Addition and Cycloaddition Reactions of $[Cp(CO)_2Re{\equiv}CTol]^+$ with *cis*-Azoarenes, Epoxides, 3,3-Dimethyloxetane, 2-Methylaziridine, Propylene Sulfide, and Benzophenone Hydrazone. Displacement of the Cyclopentadienyl Ligand from the Resultant Metallacycles by Trimethylphosphine

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The BPh_4^- salt of the carbyne complex $[Cp(CO)_2Re{\equiv}CTol]^+$, **1**, undergoes net [2 + 2] cycloaddition of *cis*-azobenzene, *cis*-azotoluene, and benzo[*c*]cinnoline to give new complexes **5a**, **5b**, and **7**, respectively, which possess four-membered metallacycles. The BCl_4^- salt of complex **1** initially reacts with *cis*-azobenzene and *cis*-azotoluene to give metallacycles **5a** and **5b**, but upon stirring these complexes abstract chloride from the BCl_4^- anion and insert a CO ligand into the Re–carbon bond of the metallacycle to give new complexes possessing five-membered metallacycles. With benzo[*c*]cinnoline, the BCl_4^- salt of complex **1** reacts to give initially the metallacycle **7** formed from the BPh_4^- salt, but upon stirring, the benzo[*c*]cinnoline group is displaced by chloride (from BCl_4^-) to yield the chlorocarbene complex $Cp(CO)_2Re{=}C(Cl)Tol$. The metallacycles **5a** and **5b** react with $[(Ph_3P)_2N]Cl$ to give new complexes (**10a,b**) that result from loss of a CO ligand and an "NPh" group from the metallacycle, coordination of Cl^- to the metal, ortho-metalation of the N-aryl group, and hydrogen migration to the remaining nitrogen atom. The BCl_4^- salt of complex **1** reacts with ethylene oxide, propylene oxide, and isobutylene oxide to form new carbene complexes of the form $Cp(CO)_2Re{=}C(Tol)OCR_2CR_2Cl$ that result from chloride-induced ring opening and addition of the epoxide to the carbyne carbon. A similar ring-opening and addition of 3,3-dimethyloxetane occurs with the BCl_4^- salt of complex **1** to form the new carbene complex $Cp(CO)_2Re{=}C(Tol)OCH_2CMe_2CH_2Cl$ (**17**). With 2-methylaziridine, carbyne complex **1** reacts to give an aziridinocarbene complex, and complex **1** abstracts sulfur from 2 equiv of propylene sulfide to give the η^2-dithiocarboxylate complex $[Cp(CO)_2Re\{\eta^2\text{-}S_2CTol\}]BPh_4$ (**19**). Carbyne complex **1** and its methylcarbyne analogue both react with benzophenone hydrazone to give the hydrazonyl carbene complexes $Cp(CO)_2Re{=}C(R)NHN{=}CPh_2$, **20** (R = Tol) and **21** (R = Me). Complex **19** reacts with PMe_3 to displace the Cp ligand as the phosphonium salt $[CpPMe_3]BPh_4$ and form the new complex *trans*-$(CO)_2(PMe_3)_2Re\{\eta^2\text{-}S_2CTol\}$. A similar reaction of PMe_3 occurs with complex **7** to give initially a *cis*-bis(phosphine) complex **24** which isomerizes upon heating to a trans derivative **25**. Complexes **5a** and **5b** react with PMe_3 to give similar Cp displacement reactions and form *trans*-bis(phosphine) complexes **26a,b** in which the metallacycles have undergone a rearrangement to form η^2-benzamidinato ligands. Complexes **10a**, **17**, **20**, **21**, **24**, **25**, and **26a** have been crystallographically characterized.

Introduction

It was earlier demonstrated in these laboratories that the highly electrophilic carbyne complex $[Cp(CO)_2Re{\equiv}CTol]^+$, **1**, readily cycloadds the unsaturated substrates PhHC=NMe and $Bu^tN{=}O$ to give the metallacycles shown in Scheme I.[1] The first step in both reactions is believed to be addition of the nucleophilic nitrogen atom of the organic substrate to the electrophilic carbyne carbon, analogous to the many other nucleophiles which have been shown to add to this carbon.[2] In an attempt to form other types of metallacycles from carbyne complex **1**, we have since reacted this species with *cis*-azobenzene, *cis*-azo-*p*-toluene, benzo[*c*]cinnoline, ethylene oxide, propylene oxide, isobutylene oxide, 3,3-dimethyloxetane, 2-methylaziridine, propylene sulfide, and benzophenone hydrazone. These reactions have led to a variety of new metallacycles and carbene complexes, and those results are described herein.

