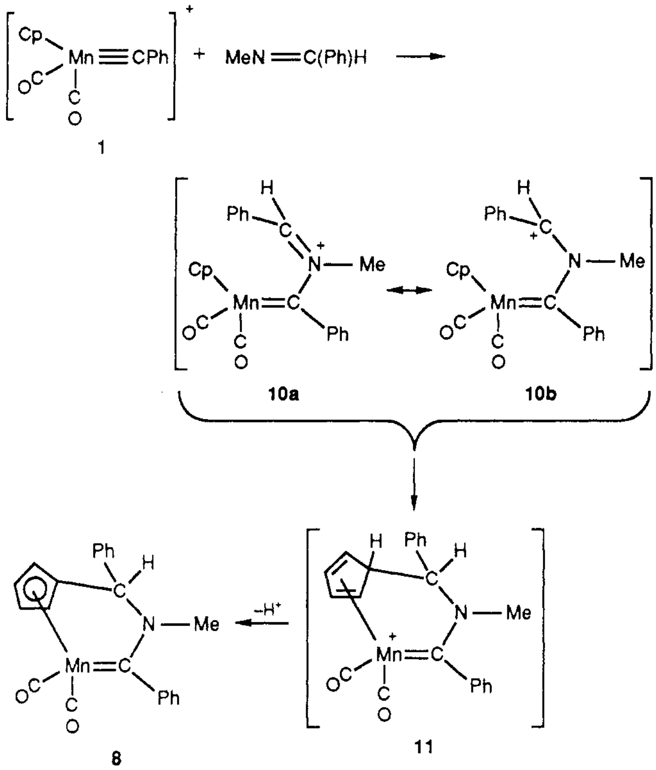


(16)

9 (56%)

Note that a proton is lost from the Cp ring during the reaction, and accordingly the yields were improved when a slight excess of NEt$_3$ was added. However, the reactions proceeded even in the absence of added base, although in lower yield, apparently because the imine reagent itself is

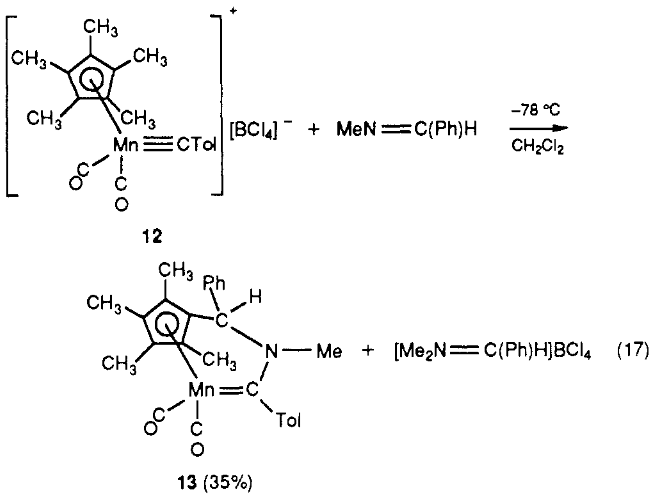
Scheme II



sufficiently basic to deprotonate the intermediate proposed in Scheme II. Both complexes **8** and **9** were isolated as microcrystalline solids and have been spectroscopically characterized. Each gave a parent ion in its mass spectrum, and the IR spectrum of each shows two ν_{CO} bands. The ^{1}H NMR spectrum of complex **8** shows four equal-intensity singlets at δ 4.25, 4.58, 4.77, and 4.95 assigned to the four inequivalent protons of the Cp ring. The benzylic and N–CH_3 protons appear as singlets at δ 5.63 and 2.69, respectively. A distinctive carbene ^{13}C NMR resonance was observed at δ 288.0 for **8** along with five resonances at δ 78.0, 80.4, 83.0, 87.0, and 109.3 due to the five inequivalent Cp ring carbons and a resonance for the benzylic carbon at δ 71.6. The spectroscopic data of complex **9** are similar to those of **8**, indicating similar structures for the two compounds.

The mechanism believed to account for the formation of these complexes is shown in Scheme II. The first step most likely involves nucleophilic attack of the imine nitrogen on the carbyne carbon of **1** to produce the cationic carbene complex **10**, since other nucleophiles add to this carbon to form similar carbene complexes.[2,10] Two resonance forms **10a** and **10b** can be written for this intermediate, with the latter indicating that the benzylic carbon should be sufficiently electrophilic to add to the Cp ring to produce intermediate **11**. Deprotonation of the latter by excess imine reagent or by added NEt_3 would yield the final product **8**.

It was reasoned that it might be possible to block the formation of complex **8** and force the imine to give a mangana–azetine complex analogous to the rhena–azetine complex **3** described above by carrying out the reaction with the η-C_5Me_5 analogue of carbyne complex **1**. However, when $[Cp^*(CO)_2Mn{\equiv}CTol]^+$, **12** ($Cp^*$ = η-C_5Me_5), was allowed to react with PhCH=NCH_3, the reaction followed the same course as that described above to give complex **13**, eq 17. The maximum yield of this reaction was obtained when 2 equiv of the imine were used, implying that the second equivalent is necessary to remove the methyl group from the Cp* ring of an intermediate



(17)

13 (35%)

analogous to **11** (Scheme II) by an S_N2 displacement reaction. The byproduct of this reaction would thus be the iminium salt $[Me_2N{=}CHPh]BCl_4$, but this species could not be separated from the intractable reaction residue. Complex **13** was isolated as a slightly air-sensitive microcrystalline yellow solid and was characterized spectroscopically. It shows a parent ion in its mass spectrum, and its IR spectrum shows two ν_{CO} bands at 1913 and 1848 cm^{-1}, similar to those observed for complex **8** except shifted to ~30 cm^{-1} lower energy because of the increased electron density as a result of the Cp ring substitution. The ^{1}H NMR spectrum of **13** shows four singlets at δ 1.19, 1.63, 1.89, and 2.14 assigned to the four inequivalent methyl groups on the cyclopentadienyl ring along with singlets at δ 2.28 and 2.90 assigned to the Tol–CH_3 and N–CH_3 groups, respectively, and a benzylic proton resonance at δ 6.07. The ^{13}C NMR spectrum of complex **13** shows two singlets at δ 10.2 and 10.9 assigned to the methyl groups of the cyclopentadienyl ring and five resonances at δ 90.9, 93.1, 97.7, 101.2, and 102.5 due to the five inequivalent ring carbons. Also observed is a characteristic carbene carbon resonance at δ 288.7 along with N–CH_3 (δ 40.1), Tol–CH_3 (δ 21.0), and aryl carbon resonances. A ^{13}C–^{1}H correlation NMR experiment confirmed the ^{1}H and ^{13}C NMR assignments given above.

Reaction of $[Cp(CO)_2Re{\equiv}CTol]BCl_4$ with Bu^{t}N=O. The reagent Bu^{t}N=O exists as a dimer in the solid state but is in equilibrium with its monomer in solution.[14] Nearly pure monomer can be formed by warming solid $[Bu^tNO]_2$ under vacuum and collecting at −78 °C the distillate as a blue solid that melts to a blue liquid upon warming to −30 °C. The monomer is stable at this temperature for several hours, although the white dimer rapidly reforms upon warming to room temperature. Unless otherwise specified, monomeric Bu^{t}N=O was used in all experiments described herein.

The BCl_4^- salt of the carbyne complex $[Cp(CO)_2Re{\equiv}CTol]^+$ slowly reacted with Bu^{t}N=O at 0 °C to form an intermediate complex **14**, which decayed to give complex **15** when the solution was warmed to 22 °C, eq 18. Complex **15** was isolated as a red, air-stable solid and has been spectroscopically and crystallographically characterized. An ORTEP drawing is shown in Figure 2. It possesses an essentially planar five-membered metallacycle assembled from the carbyne ligand, the nitroso reagent, and a carbonyl ligand, with the latter having been replaced by a chloride derived from the BCl_4^- anion. The spectroscopic

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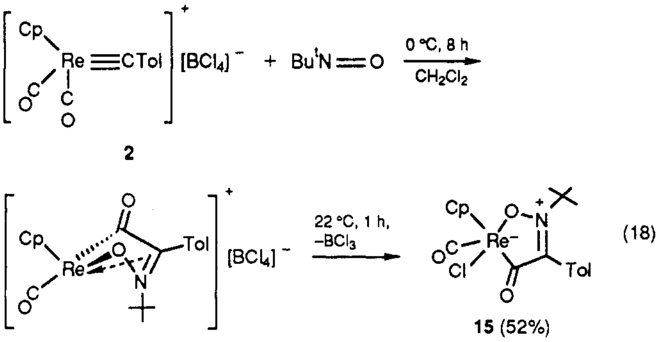
[14] (a) Janzen, E. G. *Acc. Chem. Res.* **1971**, *4*, 31. (b) Mackor, A.; Wajer, A. J. W.; deBoer, J. *Tetrahedron Lett.* **1967**, *29*, 2757.



2

14

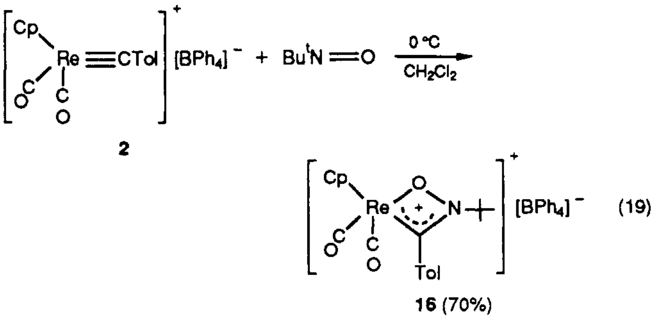
15 (52%)

(18)

data of **15** are consistent with its determined structure. Cyclopentadienyl, tolyl, and *tert*-butyl resonances are apparent in the ^{1}H and ^{13}C NMR spectra, and the latter additionally shows resonances assigned to the tolyl-substituted ring carbon (δ 160.7), the metal carbonyl (δ 204.1), and the ring carbonyl (δ 231.1), with the latter being in the typical metal acyl region. The IR spectrum of **15** shows a single band at 1930 cm^{-1} due to the carbonyl ligand, but the ν_{CO} band for the ring carbonyl is obscured by overlapping aryl vibrations.

The intermediate **14** shown in eq 18 has been isolated as a thermally unstable orange solid by evaporating the solvent from the reaction mixture at 0 °C and recrystallizing at -20 °C. It spectroscopic data indicate its overall structure to be similar to that of **15**. A single ν_{CO} band is observed at 1960 cm^{-1}, compared to the 1930 cm^{-1} band of **15**, indicating a decrease in metal electron density as compared to neutral **15**. The ^{13}C NMR spectrum of **14** shows resonances attributable to the tolyl-substituted ring carbon (δ 190.5), the metal carbonyl (δ 200.5), and the ring carbonyl (δ 218.1) in addition to Cp and *tert*-butyl resonances. Its ^{11}B NMR spectrum shows a single ^{11}B resonance at δ 6.88, identical with that observed for the carbyne complex $[Cp(CO)_2Re{\equiv}CTol]BCl_4$, implying that the BCl_4^- ion in complex **14** is not coordinated to the metal and also that the chloride has not yet been abstracted from the BCl_4^- ion. The FAB mass spectrum of **14** shows a parent ion at *m*/*z* 498, consistent with the composition of the cation drawn in eq 18. Although details of the structure of **14** are unknown, we propose the presence of a five-membered bent metallacycle with the C=N double bond coordinated to rhenium in order to achieve a satisfactory 18-electron count at the metal. The **14** to **15** interconversion presumably involves displacement of this bond by a chloride ion from the BCl_4^- anion.

Reaction of $[Cp(CO)_2Re{\equiv}CTol]BPh_4$ with Bu^{t}N=O. To circumvent the formation of complex **15** by chloride abstraction from the BCl_4^- anion, the BPh_4^- salt of $[Cp(CO)_2Re{\equiv}CTol]^+$ was allowed to react with Bu^{t}NO, and as expected the reaction took a completely different course to give complex **16** shown in eq 19. This species has



2

16 (70%)

(19)

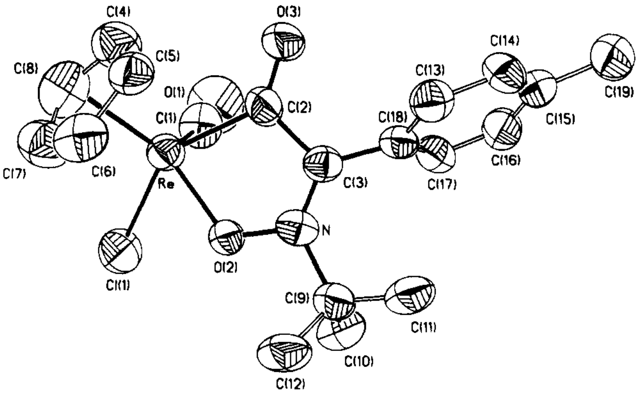


Figure 2. ORTEP diagram of Cp(CO)(Cl)Re(η^2-ON{Bu^t}C{Tol}C{O}), **15**.

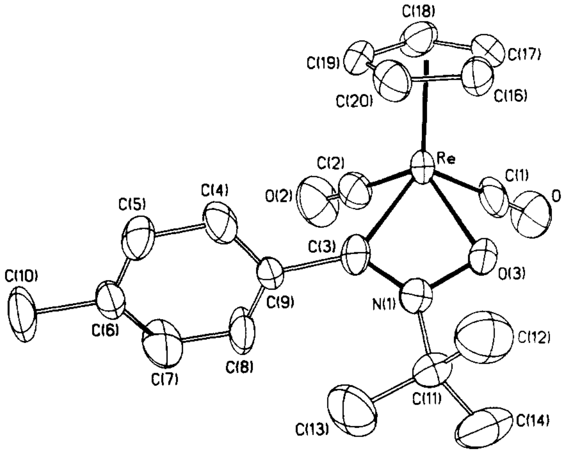
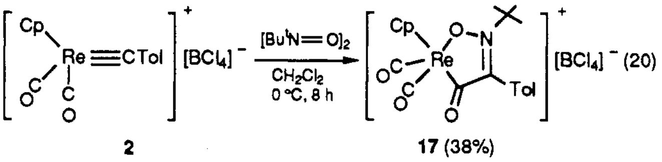


Figure 3. ORTEP diagram of [Cp(CO)$_2$Re(η^2-ON{Bu^t}C{Tol})]BPh$_4$, **16**.

formed by a net [2 + 2] cycloaddition of the N=O bond of Bu^{t}N=O across the Re≡C bond of complex **2** and is analogous to the rhena-azetine complex **3** described above which resulted from the addition of PhCH=NMe to **2**. Complex **16** was isolated as a gold, air-stable solid and has been spectroscopically and crystallographically characterized (Figure 3). Its IR spectrum shows two ν_{CO} bands at 2062 (vs) and 2000 (s) cm^{-1} at slightly higher frequencies compared to the similar bands of the rhena-azetine complex **3** (ν_{CO} 2042 (vs), 1975 (s) cm^{-1}). Its ^{1}H and ^{13}C NMR spectra show the expected Cp, tolyl, and Bu^t resonances along with ^{13}C NMR resonances for the ring carbon at δ 167.5 and metal carbonyl resonances at δ 196.7 and 198.4.

Reaction of $[Cp(CO)_2Re{\equiv}CTol]^+$ with $[Bu^tN{=}O]_2$ Dimer. In contrast to the reaction of monomeric Bu^{t}N=O with $[Cp(CO)_2Re{\equiv}CTol]^+$ which gave complexes **15** and **16** described above, the *dimer* $[Bu^tN{=}O]_2$ reacts with $[Cp(CO)_2Re{\equiv}CTol]^+$ to form the cationic complex **17** shown in eq 20, which possesses a five-membered metal-



2

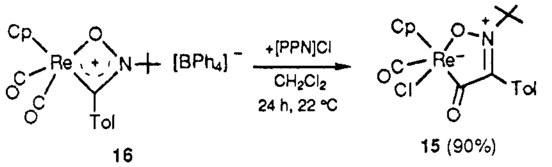
17 (38%)

(20)

lacycle resulting from insertion of a CO ligand. Although complex **17** forms under an N$_2$ atmosphere, its yield is higher when its synthesis is carried out under 1 atm of CO. When solutions of **17** were warmed to 22 °C, under either N$_2$ or CO, chloride abstraction from the BCl_4^- anion occurred to form complex **15**, described above. Complex **17** was thus never obtained in pure form, but it was spectroscopically characterized at -10 °C under 1 atm of CO.

Its ^{1}H and ^{13}C NMR spectra show characteristic Bu^t, Cp, and tolyl resonances, and the ^{13}C NMR spectrum shows an additional resonance at δ 220.8 assigned to the ring carbonyl carbon and resonances at δ 202.8 and 204.8 attributed to the metal carbonyls. The IR spectrum of **17** shows two ν_{CO} bands at 2029 (s) and 1954 (s) cm^{-1} which are in the region characteristic of cationic dicarbonyl complexes in this family of compounds (e.g., [Cp(CO)$_2$Re=CPhPMe$_3$]$^+$, ν_{CO} 2036, 1921 cm^{-1}).[15]

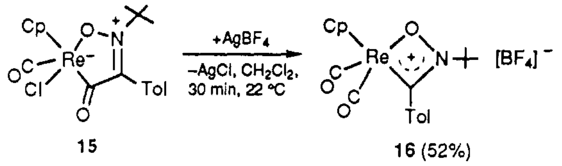
Interconversion of Complexes 15–17. The metallacycles described above were found to be interconvertible by the addition and abstraction of halide. Thus, complex **16** slowly reacts with [PPN]Cl (PPN$^+$ = (PPh$_3$)$_2$N$^+$) to form complex **15**, eq 21. This reaction is readily reversed by removing the chloride through the addition of AgBF$_4$ to **15** in the absence of added CO, eq 22. However, when complex **16** is treated with AgBF$_4$ *under a CO atmosphere*, a mixture of complexes **16** and **17** results, eq 23. This latter reaction apparently proceeds via chloride abstraction to produce a coordinatively unsaturated intermediate that either deinserts CO to form **16** or adds CO to form **17**.



(21)

16

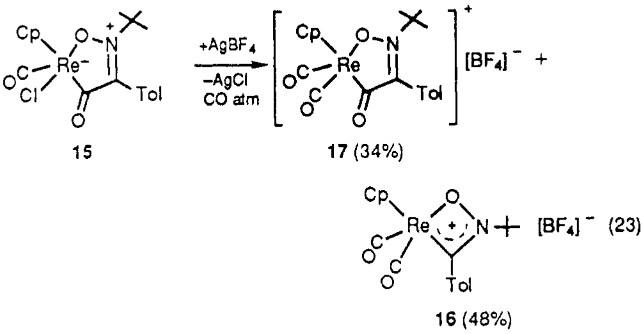
15 (90%)



(22)

15

16 (52%)



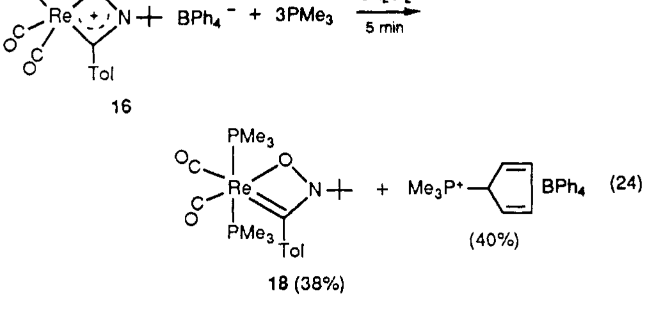
15

17 (34%)

(23)

16 (48%)

Reaction of Complex 16 with PMe$_3$. Recall that the rhena-azetine complex **3** reacted with PMe$_3$ by adding to the ring carbon of the metallacycle. In contrast, related complex **16** has been found to react with PMe$_3$ to displace the Cp ligand and form complex **18** shown in eq 24. The Cp ligand was removed in the form of the phosphonium salt shown in the equation, which was isolated from the reaction and was spectroscopically characterized. This salt gave a parent ion for the cation at m/z 141 in its FAB mass spectrum, and its ^{1}H NMR spectrum showed a doublet at δ 1.93 (J_{PH} = 14.6 Hz) assigned to the PMe$_3$ protons, a second doublet at δ 1.71 (J_{PH} = 15.0 Hz) attributed to the hydrogen on the carbon attached to the phosphorus atom, a broad singlet at δ 3.40 assigned to the Cp ligand, and resonances in the δ 6.87–7.26 region due to the BPh$_4^-$ counterion.



16

(24)

18 (38%)

(40%)

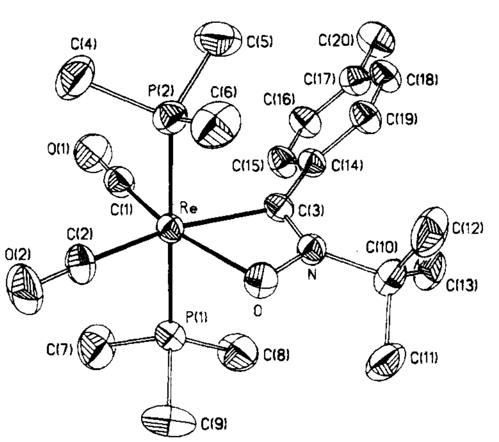


Figure 4. ORTEP diagram of (CO)$_2$(PMe$_3$)$_2$Re(η^2-ON{Bu^t}C{Tol}), **18**.

Complex **18** was isolated from the above reaction as a microcrystalline solid and was spectroscopically and crystallographically characterized (Figure 4). The complex showed a parent ion at m/z 585 in its mass spectrum and two ν_{CO} bands at 1905 and 1817 cm^{-1} in its IR spectrum. A single ^{31}P NMR resonance was observed at δ 24.95 for the trans-PMe$_3$ ligands. The ^{13}C NMR spectrum of **18** showed a triplet at δ 204.6 (J_{PC} = 9.2 Hz) for the tolyl-substituted ring carbon, in addition to PMe$_3$, CO, Bu^t, and tolyl resonances. The ^{1}H NMR spectrum of **18** also showed resonances attributed to the Bu^t, tolyl, and PMe$_3$ groups, with the latter appearing as a triplet centered at δ 1.57 (J_{PH} = 3.5 Hz) due to virtual coupling to the trans phosphorus atoms.

The reaction of **16** with PMe$_3$ is reminiscent of Cp displacement reactions reported by Casey and co-workers, who showed that CpRe(PMe$_3$)(NO)(CH$_3$) reacts with excess PMe$_3$ to form the salt [Re(PMe$_3$)$_4$(NO)(CH$_3$)]$^+$Cp$^-$.[16] The likely mechanism by which complex **18** is formed is given in Scheme III. The first step likely involves associative attack of PMe$_3$ on the rhenium center as the Cp ligand slips from an η^5 to an η^3 coordination mode to give an intermediate such as **19**. Subsequent addition of a second equivalent of PMe$_3$ and then S$_N$2 displacement of the η^1-Cp ligand by a third equivalent of PMe$_3$ would give the observed product **18**. An unstable intermediate in the conversion of **16** into **18** was observed by IR (ν_{CO} 1847, 1956 cm^{-1}) when the reaction was carried out at –10 °C with only 1 equiv of PMe$_3$, which upon warming to 22 °C rapidly decayed to give **18**.