(1) (a) Handwerker, B. M.; Garrett, K. E.; Nagle, K. L.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1990**, *9*, 1562. (b) Handwerker, B. M.; Garrett, K. E.; Geoffroy, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 369.

(2) (a) Fischer, E. O.; Chen, J.; Scherzer, K. *J. Organomet. Chem.* **1983**, *253*, 231. (b) Fischer, E. O.; Wanner, J. K. R. *Chem. Ber.* **1985**, *118*, 2489. (c) Fischer, E. O.; Schambeck, W. *J. Organomet. Chem.* **1980**, *201*, 311. (d) Fischer, E. O.; Clough, R. L.; Stückler, P. *J. Organomet. Chem.* **1976**, *120*, C6. (e) Fischer, E. O.; Frank, A. *Chem. Ber.* **1978**, *111*, 3740.

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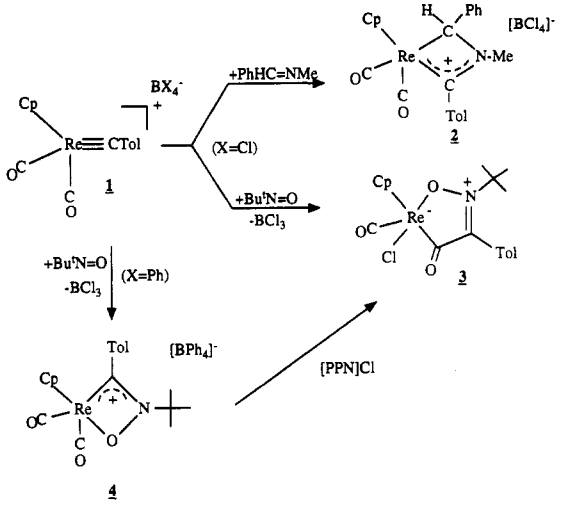
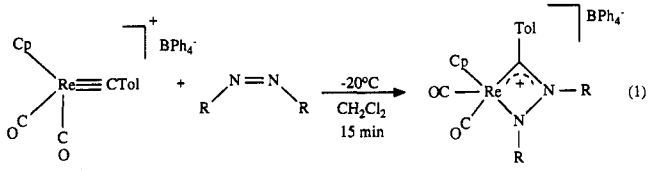
Scheme I



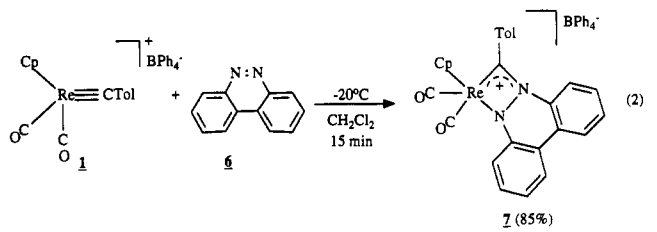
Results and Discussion

Cycloaddition of *cis*-RN=NR with the BPh_4^- Salt of $[Cp(CO)_2Re{\equiv}CTol]^+$. Although the BPh_4^- salt of carbyne complex **1** does not react with *trans*-azobenzene or *trans*-azotoluene, it readily reacts with the cis isomers of these substrates and with benzo[*c*]cinnoline (**6**), which is constrained to have a cis geometry, to form the new four-membered metallacyclic complexes **5a**, **5b**, and **7**, eqs 1 and 2. These complexes were isolated in good yields



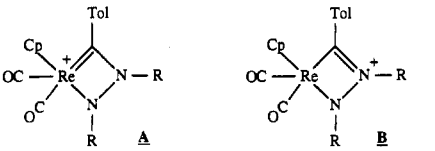
(1)

5a R=Ph (90%)
5b R=Tol (93%)

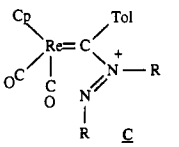


(2)

and were spectroscopically characterized. Their spectroscopic data, and those of the remainder of the new compounds described in the following paragraphs, are summarized in the Experimental Section. To our knowledge, these complexes are the first examples of metallacycles of this type, and they may be termed 3-rhena-1,2-diazetines due to their relationship to the organic diazetine ring system.[3] As illustrated in eqs 1 and 2, the complexes are formulated as hybrids of the resonance forms **A** and **B** with delocalized bonding between the Re, the tolyl-substituted ring carbon, and the ring nitrogen atom. Similar delocalized structures were indicated by the crystal structures of the related complexes **2** and **4** (Scheme I),[1] and resonance forms like those are known to be important for amino–carbene complexes.[4]