Crystal and Molecular Structures of the Complexes 3, 15, 16, and 18. The cations **3** and **16** have been structurally characterized as their BCl$_4^-$ and BPh$_4^-$ salts, respectively, and ORTEP drawings of these complexes are shown in Figures 1 and 3. Figures 3 and 4 give the ORTEP drawings of the neutral complexes **15** and **18**. Important

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(15) Kreissl, F. R. Stückler, P.; Meineke, E. W. *Chem. Ber.* **1977**, *110*, 3040.

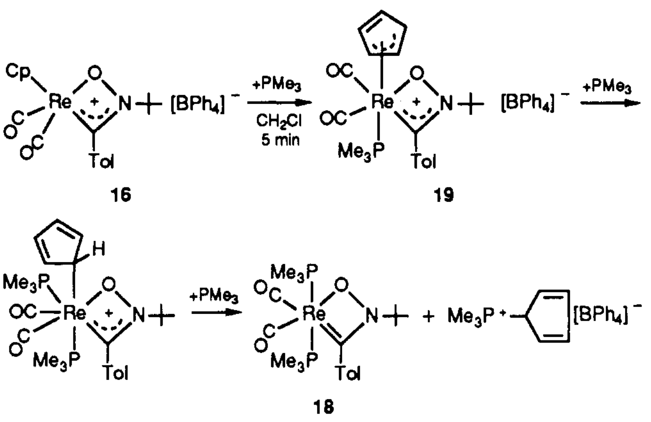
(16) Casey, C. P.; O'Connor, J. M.; Haller, K. J. *J. Am. Chem. Soc.* **1985**, *107*, 1241.

Table I. Crystallographic Data for Complexes 3, 15, 16′, and 18

	3	15	16′	18
		Crystal Parameters		
formula	$ReBC_{23}Cl_4H_{21}NO_2$	$ReC_{19}ClH_{21}NO_3$	$ReBC_{43}H_{41}NO_3$	$ReC_{20}H_{34}NP_2O_3$
fw	682.3	533.0	811.8	584.6
cryst syst	triclinic	orthorhombic	monoclinic	triclinic
space group	$P\bar{1}$	$Fdd2$	$P2_1/c$	$P\bar{1}$
a, Å	10.367 (2)	21.700 (4)	9.007 (2)	10.026 (2)
b, Å	11.306 (2)	38.016 (7)	15.003 (4)	11.075 (2)
c, Å	11.858 (2)	11.120 (2)	27.839 (6)	11.201 (2)
α, deg	83.96 (2)			85.76 (2)
β, deg	83.04 (2)		95.67 (2)	86.99 (2)
γ, deg	67.78 (2)			85.59 (2)
V, Å^3	1274.6 (5)	9173.4 (22)	3743 (2)	1235.3 (4)
Z	2	16	4	2
μ(Mo Kα), cm^{-1}	54.8	57.3	34.7	53.4
D(calc), g cm^{-3}	1.778	1.544	1.440	1.572
temp, °C	23 ± 1	24 ± 1	23	23 ± 1
size, mm	0.20 × 0.25 × 0.33	0.04 × 0.16 × 0.27	0.45 × 0.18 × 0.06	0.08 × 0.42 × 0.45
color	yellow	yellow	yellow	yellow
T(max)/T(min)	1.730	1.738	1.439	2.833
		Data Collection		
diffractometer	Nicolet R3m/μ			
monochromator	graphite			
wavelength, Å	0.71073			
radiation	Mo Kα			
scan method	Wyckoff			
scan lim, deg	$4 \le 2\theta \le 52$	$4 \le 2\theta \le 50$	$4 \le 2\theta \le 45$	$4 \le 2\theta \le 50$
data coll	$\pm h,\pm k,+l$	$+h,+k,\pm l$	$\pm h,+k,+l$	$\pm h,\pm k,l$
no. of refl coll	4804	7968	5048	4588
no. of independent ref	4489	4144	4730	4346
R(int), %	1.38	3.24	4.06	1.69
no. of indep refl	3772	3013	2792	3724
	$F_o \ge 5\sigma(F_o)$	$F_o \le 5\sigma(F_o)$	$F_o \ge 5\sigma(F_o)$	$F_o \ge 5\sigma(F_o)$
var in stds, %	11	<1	<1	<1
		Refinement Results		
R(F),[a] %	3.56	5.22	4.73	3.88
R(wF), %	4.53	5.76	4.72	4.21
Δ/σ(max)	0.01	0.03	0.04	0.01
$\Delta(\rho)$, e Å^{-3}	1.34	1.76	1.63	1.99
N_o/N_v	13.8	10.8	7.09	15.3
GOF	1.083	1.515	1.170	1.057

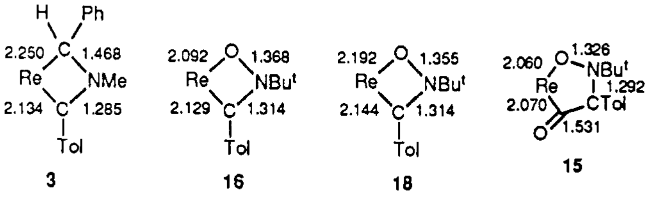
[a] $R(F) = \sum(|F_o| - |F_c|)/\sum|F_o|$; $R(wF) = \sum(w^{1/2}(|F_o| - |F_c|))/(w^{1/2}|F_o|)$; GOF $= [\sum w||F_o| - |F_c||/N_o - N_v]^{1/2}$.

Scheme III



crystallographic parameters are set out in Tables I–IX. The structues of the cationic complexes **3** and **16** are similar, with each possessing a Cp ligand and two carbonyls bonded to the rhenium atom which is part of a four-membered metallacycle. The neutral complex **18** is a derivative of **16**, with the Cp ligand having been replaced with two PMe_3 ligands and with a corresponding change in the overall charge on the complex from +1 to neutral. Complex **15** possesses a five-membered metallacycle having derived from **16** by insertion of a CO into the Re–C(Tol) bond and coordination of a chloride ligand to rhenium.

Chart I



The metallacycles of all four complexes are essentially planar, and for **3**, **16**, and **18** the maximum deviation from planarity is associated with the nitrogen atom (**3**, 0.038 Å; **16**, 0.008 Å; **18**, 0.023 Å). For **15**, the maximum deviation is associated with the carbonyl carbon (0.076 Å).

The important bond distances within the metallacycles are illustrated in Chart I. The Re–C(Tol) distances in the three complexes **3**, **16**, and **18** are similar and appear intermediate in length between typical Re–carbon single (e.g., $Cp(NO)(PPh_3)ReCH_2Ph$, Re–C = 2.203 (8) Å)[17] and double bond values (e.g., $[Cp(NO)(PPh_3)Re{=}CHPh]^+$, Re–C = 1.949 (6) Å).[18] Each is significantly shorter than the Re–CHPh bond length of 2.250 (6) Å found in complex **3**. The C(Tol)–N bond distances in all four of complexes

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(17) Merrifield, J. H.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1204.

(18) Kiel, W. A.; Lin, G.-Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4865.

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for [Cp(CO)$_2$Re(η^2-CH{Ph}N{CH$_3$}C{Tol})]BCl$_4$, 3

	x	*y*	*z*	*U*[a]
Re	2488.5 (3)	768.2 (2)	3080.5 (2)	42.7 (1)
B	1143 (10)	1914 (8)	8444 (9)	68 (4)
Cl(1)	2301 (2)	2420 (2)	9181 (2)	76 (1)
Cl(2)	1956 (3)	175 (2)	8301 (3)	109 (1)
Cl(3)	−538 (3)	2304 (3)	9354 (3)	121 (2)
Cl(4)	805 (5)	2764 (3)	7084 (3)	161 (2)
N	1062 (5)	3091 (5)	2059 (4)	42 (2)
O(1)	738 (6)	753 (6)	5377 (4)	74 (3)
O(2)	4230 (7)	1517 (6)	4580 (6)	94 (3)
C(1)	1367 (8)	795 (7)	4537 (6)	56 (3)
C(2)	3577 (8)	1226 (7)	4023 (7)	63 (3)
C(3)	2306 (11)	−442 (8)	1701 (9)	89 (5)
C(4)	2472 (10)	−1175 (7)	2735 (8)	77 (4)
C(5)	3775 (10)	−1339 (7)	3071 (9)	81 (4)
C(6)	4391 (9)	−731 (8)	2242 (9)	87 (4)
C(7)	3496 (11)	−152 (8)	1411 (8)	87 (4)
C(8)	2353 (6)	2583 (5)	2269 (5)	41 (2)
C(9)	410 (10)	2197 (6)	2590 (5)	44 (2)
C(10)	292 (7)	4270 (6)	1380 (6)	54 (3)
C(11)	−772 (5)	3752 (5)	4114 (4)	70 (4)
C(12)	−1928	4346	4869	82 (4)
C(13)	−3103	4014	4944	85 (4)
C(14)	−3122	3086	4264	81 (4)
C(15)	−1965	2491	3510	59 (3)
C(16)	−791	2824	3435	49 (3)
C(21)	4717 (7)	2548 (6)	1554 (6)	54 (3)
C(22)	5677 (7)	3159 (7)	1298 (7)	65 (3)
C(23)	5280 (7)	4447 (7)	1490 (7)	61 (3)
C(24)	3922 (8)	5103 (7)	1925 (7)	61 (3)
C(25)	2953 (7)	4523 (7)	2163 (6)	53 (3)
C(26)	3354 (6)	3219 (5)	1975 (5)	42 (2)
C(27)	6321 (9)	5097 (9)	1294 (9)	88 (5)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Selected Bond Distances and Angles for [Cp(CO)$_2$Re(η^2-CH{Ph}N{CH$_0$}C{Tol})]BCl$_4$, 3

	Bond Lengths, Å		
Re–C(1)	1.958 (7)	C(3)–C(4)	1.396 (13)
Re–C(2)	1.913 (9)	C(3)–C(7)	1.388 (17)
Re–C(8)	2.134 (6)	C(4)–C(5)	1.394 (15)
Re–C(9)	2.250 (6)	C(5)–C(6)	1.373 (14)
Re–CNT[a]	1.947 (9)	C(6)–C(7)	1.374 (14)
B–Cl(1)	1.848 (12)	C(8)–C(26)	1.46 (10)
B–Cl(2)	1.840 (9)	C(9)–C(16)	1.495 (7)
B–Cl(3)	1.860 (10)	C(21)–C(22)	1.401 (12)
B–Cl(4)	1.789 (10)	C(21)–C(26)	1.385 (8)
N–C(8)	1.285 (8)	C(22)–C(23)	1.391 (11)
N–C(9)	1.468 (9)	C(23)–C(24)	1.384 (9)
N–C(10)	1.479 (8)	C(23)–C(27)	1.505 (14)
O(1)–C(1)	1.129 (9)	C(24)–C(25)	1.383 (12)
O(2)–C(2)	1.151 (12)	C(25)–C(26)	1.406 (10)
	Bond Angles, deg		
C(1)–Re–C(2)	80.8 (4)	C(9)–N–C(10)	122.6 (5)
C(1)–Re–C(8)	116.5 (3)	C(8)–N–C(10)	131.4 (6)
C(2)–Re–C(8)	79.9 (3)	N–C(9)–C(16)	111.7 (5)
C(8)–Re–C(9)	60.1 (3)	N–C(8)–C(26)	123.6 (5)
CNT–Re–C(1)	121.4 (3)	Re–C(8)–N	102.3 (5)
CNT–Re–C(2)	121.6 (3)	Re–C(8)–C(26)	134.0 (4)
CNT–Re–C(8)	120.3 (3)	Re–C(9)N	91.4 (4)
CNT–Re–C(9)	116.4 (3)	Re–C(9)–C(16)	123.5 (4)
C(8)–N–C(9)	105.8 (5)		

[a] CNT = centroid of η^5-C$_5$H$_5$ ring.

Table IV. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for Cp(CO)(Cl)Re(η^2-ON{Bu^t}C{Tol}C{O}), 15

	x	*y*	*z*	*U*[a]
Re	688.7 (3)	950.2 (2)	0	53.6 (2)
Cl(1)	910 (3)	732 (1)	2033 (4)	85 (2)
N	1504 (6)	441 (4)	−1197 (11)	56 (5)
O(1)	−482 (7)	516 (4)	70 (21)	118 (7)
O(2)	1453 (5)	634 (3)	−209 (9)	57 (3)
O(3)	263 (5)	841 (3)	−2561 (13)	76 (4)
C(1)	−13 (8)	660 (5)	43 (22)	77 (7)
C(2)	616 (7)	761 (5)	−1740 (15)	58 (6)
C(3)	1084 (7)	470 (4)	−2015 (14)	53 (5)
C(4)	187 (10)	1415 (6)	−596 (25)	84 (9)
C(5)	794 (9)	1452 (5)	−1051 (17)	68 (7)
C(6)	1186 (8)	1508 (4)	−44 (24)	75 (6)
C(7)	826 (13)	1484 (7)	957 (25)	93 (10)
C(8)	225 (11)	1439 (6)	947 (26)	92 (10)
C(9)	2059 (8)	197 (5)	−1088 (15)	61 (6)
C(10)	1846 (8)	−118 (5)	−335 (21)	82 (8)
C(11)	2291 (9)	78 (6)	−2307 (20)	94 (8)
C(12)	2568 (7)	396 (5)	−450 (18)	77 (7)
C(13)	1172 (5)	412 (2)	−4425 (10)	63 (6)
C(14)	1070	230	−5296	68 (7)
C(15)	816	−107	−5269	65 (7)
C(16)	664	−262	−4171	65 (6)
C(17)	766	−80	−3100	61 (6)
C(18)	1020	257	−3127	53 (5)
C(19)	700 (9)	−293 (6)	−6456 (20)	91 (9)
Cl(2)	8446 (4)	1055 (2)	2109 (9)	146 (4)
Cl(3)	7136 (3)	1159 (2)	1994 (10)	154 (4)
Cs	4840 (9)	1366 (6)	2182 (23)	97 (9)

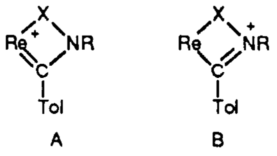
[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table V. Selected Bond Distances and Angles for Cp(CO)(Cl)Re(η^2-ON{Bu^t}C{Tol}C{O}), 15

	Bond Lengths, Å		
Re–Cl(1)	2.455 (5)	Re–O(2)	2.06 (10)
Re–C(1)	1.880 (18)	Re–C(2)	2.070 (17)
Re–C(4)	2.180 (23)	Re–C(5)	2.250 (18)
Re–C(6)	2.380 (16)	Re–C(7)	2.310 (27)
Re–C(8)	2.232 (25)	N–O(2)	1.326 (16)
N–C(3)	1.292 (20)	N–C(9)	1.526 (22)
O(1)–C(1)	1.155 (24)	O(3)–C(2)	1.229 (21)
C(2)–C(3)	1.531 (22)	C(3)–C(18)	1.486 (19)
C(4)–C(5)	1.420 (31)	C(4)–C(8)	1.388 (40)
C(5)–C(6)	1.422 (30)	C(6)–C(7)	1.362 (37)
C(7)–C(8)	1.361 (38)	C(9)–C(10)	1.531 (26)
C(9)–C(11)	1.515 (27)	C(9)–C(12)	1.517 (24)
C(19)–C(15)	1.519 (24)	Cl(2)–Cs	1.770 (23)
Cl(3)–Cs	1.731 (22)	Re–CNT[a]	1.939 (15)
	Bond Angles, deg		
Cl(1)–Re–C(2)	75.3 (3)	Cl(1)–Re–C(2)	139.3 (5)
O(2)–Re–C(2)	75.7 (5)	Cl(1)–Re–C(2)	76.0 (8)
O(2)–N–C(3)	118.4 (13)	O(2)–N–C(9)	109.7 (11)
C(3)–N–C(9)	131.8 (13)	Re–O(2)–N	118.9 (8)
Re–C(2)–C(3)	112.7 (10)	Re–C(2)–O(3)	131.0 (13)
N–C(3)–C(2)	113.0 (14)	O(3)–C(2)–C(3)	116.3 (14)
Cl(1)–Re–C(1)	86.4 (7)	N–C(3)–C(18)	127.1 (13)
CNT–Re–Cl(1)	110.9 (7)	CNT–Re–C(2)	109.5 (9)
CNT–Re–C(1)	123.0 (10)	CNT–Re–O(2)	128.5 (8)

[a] CNT = centroid of η^5-C$_5$H$_5$ ring.

are similar and in the range of typical C–N double-bond values in organic compounds (1.29 Å).[19] Each is significantly shorter than the N–CHPh bond distance in **3**, which is a typical N–C single-bond value. These data indicate that the metallacycles of complexes **3**, **16**, and **18** are best described as resonance hybrids of the two structures A and B but with B dominant.



3, X = CHPh
16, **18**, X = O

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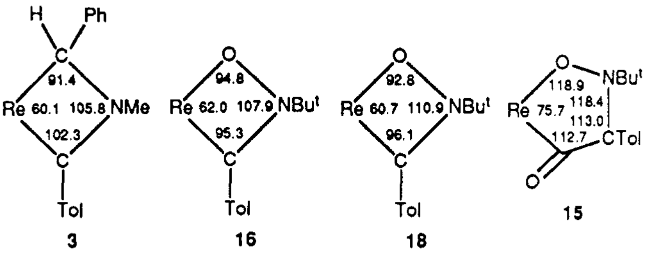
(19) Nyburg, S. C. *X-Ray Analysis of Organic Structures*; Academic Press: New York, 1961; p 297.

Table VI. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for [Cp(CO)$_2$Re(η^2-O{N-Bu^t}C{Tol}BPh$_4$, 16′

	x	*y*	*z*	*U*[a]
Re	4852 (1)	1824 (1)	523 (1)	50 (1)
O(1)	5155 (12)	919 (7)	−469 (3)	101 (5)
O(2)	1930 (11)	742 (7)	456 (4)	117 (5)
O(3)	6933 (9)	1205 (5)	658 (3)	62 (3)
N(1)	6624 (11)	829 (6)	1085 (4)	60 (4)
C(1)	5022 (15)	1248 (8)	−118 (5)	77 (6)
C(2)	3040 (16)	1134 (9)	483 (5)	74 (6)
C(3)	5251 (13)	1047 (8)	1159 (4)	54 (4)
C(4)	3953 (15)	1424 (8)	1858 (5)	76 (6)
C(5)	3148 (15)	1210 (9)	2243 (4)	66 (5)
C(6)	2675 (14)	367 (9)	2308 (4)	60 (5)
C(7)	2989 (2)	−270 (9)	1983 (6)	118 (9)
C(8)	3860 (18)	−62 (9)	1602 (5)	97 (7)
C(10)	1786 (19)	159 (10)	2731 (5)	111 (8)
C(12)	9145 (17)	1131 (10)	1432 (6)	107 (8)
C(13)	7599 (20)	68 (13)	1847 (6)	142 (10)
C(14)	8491 (16)	−333 (9)	1057 (6)	114 (8)
C(16)	6165 (14)	3185 (8)	625 (4)	66 (5)
C(17)	5241 (17)	3224 (8)	209 (6)	78 (6)
C(18)	3718 (16)	3134 (9)	288 (5)	70 (5)
C(19)	3749 (14)	3033 (7)	801 (5)	64 (5)
C(20)	5226 (15)	3066 (8)	997 (4)	65 (5)
C(9)	4352 (13)	775 (7)	1558 (4)	51 (4)
C(11)	7949 (13)	398 (8)	1359 (4)	63 (5)
B	2823 (15)	6227 (9)	1270 (5)	46 (5)
C(21)	3393 (7)	4767 (5)	1785 (3)	53 (5)
C(22)	3027	3942	1973	62 (5)
C(23)	1657	3546	1823	73 (6)
C(24)	654	3975	1485	66 (6)
C(25)	1020	4799	1297	51 (5)
C(26)	2389	5195	1447	47 (4)
C(31)	5257 (8)	5543 (4)	956 (3)	55 (5)
C(32)	6711	5589	826	65 (5)
C(33)	7525	6378	895	73 (6)
C(34)	6886	7120	1095	80 (6)
C(35)	5432	7074	1226	64 (5)
C(36)	4618	6285	1157	48 (4)
C(41)	1453 (9)	5969 (4)	379 (3)	49 (5)
C(42)	731	6269	−57	73 (6)
C(43)	431	7174	−125	79 (6)
C(44)	852	7781	243	88 (7)
C(45)	1574	7481	679	64 (5)
C(46)	1875	6575	748	49 (5)
C(51)	880 (8)	7089 (6)	1750 (3)	77 (6)
C(52)	421	7533	2150	84 (7)
C(53)	1460	7752	2537	53 (7)
C(54)	2958	7527	2524	97 (7)
C(55)	3417	7082	2125	85 (7)
C(56)	2378	6863	1737	48 (4)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Chart II



3 16 18 15

The Re–O bonds in complexes **15**, **16**, and **18** are similar to each other and appear to represent a Re–O single bond (e.g., Re(O)(OPh)(MeC≡CMe)$_2$, Re–OPh = 1.966 (14) Å).[20]

Table VII. Selected Bond Distances and Angles for [Cp(CO)$_2$Re(η^2-O{N-Bu^t}C{Tol}]BPh$_4$, 16′

	Bond Lengths, Å		
Re–O(3)	2.092 (8)	Re–C(1)	2.002 (14)
Re–C(2)	1.926 (14)	Re–C(3)	2.129 (11)
Re–C(16)	2.364 (12)	Re–C(17)	2.315 (14)
Re–C(18)	2.281 (13)	Re–C(19)	2.243 (12)
Re–C(20)	2.290 (12)	O(1)–C(1)	1.111 (17)
O(2)–C(2)	1.156 (17)	O(3)–N(1)	1.368 (13)
N(1)–C(3)	1.314 (16)	N(1)–C(11)	1.498 (15)
C(3)–C(9)	1.496 (17)	C(4)–C(5)	1.390 (19)
C(4)–C(9)	1.354 (18)	C(5)–C(6)	1.353 (19)
C(6)–C(7)	1.364 (20)	C(6)–C(10)	1.519 (20)
C(7)–C(8)	1.415 (24)	C(8)–C(9)	1.342 (17)
C(12)–C(11)	1.539 (19)	C(13)–C(11)	1.510 (22)
C(14)–C(11)	1.492 (20)	C(16)–C(17)	1.359 (20)
C(16)–C(20)	1.413 (19)	C(17)–C(18)	1.417 (21)
C(18)–C(19)	1.433 (18)	C(19)–C(20)	1.388 (18)
B–C(26)	1.682 (15)	B–C(36)	1.679 (15)
B–C(46)	1.694 (15)	B–C(56)	1.694 (16)
CNT–Re[a]	1.966 (11)		
	Bond Angles, deg		
C(1)–Re–C(2)	81.8 (6)	C(3)–Re–O(3)	62.0 (4)
C(1)–Re–C(3)	119.1 (5)	Re–C(1)–O(1)	178.0 (12)
C(1)–Re–O(3)	79.9 (4)	Re–C(2)–O(2)	178.0 (12)
C(2)–Re–C(3)	79.9 (5)	Re–C(3)–N(1)	95.3 (7)
C(2)–Re–O(3)	120.7 (5)	Re–O(3)–N(1)	94.8 (6)
C(3)–N(1)O(3)	107.9 (9)	CNT–Re–C(1)	120.7 (8)
CNT–Re–C(2)	121.3 (9)	CNT–Re–C(3)	118.5 (9)
CNT–Re–O(3)	116.5 (10)		

[a] CNT = centroid of η^5-C$_5$H$_5$ ring.