The initial step in these formal [2 + 2] cycloaddition reactions likely involves addition of one nitrogen atom of the substrate to the electrophilic carbyne carbon of **1** to give intermediate **C** which then undergoes ring closure to



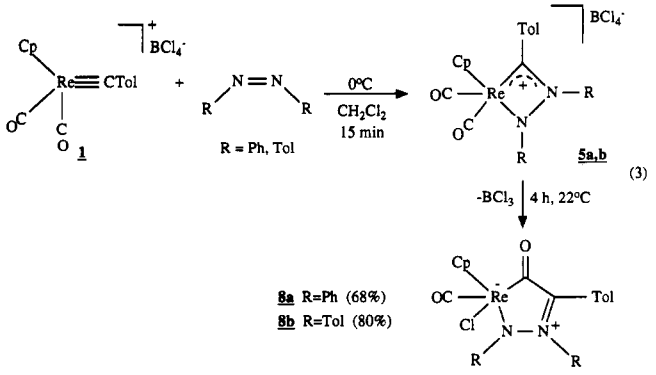
give **5** and **7**. Carbyne complex **1** and its manganese analogue are known to add a variety of nucleophiles to the carbyne carbon to give carbene derivatives similar to **C**,[2] and analogous intermediates were proposed to account for the formation of **2** and **4** illustrated in Scheme I.[1] Azobenzene is also known to react with electrophilic carbene complexes to give products that have been proposed to result from initial addition of one of the azobenzene nitrogen atoms to a carbene carbon.[5] It should be noted that reaction 1 can be induced either by using the pure *cis*-azoarenes formed by UV-irradiation of the trans isomers or by directly irradiating mixtures of **1** and the *trans*-azoarenes. In contrast, photolysis of **1** in the presence of *trans*-$Bu^tN{=}NBu^t$ gave no reaction, apparently because of the instability of *cis*-$Bu^tN{=}NBu^t$ due to the bulky *tert*-butyl substituents. Also, reaction 1 is not readily reversible since complex **5b** did not form when **5a** was stirred with *cis*-TolN=NTol nor was **5a** produced when **5b** was stirred with *cis*-PhN=NPh. In contrast, loss of the benzo[*c*]cinnoline group from **7** does occur as indicated by the slow transformation of **7** into **5b** when stirred at room temperature with 1.1 equiv of *cis*-TolN=NTol (50% conversion after 24 h). As shown below, the benzo[*c*]cinnoline group in **7** can also be displaced by chloride ion.

Cycloaddition of *cis*-RN=NR with the BCl_4^- Salt of $[Cp(CO)_2Re{\equiv}CTol]^+$. The BCl_4^- salt of complex **1** also reacted with *cis*-RN=NR but gave final products different from those described above with the BPh_4^- salt. IR monitoring indicated that the initial products of the reactions with both *cis*-PhN=NPh and *cis*-TolN=NTol were the same four-membered metallacycles **5a** and **5b** formed in eq 1, but these species subsequently extracted a chloride ion from the BCl_4^- anion and underwent insertion of a CO ligand into the Re–C(Tol) bond to give complexes **8a** and **8b** which possess five-membered metallacycles, eq 3. These latter complexes were isolated in good yields as spectroscopically characterized microcrystalline solids and are similar to the crystallographically characterized complex **3** shown in Scheme I that resulted

(3) *Small Ring Heterocycles, Part II: Azetidines, β-Lactams, Diazetidines and Diaziridines*; Hassner, A., ed.; John Wiley and Sons: New York, 1983; Vol. 42, p 444.

(4) Dötz, K. H.; Fischer, H.; Hoffman, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, 1983.