Table VIII. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for (CO)$_2$(PMe$_3$)$_2$Re(η^2-ON{Bu^t}C{Tol}), 18

	x	*y*	*z*	*U*[a]
Re	3479.7 (3)	2512.6 (2)	2492.4 (2)	49.8 (1)
P(1)	3263 (2)	4669 (2)	2587 (2)	62 (1)
P(2)	3632 (2)	352 (2)	2551 (2)	66 (1)
O	1493 (5)	2535 (5)	3409 (4)	61 (2)
O(1)	5728 (7)	2635 (7)	572 (6)	101 (3)
O(2)	5376 (8)	2482 (8)	4559 (7)	118 (3)
N	861 (6)	2604 (5)	2365 (5)	54 (2)
C(1)	4893 (8)	2590 (7)	1345 (7)	63 (3)
C(2)	4679 (8)	2476 (8)	3776 (7)	69 (3)
C(3)	1739 (7)	2555 (6)	1453 (5)	50 (2)
C(4)	5264 (10)	−385 (9)	2911 (13)	112 (5)
C(5)	3281 (14)	−345 (10)	1196 (11)	111 (5)
C(6)	2525 (12)	−379 (9)	3663 (10)	102 (4)
C(7)	4803 (11)	5429 (10)	2319 (14)	122 (6)
C(8)	2130 (12)	5623 (9)	1648 (11)	106 (5)
C(9)	2721 (15)	5146 (10)	4070 (10)	118 (6)
C(10)	−657 (8)	2814 (8)	2502 (7)	68 (3)
C(11)	−950 (10)	3659 (11)	3522 (9)	106 (5)
C(12)	−1222 (10)	1564 (10)	2857 (12)	108 (5)
C(13)	−1259 (9)	3433 (9)	1370 (8)	82 (3)
C(14)	1467 (7)	2476 (6)	177 (6)	54 (2)
C(15)	2215 (8)	3138 (7)	−677 (6)	64 (3)
C(16)	2092 (9)	3041 (7)	−1892 (7)	69 (3)
C(17)	1244 (9)	2264 (7)	−2291 (6)	67 (3)
C(18)	527 (9)	1571 (8)	−1457 (7)	72 (3)
C(19)	625 (8)	1675 (7)	−224 (7)	67 (3)
C(20)	1138 (12)	2139 (10)	−3627 (8)	100 (4)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

The O–N bond distances in the three compounds also compare favorably and are near the value characteristic of N–O single bonds in organic compounds (1.40 Å).[19]

The drawings in Chart II compare the bond angles within the metallacycles of **3**, **15**, **16**, and **18**. The bond angles within the four-membered rings are similar, but as expected these rings are considerably more strained than the five-membered ring of **15**.

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(20) Erikson, T. K. J.; Bryan, J. C.; Mayer, J. M. *Organometallics* **1988**, *7*, 1930.

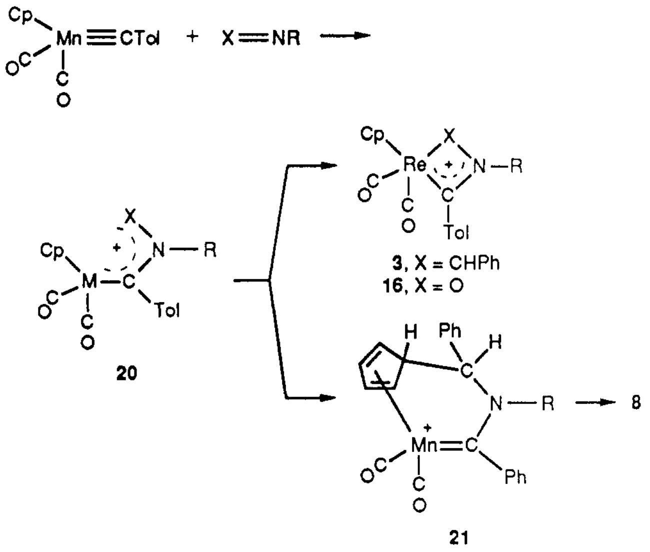
(21) Wong, W. K.; Tam, W.; Strouse, C. E. Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1979**, 530.

Table IX. Selected Bond Distances and Angles for $(CO)_2(PMe_3)_2Re(\eta^2\text{-}ON\{Bu^t\}C\{Tol\})$, 18

Bond Lengths, Å			
Re-P(1)	2.392 (2)	Re-C(3)	2.144 (7)
Re-P(2)	2.382 (2)	C(1)-O(1)	1.173 (10)
Re-O	2.192 (5)	C(2)-O(2)	1.151 (12)
Re-C(1)	1.865 (8)	C(3)-N	1.314 (8)
Re-C(2)	1.918 (8)	N-O	1.353 (7)

Bond Angles, deg			
P(1)-Re-P(2)	175.7 (1)	O-Re-C(1)	164.3 (3)
P(1)-Re-O	85.7 (1)	O-Re-C(2)	103.7 (3)
P(1)-Re-C(1)	92.4 (2)	O-Re-C(3)	60.7 (2)
P(1)-Re-C(2)	86.8 (3)	C(1)-Re-C(2)	91.7 (3)
P(1)-Re-C(3)	91.7 (2)	C(1)-Re-C(3)	103.9 (3)
P(2)-Re-O	91.2 (1)	C(2)-Re-C(3)	164.4 (3)
P(2)-Re-C(1)	91.4 (2)	Re-O-N	92.8 (3)
P(2)-Re-C(2)	91.1 (3)	O-N-C(3)	110.3 (5)
P(2)-Re-C(3)	89.4 (2)	Re-C(3)-N	96.1 (4)

Scheme IV



Concluding Remarks

Prior to the work reported herein, only alkynes[3] and CO$_2$[5] had been shown to undergo [2 + 2] cycloaddition across a metal–carbon triple bond to form stable metallacycles, but now imines and Bu^{t}N=O can be added to that list on the basis of the above-described reactions of these substrates with $[Cp(CO)_2Re{\equiv}CTol]^+$, 2. This latter complex is ideally suited for cycloaddition with polar organic molecules because of the documented facility with which it adds nucleophiles to the carbyne carbon.[10] The nucleophilic character of the substrate is critically important for cycloaddition with 2 since nonpolar substrates such as olefins and alkynes fail to react with this complex, even when activated by electron releasing groups (e.g., $CH_2{=}CHOEt$, $MeC{\equiv}CMe$). As illustrated in Scheme IV, the first step in the transformations described herein is likely nucleophilic addition of the imine or nitroso nitrogen atom to the carbyne carbon to form an intermediate such as 20. This species can then either undergo ring closure by addition to the metal atom to give complexes 3 and 16 or in the case of manganese can nucleophilically attack the Cp ring to give complex 21. That ring closure occurs with Re but not with Mn may reflect the larger size of the former metal. The covalent radius of manganese is 1.46 Å, whereas that of rhenium is 1.59 Å,[22] suggesting that the rhenium center is better able to accept an expanded coordination sphere in its products than is manganese. Another important factor in these reactions may be the known differences in susceptibility of the Cp ligand to electrophilic attack as evidenced by Fischer and co-workers demonstration that the Cp ligand of CpMn(CO)$_3$ is far more reactive toward Friedel–Crafts acylation than is the Cp ligand in CpRe(CO)$_3$.[23]

There are also some remarkable differences in the behavior of the rhenium complexes 3 and 16, both of which possess similar four-membered metallacycles. Complex 16, formed from the combination of 2 with Bu^{t}N=O, rapidly undergoes ring expansion when treated with a chloride source, but complex 3 fails to give similar chemistry even when stirred for prolonged periods with excess chloride. The differing reactivity is apparently electronic in origin since the crystallographic results show that the two compounds have very similar structures with comparable degrees of ring strain. The key difference in the two compounds is binding of an oxygen atom to rhenium in the metallacycle of 16 whereas this atom is replaced by a CHPh group in 3. There is a great deal of electronic difference in these two substituents, and in particular, the oxygen atom has unpaired electrons that can be donated to the rhenium center to stabilize the coordinatively unsaturated transition state that must form in the CO migratory insertion step leading to the ring-expanded product 15. Note that the crystal structure of the latter compound (Figure 2) shows that the chloride ligand is trans to the oxygen atom, suggesting that it was the carbonyl ligand in this position in 16 that underwent the migratory insertion. The differing electronic character of the metallacycles 3 and 16 also manifests itself in their differing reactivity with PMe$_3$. Recall that this reagent adds to the tolyl-substituted ring carbon of the metallacycle in 3, whereas with 16 displacement of the Cp ligand occurs to form complex 18, which retains the original metallacycle. This result suggests that the positive charge is more localized on the metallacycle ring carbon in 3 than it is in 16. A detailed electronic structural analysis would thus appear warranted to more carefully probe the electronic differences between these two compounds.

Experimental Section

General Procedure. The complexes $[Cp(CO)_2Mn{\equiv}CPh][BCl_4]$,[26a] Cp*Mn(CO)$_3$,[26b] and CpRe(CO)$_3$[27] were prepared by literature procedures. The complex $[Cp^*(CO)_2Mn{\equiv}CTol][BCl_4]$ was prepared from Cp*Mn(CO)$_3$ by the same procedure reported for the Cp analogue.[26a] Solvents were dried by refluxing over Na/benzophone ketyl (THF, Et$_2$O) or CaH$_2$ (CH$_2$Cl$_2$, pentane,

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hexane) and were freshly distilled prior to use. The reagents $PhCH{=}N{-}N{=}CHPh$ (Pfaltz and Bauer, Inc.), $Re_2(CO)_{10}$, $CpMn(CO)_3$ (Strem Chemicals), NEt_3, $PhCH{=}NCH_3$, [PPN]Cl, $AgBF_4$, Me_3SiCl, PMe_3, and $[Bu^tN{=}O]_2$ (Aldrich Chemical Co.) were purchased and used as received except for $PhCH{=}NCH_3$, which was freshly distilled before use. All manipulations were performed under N_2 using standard Schlenk techniques. IR spectra were recorded on an IBM FTIR-32 spectrometer operated in the absorbance mode, NMR spectra were recorded on a Brucker AM 300 FT NMR spectrometer, and electron impact (EI) and fast atom bombardment (FAB) mass spectra were respectively recorded on AEI-MS9 and AFAB-MS9 mass spectrometers. Field desorption (FD) mass spectra were obtained by G. Steinmetz and R. J. Hale at the Tennessee Eastman Co. Elemental analyses were obtained from Schwarzkopf Microanalytical Laboratories, Woodside, NY.

Preparation of Monomeric $Bu^tN{=}O$ from $[Bu^tN{=}O]_2$. For the reactions described below using $Bu^tN{=}O$, an apparatus was assembled consisting of two Schlenk flasks connected by a glass U-tube. The glassware was flame-dried, solid $[Bu^tN{=}O]_2$ was added to one of the Schlenk flasks, and the metal complex to be studied and its solvent were added to the other. The apparatus was evacuated, and the flask containing the metal complex was cooled to −78 °C while the flask containing solid $[Bu^tN{=}O]_2$ was gently warmed with a heat gun. Monomeric $Bu^tN{=}O$ distilled into the cooled vessel over 10 min.

Modified Syntheses of $[Cp(CO)_2Re{\equiv}CTol]BCl_4$ and $[Cp(CO)_2Re{\equiv}CTol]BPh_4$. These complexes were prepared by a modification of the original Fischer synthesis.[28] The complex $CpRe(CO)_3$ (2.6 g, 7.74 mmol) was dissolved in dry Et_2O (100 mL) in a three-necked round-bottom flask under N_2. Tolyl lithium (7.74 mmol) was added over 30 min via a dropping funnel, and the reaction mixture was allowed to stir for 30 min. To the resulting yellow solution of the acyl complex $Li[Cp(CO)_2Re{-}C\{O\}Tol]$ was added Me_3SiCl (0.84 mL, 7.74 mmol) via syringe, and the reaction mixture was stirred for 1 h. The solvent was removed under vacuum to yield the brown-red carbene complex $Cp(CO)_2Re{=}C(OSiMe_3)Tol$. This complex was dissolved in dry pentane (200 mL), and the solution was filtered through a pad of Celite on a glass frit. The filtrate was cooled to −20 °C, and BCl_3 gas was bubbled through the solution to induce formation of the salt $[Cp(CO)_2Re{\equiv}CTol]BCl_4$, which precipitated as a yellow solid. The pentane was removed by cannula, and the solid residue was washed with pentane (3 × 50 mL, −20 °C) and then dried under vacuum at −20 °C. Spectroscopic data were similar to those previously reported[25] for the related complex $[Cp(CO)_2Re{\equiv}CPh]BCl_4$.

$[Cp(CO)_2Re{\equiv}CTol]BCl_4$: ^1H NMR (−10 °C, CD_2Cl_2) δ 2.48 (s, 3 H, Tol-C*H*$_3$), 6.24 (s, 5 H, Cp), 7.32–7.88 (m, 4 H, Tol). ^{13}C NMR (−10 °C, CD_2Cl_2) δ 23.1 (Tol-*C*H$_3$), 93.8 (Cp), 129.9, 134.0, 142.8, 151.4 (Tol), 186.1 (*C*O), 316.3 (Re≡*C*). IR (CD_2Cl_2) ν_{CO} 2033, 2087 cm^{-1}.

The salt $[Cp(CO)_2Re{\equiv}CTol]BPh_4$ was prepared by dissolving $[Cp(CO)_2Re{\equiv}CTol]BCl_4$ (200 mg, 0.356 mmol) in THF (50 mL) at −20 °C and adding $Na[BPh_4]$ (0.181 mg, 0.534 mmol). After stirring for 1 h, the solvent was removed by vacuum evaporation to leave a mixture of $[Cp(CO)_2Re{\equiv}CTol]BPh_4$ and $Na[BCl_4]$. The complex salt was extracted from the residue with CH_2Cl_2 at −20 °C. Addition of hexane to the CH_2Cl_2 extract induced precipitation of yellow microcrystalline $[Cp(CO)_2Re{\equiv}CTol]BPh_4$ (52% yield, 136 mg, 0.186 mmol). IR (CH_2Cl_2) 2033, 2087 cm^{-1}. ^1H NMR (CD_2Cl_2) δ 2.47 (s, 3 H, Tol-C*H*$_3$), 5.63 (s, 5 H, Cp), 6.85–7.79 (m, 24 H, aryl). ^{13}C NMR (CD_2Cl_2) δ 23.2 (Tol-*C*H$_3$), 93.3 (Cp), 122.1–151.8 (aryl), 186.1 (*C*O), 316.9 (Re≡*C*).

Reaction of $[Cp(CO)_2Re{\equiv}CTol]BCl_4$ with $PhCH{=}NMe$. The salt $[Cp(CO)_2Re{\equiv}CTol]BCl_4$ (50 mg, 0.089 mmol) was dissolved in CH_2Cl_2 (20 mL) at −20 °C. *N*-Benzylidenemethylamine (0.011 mL, 0.089 mmol) was added via syringe, and the reaction mixture was stirred for 15 min. The solvent was reduced in vacuo to 10 mL, and sufficient hexane was added to induce crystallization of $[Cp(CO)_2Re(\eta^2\text{-}CH\{Ph\}N\{CH_3\}C\{Tol\})]BCl_4$, **3**. The supernatant was removed by cannula, and the product was washed with hexane (3 × 10 mL) to give light green microcrystalline **3** in 83% yield (51 mg, 0.075 mmol) as a 1:1.8 mixture of two diastereomers **3a** and **3b**.

3a and **3b**: Anal. Calcd for $C_{23}H_{16}BCl_4NO_2Re{\cdot}C_6H_{12}$ (%): C, 45.32; H, 4.59. Found: C, 44.87; H, 4.14. IR (CH_2Cl_2) ν_{CO} 2042 (s), 1975 (m) cm^{-1}. MS (FAB, 3-nitrophenyl oxtyl ether matrix) *m/z* 530 (M$^+$), 411 (M$^+$ − $CH_3N{=}CHPh$).

3a: ^1H NMR (acetone-d_6) δ 2.46 (s, 3 H, Tol-C*H*$_3$), 3.58 (s, 3 H, NC*H*$_3$), 5.48 (s, 1 H, C*H*Ph), 5.81 (s, 5 H, Cp), 7.19–7.67 (m, 9 H, aryl). ^{13}C NMR (CD_2Cl_2) δ 20.1 (*C*HPh), 21.6 (Tol-*C*H$_3$), 45.5 (N-*C*H$_3$), 95.3 (Cp), 124.7–144.0 (aryl), 200.2 (*C*-Tol), 201.2, 201.4 (*C*O).

3b: ^1H NMR (acetone-d_6) δ 2.46 (s, 3 H, Tol-C*H*$_3$), 3.47 (s, 3 H, NC*H*$_3$), 5.61 (s, 1 H, C*H*Ph), 6.45 (s, 5 H, Cp), 7.19–7.67 (m, 9 H, aryl). ^{13}C NMR (CD_2Cl_2) δ 16.2 (*C*HPh), 21.6 (Tol-*C*H$_3$), 46.6 (N-*C*H$_3$), 93.5 (Cp), 124.7–144.0 (aryl), 200.2 (*C*-Tol), 197.3, 199.0 (*C*O).

Reaction of $[Cp(CO)_2Re{\equiv}CTol]BCl_4$ with $PhCH{=}N{-}N{=}CHPh$. The salt $[Cp(CO)_2Re{\equiv}CTol]BCl_4$ (103 mg, 0.183 mmol) was dissolved in CH_2Cl_2 (20 mL) at −20 °C. The reagent $PhCH{=}N{-}N{=}CHPh$ (38 mg; 0.183 mmol) was added, and the reaction mixture was stirred for 3 h. The solvent was reduced under vacuum to 10 mL, and hexane was added until crystals of $[Cp(CO)_2Re(\eta^2\text{-}CH\{Ph\}N\{{-}N{=}CHPh\}C\{Tol\})]BCl_4$, **4**, precipitated. The supernatant was removed by cannula, and the product was washed with hexane (3 × 10 mL) to yield **4** as a yellow microcrystalline solid in 76% yield (107 mg; 0.139 mmol) as a 1:2 mixture of two diastereomers, **4a** and **4b**.

4: Anal. Calcd for $C_{29}H_{24}BCl_4N_2O_2Re{\cdot}C_6H_{14}$ (%): C, 49.02; H, 4.47. Found: C, 48.74; H, 3.90. IR (CH_2Cl_2) ν_{CO} 2047 (s), 1977 (m) cm^{-1}. MS (FAB, 18-crown-6 matrix) *m/z* 619 (M$^+$).

4a: ^1H NMR (CD_2Cl_2) δ 2.55 (s, 3 H, Tol-C*H*$_3$), 5.00 (s, 1 H, C*H*Ph), 5.60 (s, 5 H, Cp), 7.11–8.11 (m, 14 H, aryl), 9.33 (s, 1 H, exocyclic C*H*Ph). ^{13}C NMR (CD_2Cl_2) δ 15.7 (*C*HPh), 21.9 (Tol-*C*H$_3$), 96.1 (Cp), 124.5–147.5 (aryl), 157.1 (exocyclic *C*HPh), 194.7 (*C*-Tol), 199.0, 200.4 (*C*O).

4b: ^1H NMR (CD_2Cl_2) δ 2.52 (s, 3 H, Tol-C*H*$_3$), 5.37 (s, 1 H, C*H*Ph), 6.20 (s, 5 H, Cp), 7.11–8.11 (m, 14 H, aryl), 8.55 (s, 1 H, exocyclic C*H*Ph). ^{13}C NMR (CD_2Cl_2) δ 20.7 (*C*HPh), 21.9 (Tol-*C*H$_3$), 98.7 (Cp), 124.5–147.5 (aryl), 157.6 (exocyclic *C*HPh), 194.7 (*C*-Tol), 201.2, 201.6 (*C*O).

Attempted Imine Exchange in Complexes 3 and 4. Complex **3** (50 mg; 0.073 mmol) was dissolved in CH_2Cl_2 (20 mL) followed by addition of $PhCH{=}N{-}N{=}CHPh$ (30 mg, 0.146 mmol). After stirring for 24 h at 22 °C, the solvent was removed and the product recrystallized. ^1H NMR analysis showed only the presence of **3** with no **4** present. A similar experiment employing complex **4** with excess $PhCH{=}NCH_3$ showed that after stirring for 24 h at 22 °C, only complex **4** was present.

Photoinduced Conversion of $[Cp(CO)_2Re(\eta^2\text{-}CH\{Ph\}N\{CH_3\}C\{Tol\})]BCl_4$, 3, into $Cp(CO)ClRe(\eta^2\text{-}CH\{Ph\}N\{CH_3\}C\{Tol\}C\{O\})$, 5. Complex **3** (50 mg, 0.073 mmol) was dissolved in CH_2Cl_2 (10 mL) in a 50-mL Schlenk flask. The solution was cooled to 0 °C in an ice-water bath and was irradiated with Pyrex-filtered broad-band irradiation from a 450-W medium-pressure Hg vapor lamp (Hanovia) for 30 min, during which time the color changed from pale green to bright yellow. The solvent was removed in vacuo, and the residue was chromatographed on silica gel (0.5 in. × 1.5 ft column) using CH_2Cl_2 as eluent. This gave one bright yellow band, which upon removal of solvent left complex **5** (7.0 mg, 0.013 mmol) as yellow microcrystals in 18% yield. A yellow-orange band was then eluted, which upon evaporation of solvent gave $CpRe(CO)_2Cl_2$[13] as gold microcrystals (3.7 mg, 13%).

5: Anal. Calcd for $C_{22}H_{21}ClNORe{\cdot}CH_2Cl_2$ (%): C, 44.41; H, 3.73. Found: C, 45.06; H, 4.10. IR (CH_2Cl_2) ν_{CO} 1930 (s) cm^{-1}. ^1H NMR (CD_2Cl_2) δ 2.43 (s, 3 H, Tol-C*H*$_3$), 3.37 (s, 3 H, NC*H*$_3$), 4.91 (s, 5 H, Cp), 5.20 (s, 1 H, C*H*Ph), 7.10–7.36 (m, 9 H, aryl). ^{13}C NMR (CD_2Cl_2) δ 21.6 (Tol-*C*H$_3$), 42.1 (*C*HPh), 42.4 (N*C*H$_3$), 93.6 (Cp), 124–147.1 (aryl), 211.2 (*C*O), 216.7 (Re=*C*). MS (EI), *m/z* 537 (M$^+$), 419 (M$^+$ − $CH_3N{=}CHPh$).

$CpRe(CO)_2Cl_2$: MS (EI) *m/z* 378 (M$^+$). IR (CH_2Cl_2) 2013 (s), 2079 (s) cm^{-1} (lit.[13] ν_{CO} 2012 (s), 2078 (s) cm^{-1}).