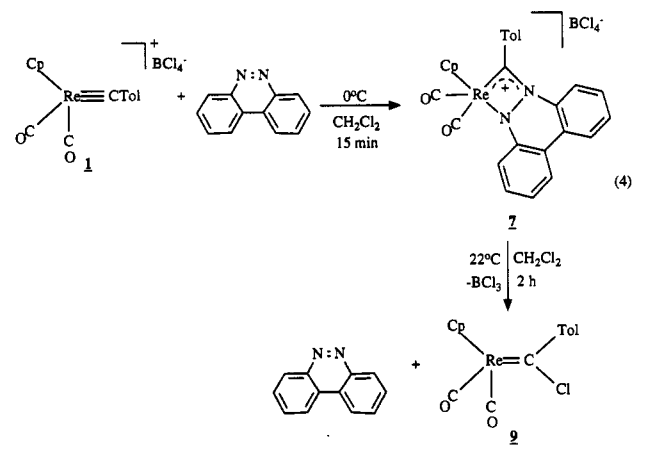
(5) (a) Hegedus, L. S.; Lundmark, B. R. *J. Am. Chem. Soc.* **1989**, *111*, 9194. (b) Sleiman, H. F.; McElwee-White, L. *J. Am. Chem. Soc.* **1988**, *110*, 8700. (c) Sleiman, H. F.; Mercer, S.; McElwee-White, L. *J. Am. Chem. Soc.* **1989**, *111*, 8007. (d) Sleiman, H. F.; Arndtsen, B. A.; McElwee-White, L. *Organometallics* **1991**, *10*, 541. (e) Maxey, C. T.; Sleiman, H. F.; Massey, S. T.; McElwee-White, L. *J. Am. Chem. Soc.* **1992**, *114*, 5153. (f) Peng, W.-J.; Gamble, A. S.; Templeton, J. L.; Brookhart, M. *Inorg. Chem.* **1990**, *29*, 463.



from an analogous reaction of [Cp(CO)$_2$Re≡CTol][BCl$_4$] with Bu^{t}N=O.[1]

The **5a** to **8a** conversion shown in eq 3 can be reversed by treating **8a** with AgBF$_4$ to abstract the chloride and induce deinsertion of CO from the ring to form the BF$_4^-$ salt of **5a** in modest yield (62%). Similarly, addition of HBF$_4$·Et$_2$O to **8a** also rapidly induced its conversion into **5a** by loss of HCl.

In contrast to the above results, a complex analogous to **8a,b** did not result when benzo[*c*]cinnoline was allowed to react with the BCl$_4^-$ salt of [Cp(CO)$_2$Re≡CTol]$^+$. IR monitoring indicated that the BCl$_4^-$ salt of the rhenadiazetine complex **7** was formed initially, but continued reaction over 2 h gave displacement of the benzo[*c*]cinnoline by a chloride ion abstracted from the BCl$_4^-$ anion to form the chlorocarbene complex **9**, eq 4. The phenyl



analogue of **9** was earlier shown to result from addition of Cl$^-$ to [Cp(CO)$_2$Re≡CPh]$^+$,[2a] and complex **9** also formed

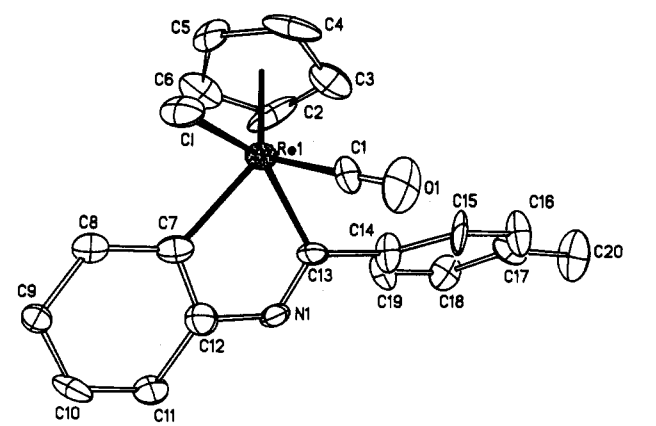
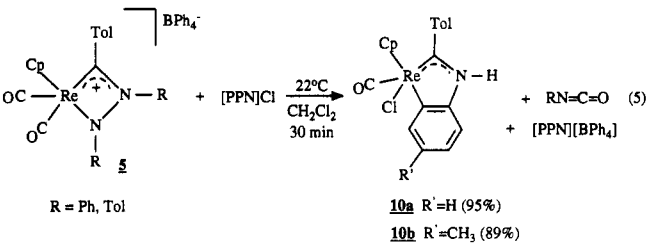


Figure 1. ORTEP drawing for **10a**. Thermal ellipsoids are drawn at the 35% probability level.

when the BPh$_4^-$ salt of **7** was treated with [PPN]Cl. The driving force for the overall conversion of **1** into **9** must be the formation of a Lewis acid–base complex between the released BCl$_3$ and the benzo[*c*]cinnoline since the BCl$_4^-$ salt of carbyne complex **1** is stable and does not transform on its own accord into **9** and BCl$_3$. Consistent with this proposal is the observation (by IR) that complex **9** slowly formed when the BCl$_4^-$ salt of carbyne complex **1** was allowed to stir in the presence of NEt$_3$.