Hydrolysis of $[Cp(CO)_2Re(\eta^2\text{-}CH\{Ph\}N\{CH_3\}C\{Tol\})]BCl_4$, 3, To Form $Cp(CO)_2Re{=}C(NHCH_3)(Tol)$, 6, and Benzaldehyde. Complex **3** (70 mg, 0.10 mmol) was dissolved in CH_2Cl_2 (20 mL). Aqueous NaOH was added (0.09 M, 7 mL), and the

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[28] Fischer, E. O.; Clough, R. L.; Stückler, P. *J. Organomet. Chem.* **1976**, *120*, C6.

solution was stirred for 50 min. IR analysis showed the presence of complex **6** along with PhCHO (ν_{CO} 1705 cm^{-1}). The resulting mixture was extracted with CH_2Cl_2 (3 × 20 mL), and the combined CH_2Cl_2 washings were dried over $MgSO_4$ and filtered. The solvent was removed under vacuum, and the residue was chromatographed on silica gel (0.5 in. × 1 ft column) with 50:50 CH_2Cl_2/hexane as eluent. A clear fraction first eluted, which upon removal of solvent gave PhCHO (5 mg, 0.047 mmol, 46%, ν_{CO} 1705 cm^{-1}, *m/z* 106 (M^+)) as a clear liquid. Next, a pale yellow band eluted with 1:1 CH_2Cl_2/acetone as eluent. This gave upon removal of solvent complex **6** (22 mg, 0.055 mmol) as pale yellow microcrystals in 49% yield.

6: Anal. Calcd for $C_{16}H_{16}NO_2Re$ (%): C, 43.63; H, 3.66. Found: C, 43.50; H, 3.71. IR (CH_2Cl_2) ν_{CO} 1842 (s), 1919 (s) cm^{-1}. ^1H NMR (CD_2Cl_2) δ 2.34 (s, 3 H, Tol-CH_3), 3.36 (s, 3 H, NCH_3), 4.96 (s, 5 H, Cp), 6.80–7.10 (m, 4 H, Tol), 7.70 (s, 1 H, N*H*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 21.1 (Tol-CH_3), 39.7 (N-CH_3), 87.5 (Cp), 123.2, 128.4, 136.9, 155.6 (Tol), 205.7 (*C*O), 245.3 (Re=*C*). MS (EI) *m/z* 441 (M^+).

Reaction of [Cp(CO)$_2$Re(η^2-CH{Ph}N{CH$_3$}C{Tol})]BCl$_4$, 3, with PMe$_3$. The BPh_4^- salt of complex **3** (240 mg, 0.284 mmol) was dissolved in CH_2Cl_2 (20 mL). Excess PMe_3 (0.088 mL, 0.852 mmol) was added, and the reaction mixture was stirred for 1 h. The solution was concentrated to 10 mL and filtered, and hexane was added until crystals of complex **7** precipitated. The supernatant was removed by cannula, and the product was washed with hexane (3 × 10 mL) to give **7** as a yellow microcrystalline solid in 61% yield (160 mg; 0.173 mmol) as a 2:1 mixture of isomers.

7: Anal. Calcd for $C_{50}H_{50}BNO_2PRe$ (%): C, 64.93; H, 5.45. Found: C, 65.01; H, 5.63. IR (CH_2Cl_2) 1842 (s), 1930 (s) cm^{-1}. MS (FAB, 18-crown-6 matrix), *m/z* 606 (M^+). Major Isomer: ^1H NMR (CD_2Cl_2) δ 1.38 (d, 9 H, P(CH_3)$_3$, J_{PH} = 13.2 Hz), 2.41 (s, 9 H, Tol-CH_3), 2.62 (s, 3 H, NCH_3), 3.68 (s, 1 H, C*H*Ph), 4.95 (s, 5 H, Cp), 6.49–7.56 (Ar). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 8.4 (d, P(CH_3)$_3$, J_{PC} = 50.7 Hz), 21.1 (Tol-CH_3), 40.7 (N-CH_3), 70.6 (*C*HPh), 89.5 (Cp), 120.4–152.1 (Ar), 163.8 (d, *C*(Tol)PMe$_3$, J_{PC} = 48.4 Hz), 202.0, 207.8 (*C*O). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 49.5. Minor Isomer: ^1H NMR (CD_2Cl_2) δ 1.00 (d, 9 H, P(CH_3)$_3$, J_{PH} = 13.0 Hz), 2.41 (s, 9 H, Tol-CH_3), 2.62 (s, 3 H, NCH_3), 3.68 (s, 1 H, C*H*Ph), 4.92 (s, 5 H, Cp), 6.49–7.56 (Ar). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 8.7 (d, P(CH_3)$_3$, J_{PC} = 49.7 Hz), 21.1 (Tol-CH_3), 40.7 (N-CH_3), 72.5 (*C*HPh), 89.7 (Cp), 120.4–152.1 (Ar), 165.1 (d, *C*(Tol)PMe$_3$, J_{PC} = 49.6 Hz), 204.7, 205.9 (*C*O). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 50.3.

Reaction of [Cp(CO)$_2$Mn≡CPh][BCl$_4$] with PhCH=NMe. To a −30 °C CH_2Cl_2 (20 mL) solution of [Cp(CO)$_2$Mn≡CPh][BCl$_4$] (0.505 g, 1.91 mmol) was added PhCH=NMe (0.23 mL, 1.91 mmol), followed by addition of NEt_3 (0.27 mL, 1.91 mmol). The orange solution was allowed to warm to room temperature and was stirred for an additional hour. The solvent was removed under vacuum, and the resulting orange oil was chromatographed on silica gel eluting with 2:1 pentane/CH_2Cl_2. One yellow band eluted which gave yellow microcrystalline **8** after evaporation of solvent (0.327 g, 0.853 mmol, 45% yield).

8: Anal. Calcd for $C_{22}H_{18}O_2NMn$ (%): C, 68.99; H, 4.74. Found: C, 68.33; H, 5.13. IR (CH_2Cl_2) ν_{CO} 1930 (s), 1863 (s) cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.69 (s, 3 H, NCH_3), 4.25, 4.58, 4.77, 4.95 (s, 1 H, Cp), 5.63 (s, 1 H, C*H*Ph), 6.94–7.42 (m, 10 H, aryl). ^{13}C NMR ($CDCl_3$) δ 40.1 (NCH_3), 71.6 (*C*HPh), 78.0, 80.4, 83.0, 87.0, 109.3 (Cp), 109.3–149.8 (aryl), 233.2, 233.4 (*C*O), 288.0 (Mn=*C*). MS (EI), *m/z* 383 (M^+).

Reaction of [Cp*(CO)$_2$Mn≡CTol][BCl$_4$] with PhCH=NMe. To a −30 °C CH_2Cl_2 (20 mL) solution of [Cp*(CO)$_2$Mn≡CTol][BCl$_4$] (0.370 g, 0.974 mmol) was added PhCH=NMe (0.24 mL, 1.95 mmol). The yellow solution was allowed to warm to room temperature and was stirred for an additional hour. The solvent was removed under vacuum, and the resulting yellow oil was chromatographed on silica gel eluting with 2:1 pentane/CH_2Cl_2. The solvent was evaporated from the one yellow band which eluted to yield complex **13** as a yellow microcrystalline solid in 35% yield (0.155 g, 0.343 mmol).

13: Anal. Calcd for $C_{27}H_{28}O_2NMn$ (%): C, 71.60; H, 6.20. Found: C, 71.99; H, 6.85. IR (CH_2Cl_2) ν_{CO} 1913 (s), 1848 (s) cm^{-1}. ^1H NMR (CD_2Cl_2) δ 1.19, 1.63, 1.89, 2.14 (s, 3 H each, C_5\{CH_3\}$_4$), 2.28 (s, 3 H, Tol-CH_3), 2.90 (s, 3 H, NCH_3), 6.07 (s, 1 H, C*H*Ph), 6.80–7.50 (m, 9 H, aryl). ^{13}C NMR (CD_2Cl_2) δ 10.2, 10.9 (C_5\{CH_3\}$_4$), 21.0 (Tol-CH_3), 40.1 (NCH_3), 71.1 (*C*HPh), 90.9, 93.1, 97.7, 101.2, 102.5 (*C*$_5$\{CH_3\}$_4$), 128.5–149.3 (aryl), 234.9, 235.5 (*C*O), 288.7 (Mn=*C*). MS (EI), *m/z* 453 (M^+).

Reaction of [Cp(CO)$_2$Mn≡CPh][BCl$_4$] with PhCH=N—N=CHPh. To a −30 °C CH_2Cl_2 (20 mL) solution of [Cp(CO)$_2$Mn≡CPh][BCl$_4$] (0.226 g, 0.723 mmol) was added PhCH=N—N=CHPh (0.32 mg, 1.53 mmol). The orange solution was allowed to warm to room temperature and was stirred for an additional 12 h. The solvent was removed under vacuum, and the resulting orange oil was chromatographed on silica gel eluting with 2:1 pentane/CH_2Cl_2. The solvent was evaporated from the single orange band to yield complex **9** as an orange microcrystalline solid in 56% yield (0.200 g, 0.424 mmol).

9: Anal. Calcd for $C_{28}H_{21}N_2O_2Mn{\cdot}0.25CH_2Cl_2$ (%): C, 68.83; H, 4.40. Found: C, 68.72; H, 4.54. IR (CH_2Cl_2) ν_{CO} 1942 (s), 1878 (s) cm^{-1}. ^1H NMR (acetone-d_6) δ 4.48, 4.50, 5.02, 5.15 (s, 4 H, Cp), 6.87 (s, 1 H, C*H*Ph), 7.04–7.56 (m, 15 H, aryl), 7.69 (s, 1 H, N=C*H*Ph). ^{13}C NMR (acetone-d_6) δ 66.1 (*C*HPh), 80.3, 82.9, 85.7, 89.9, 106.3 (Cp), 123.5–143.8 (aryl), 152.2 (N=*C*PhH), 233.4, 234.1 (*C*O), 294.6 (Mn=*C*). MS (EI), *m/z* 472 (M^+).

Reaction of [Cp(CO)$_2$Re≡CTol]BCl$_4$ with Bu^{t}N=O To Form [Cp(CO)Re(η^2-ON{Bu^t}C{Tol}C{O})]BCl$_4$, 14, and Cp(CO)ClRe(η^2-ON{Bu^t}C{Tol}C{O}), 15. A solution containing the salt [Cp(CO)$_2$Re≡CTol]BCl$_4$ (50 mg, 0.089 mmol) in CH_2Cl_2 (20 mL) was cooled to −78 °C, and Bu^{t}N=O (7.7 mg of dimer, 0.089 mmol) was condensed into the flask by the method described above. The solution was stirred for 8 h at 0 °C and then warmed to room temperature and stirred for 1 h. Chromatography on a 0.5 in. × 1.5 ft silica gel column with 1:3 acetone/CH_2Cl_2 eluent gave a single red band which upon evaporation of the solvent left complex **15** (25 mg, 52%) as red microcrystals.

Complex **14** was obtained by repeating this reaction exactly as described above with 179 mg of [Cp(CO)$_2$Re≡CTol]BCl$_4$ except that the solution was never allowed to warm above 0 °C. Evaporation of solvent at this temperature left an orange residue which was recrystallized from CH_2Cl_2/hexane at −20 °C to give orange microcrystalline **14** in 47% yield (97 mg, 0.15 mmol).

15: Anal. Calcd for $C_{19}H_{21}NO_3ClRe{\cdot}CH_2Cl_2{\cdot}(CH_3)_2CO$ (%): C, 40.86; H, 4.32. Found: C, 41.14; H, 3.95. ^1H NMR (CD_2Cl_2) δ 1.45 (s, Bu^t), 2.40 (s, Tol-CH_3), 5.54 (s, Cp), 7.02–7.27 (m, Tol). ^{13}C NMR (CD_2Cl_2) δ 21.5 (Tol-CH_3), 30.0 (C(CH_3)$_3$), 74.5 (*C*(CH$_3$)$_3$), 125.3, 129.2, 130.2, 140.9 (Tol), 160.7 (*C*-Tol), 204.1 (*C*O), 231.1 (ring *C*O). IR (CH_2Cl_2) ν_{CO} 1930 (s) cm^{-1}. MS (EI), *m/z* 533 (M^+). MS (FAB, 3-nitrophenyl oxtyl ether matrix), *m/z* 498 (M^+ − Cl).

14: Anal. Calcd for $C_{19}H_{21}BCl_4NO_3Re{\cdot}C_6H_{14}$ (%): C, 40.77; H, 4.80. Found: C, 40.08; H, 4.50. ^1H NMR (−10 °C, CD_2Cl_2) δ 1.33 (s, Bu^t), 2.35 (s, Tol-CH_3), 5.37 (s, Cp), 7.08–7.16 (m, Tol). ^{13}C NMR (−10 °C, CD_2Cl_2) δ 22.8 (Tol-CH_3), 30.5 (C(CH_3)$_3$), 72.5 (*C*(CH$_3$)$_3$), 92.0 (Cp), 123.7, 127.8, 137.5, 139.9 (Tol), 190.5 (*C*-Tol), 200.5 (*C*O), 218.1 (ring *C*O). ^{11}B NMR (CD_2Cl_2) δ 6.88 (referenced to $BF_3{\cdot}Et_2O$). IR (CH_2Cl_2) ν_{CO} 1960 (s) cm^{-1}. MS (FAB, 18-crown-6 matrix), *m/z* 498 (M^+).

Reaction of Cp(CO)ClRe(η^2-ON{Bu^t}C{Tol}C{O}) with AgBF$_4$ To Form [Cp(CO)$_2$Re(η^2-ON{Bu^t}C{Tol})]BF$_4$, 16. The complex Cp(CO)ClRe(η^2-ON{Bu^t}C{Tol}C{O}) (118 mg, 0.210 mmol) was dissolved in CH_2Cl_2 (40 mL) and solid $AgBF_4$ (45 mg, 0.231 mmol) was added. The solution was stirred for 30 min and then filtered through Celite to remove the precipitated AgCl. The solvent was removed in vacuo to give a gold colored residue which was recrystallized from CH_2Cl_2/hexane to yield [Cp(CO)$_2$Re(η^2-ON{Bu^t}C{Tol})]BF$_4$ in 52% yield (63 mg) as gold microcrystals.

16: Anal. Calcd for $C_{19}H_{21}BF_4NO_3Re$ (%): C, 39.05; H, 3.62. Found: C, 39.48; H, 4.13. ^1H NMR (CD_2Cl_2) δ 1.25 (s, Bu^t), 2.41 (s, Tol-CH_3), 6.27 (s, Cp), 7.19–7.36 (m, Tol). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 21.5 (Tol-CH_3), 27.4 (C(CH_3)$_3$), 76.4 (*C*(CH$_3$)$_3$), 95.8 (Cp), 125.5, 130.1, 134.8, 141.2 (Tol), 167.5 (*C*-Tol), 196.7, 198.4 (*C*O). IR (CH_2Cl_2) ν_{CO} 2000 (s), 2062 (vs) cm^{-1}. MS (FAB, 18-crown-6 matrix), *m/z* 498 (M^+).

Reaction of [Cp(CO)$_2$Re≡CTol]BCl$_4$ with [Bu^{t}N=O]$_2$ To Form [Cp(CO)$_2$Re(η^2-ON{Bu^t}C{Tol}C{O})]BCl$_4$, 17. The salt [Cp(CO)$_2$Re≡CTol]BCl$_4$ (53 mg, 0.094 mmol) was dissolved in CH_2Cl_2 (20 mL) at −10 °C. Solid [Bu^{t}N=O]$_2$ (20 mg, 0.12 mmol) was added, and the flask was quickly evacuated and back-filled with CO. The mixture was stirred at 0 °C for 8 h until the IR spectrum of the solution showed the disappearance of the carbyne complex. The solvent was removed under vacuum, and the resulting yellow oil was recrystallized under CO from CH_2Cl_2/hexane at −20 °C to give yellow microcrystalline **17** in 38% yield (24 mg, 0.036 mmol).

17: ^1H NMR (CD_2Cl_2) δ 1.63 (s, 9 H, Bu^t), 2.34 s, 3 H, Tol-C*H*$_3$), 6.00 (s, 5 H, Cp), 7.18–7.48 (m, 4 H, Tol). ^{13}C NMR (CD_2Cl_2) δ 21.8 (Tol-CH_3), 26.3 ($C(CH_3)$), 70.0 (*C*(CH_3)), 98.1 (Cp), 128.5, 128.7, 130.0, 142.5 (Tol), 202.3, 204.5 (*C*O), 221.0 (Re=*C*). IR (CH_2Cl_2) ν_{CO} 1954 (s), 2029 (s) cm^{-1}. MS (FAB, 18-crown-6 matrix), *m/z* 498 (M^+).

Reaction of $[Cp(CO)_2Re{\equiv}CTol]BPh_4$ with $Bu^tN{=}O$ To Form $[Cp(CO)_2Re(\eta^2\text{-}ON\{Bu^t\}C\{Tol\})]BPh_4$, 16′. The salt $[Cp(CO)_2Re{\equiv}CTol]BPh_4$ (132 mg, 0.181 mmol) was dissolved in CH_2Cl_2 (20 mL), and the solution was cooled to −78 °C. The reagent $Bu^tN{=}O$ (11 mg of $[Bu^tN{=}O]_2$, 0.181 mmol) was condensed into the flask by the method described above. The solution was stirred for 8 h at 0 °C as the color changed from yellow to gold. Evaporation of solvent left a gold-colored residue which was recrystallized from CH_2Cl_2/hexane to yield $[Cp(CO)_2Re(\eta^2\text{-}ON\{Bu^t\}C\{Tol\})]BPh_4$, **16′** (70%, 103 mg, 0.126 mmol) as gold microcrystals.

16′: Anal. Calcd for $C_{43}H_{41}BNO_3Re{\cdot}{}^1/_2CH_2Cl_2$ (%): C, 60.80; H, 4.93. Found: C, 61.30; H, 5.69. Spectroscopic data of this salt were identical with those of the BCl_4^- (**16**) salt given above.

Reaction of $[Cp(CO)_2Re(\eta^2\text{-}ON\{Bu^t\}C\{Tol\})]BCl_4$, 16, with PMe_3 To Form $(CO)_2(PMe_3)_2Re(\eta^2\text{-}ON\{Bu^t\}C\{Tol\})$, 18. The salt $[Cp(CO)_2Re(\eta^2\text{-}ON\{Bu^t\}C\{Tol\})]BCl_4$ (212 mg, 0.260 mmol) was dissolved in CH_2Cl_2 (20 mL), the solution was cooled to −10 °C, and PMe_3 (0.026 mL, 0.260 mmol) was added. The solution was stirred for 5 min, after which time the IR spectrum showed the presence of complex **18** (ν_{CO} 1817, 1905 cm^{-1}) and an intermediate species (ν_{CO} 1847, 1956 cm^{-1}). Addition of a second equivalent of PMe_3 (0.026 mL, 0.260 mmol) converted the intermediate species completely to complex **18**. The solvent was removed from this solution under vacuum to yield a yellow oil. The oil was dissolved in 1 mL of CH_2Cl_2 and chromatographed on silica gel (0.5 in. × 1 ft column) using CH_2Cl_2 as eluent. A single yellow band eluted which upon evaporation of solvent gave complex **18** as gold microcrystals (57 mg, 38%). The intermediate complex could not be isolated due to its rapid conversion to complex **18**.

18: Anal. Calcd for $C_{20}H_{34}NO_3P_2Re$ (%): C, 41.02; H, 6.02. Found: C, 41.24; H, 5.92. IR (CH_2Cl_2) ν_{CO} 1817 (s), 1905 (s) cm^{-1}. ^1H NMR (CD_2Cl_2) δ 1.33 (s, 9 H, Bu^t), 1.57 (t, 18 H, P(C*H*$_3$)$_3$, J_{PH} = 3.5 Hz), 2.34 (s, 3 H, Tol-C*H*$_3$), 6.95–7.15 (m, 4 H, Tol). ^{13}C NMR (CD_2Cl_2) δ 18.8 (t, PCH_3, J_{PC} = 14.93), 21.1 (Tol-CH_3), 29.1 ($C(CH_3)_3$), 71.7 (*C*(CH_3)$_3$), 122.2, 126.3, 128.6, 136.2 (Tol), 204.6 (t, Re=*C*, J_{PC} = 9.2 Hz), 205.8 (t, *C*O, J_{PC} = 7.4 Hz), 206.0 (t, *C*O, J_{CP} = 6.10 Hz). ^{31}P NMR (CD_2Cl_2) δ 24.95. MS (EI), *m/z* 585 (M^+).

X-ray Crystallographic Characterization of Complexes 3, 15, 16′, and 18. General Methods. Crystallographic data for the four complexes are contained in Table I. Specimens of suitable quality were mounted on glass fibers, and unit-cell parameters were obtained from the angular settings of 25 reflections (15° ≤ 2 θ ≤ 25°). All were empirically corrected for absorption (ψ-scans, six reflections, 216 data). The Re atom in each was located by heavy-atom methods. All non-hydrogen atoms were anisotropically refined, and all hydrogen atoms were treated as idealized isotropic contributions. All calculations used SHELXTL software (G. S. Sheldrick, Nicolet XRD, Madison, WI).

$[Cp(CO)_2Re(\eta^2\text{-}CH\{Ph\}N\{CH_3\}C\{Tol\})]BCl_4$, 3: The centrosymmetric space group was initially assumed and later confirmed by the results of refinement. A correction was applied for an 11% decrease in the standard reflections. The phenyl ring, C(11–16), was constrained to a rigid planar hexagon, d_{CC} = 1.395 Å.

$Cp(CO)(Cl)Re(\eta^2\text{-}ON\{Bu^t\}C\{Tol\}C\{O\})$, 15: The noncentrosymmetric space group *Fdd*2 was uniquely determined by systematic absences in the diffraction data. The aromatic ring, C(13–18), was constrained to a rigid planar hexagon, d_{CC} = 1.395 Å. The enantiomorph reported produced a multiplicative factor for $\Delta f''$ that refined to 1.02 (4), indicating the correctness of the handedness.

$[Cp(CO)_2Re(\eta^2\text{-}ON\{Bu^t\}C\{Tol\})]BPh_4$, 16′: Systematic absences unambiguously established the space group as $P2_1/c$. The thin-plate habit (major face 0,0,1) of the crystal necessitated an absorption correction that eliminated reflections making a shallow (≤3°) glancing angle to the crystal; these reflections were found to contain excessive edge effects. Of 216 ψ-scan reflections, 12 data were ignored; of 4730 general data, 354 were discarded. The phenyl rings of the anion were treated as rigid, planar hexagons, d_{CC} = 1.395 Å.

$(CO)_2(PMe_3)_2Re(\eta^2\text{-}ON\{Bu^t\}C\{Tol\})$, 18: The centrosymmetric space group was initially assumed correct; the chemically reasonable results of refinement confirmed this assumption.

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Supplementary Material Available: For 3, 15, 16′, and 18, tables of anisotropic temperature factors, complete bond lengths and bond angles, and calculated hydrogen atom positions (15 pages); lists of structural factors (80 pages). Ordering information is given on any current masthead page.