Reaction of 5a and 5b with [PPN]Cl. In view of the observation described above that complex **5** abstracted a chloride ion from the BCl$_4^-$ anion to form complex **8**, we considered the possibility of directly inducing the **5** to **8** conversion by adding [PPN]Cl to the [BPh$_4$]$^-$ salt of **5** (see Scheme I for an analogous reaction). However, the products of this reaction with both **5a** and **5b** were not the expected complexes **8a** and **8b**, but rather the new complexes **10a** and **10b** shown in eq 5. Analogous products



formed when [Et$_4$N]Cl was added to solutions of **5a** and **5b**. Complexes **10a,b** result from loss of a CO ligand and an "NPh" group from the metallacycle, coordination of Cl$^-$ to the metal, metalation of the N-aryl group, and hydrogen migration to the remaining nitrogen atom. The "NR" and CO groups are lost as arylisocyanate which was detected by IR (PhN=C=O, ν_{CO} = 2263 cm^{-1}; TolN=C=O, ν_{CO} = 2274 cm^{-1}). Complexes **10a,b** were isolated in excellent yields as microcrystalline solids and were spectroscopically characterized. Complex **10a** was further defined by an X-ray diffraction study (see Figure 1 and below).

The mechanism proposed to account for the transformation of **5** into **10** is illustrated in Scheme II. We suggest that chloride adds to complex **5** to induce insertion of CO into the Re–N bond to form the five-membered metallacyclic complex **11**. Extrusion of RN=C=O from this metallacycle would give the iminoacyl complex **12**, and insertion of Re into an aryl C–H bond of this species followed by a 1,3-hydrogen migration to the ring nitrogen atom would give the observed product **10**.

It is surprising that the source of the chloride ion so dramatically influences the reactivity of **5**. Recall that

Scheme II

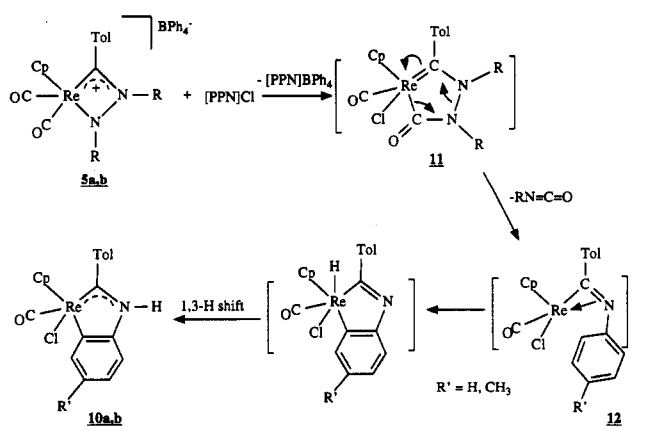
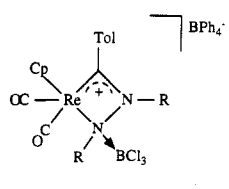


Table I. Crystallographic Parameters for Complexes 10a, 17, 20, and 21[a]

	10a	17	20	21
		(a) Crystal Parameters		
formula	$C_{20}H_{16}NOClRe$	$C_{20}H_{22}O_3ClRe$	$C_{28}H_{28}N_2O_2Re$	$C_{22}H_{19}N_2O_2Re$
formula wt	508.0	520.0	605.7	529.6
cryst sys	orthorhombic	monoclinic	triclinic	triclinic
space gp	*Pccn*	$P2_1/c$	*P*1(bar)	*P*1(bar)
a, Å	21.083(5)	8.622(1)	6.716(2)	9.765(2)
b, Å	29.388(7)	20.682(3)	11.289(4)	10.238(2)
c, Å	11.489(3)	11.985(2)	16.705(7)	11.700(2)
α, deg			77.61(3)	107.41(3)
β, deg		109.86(1)	89.88(3)	107.73(3)
γ, deg			77.73(3)	104.58(3)
V, Å	7119(3)	2010.1(5)	1207.6(7)	984.5(3)
Z	16	4	2	2
cryst dimens, mm	0.10 × 0.30 × 0.38	0.21 × 0.22 × 0.38	0.24 × 0.25 × 0.33	0.28 × 0.32 × 0.40
cryst color	red	yellow	yellow	yellow
D(calcd), g cm^{-3}	1.93	1.72	1.67	1.79
μ(Mo Kα), cm^{-1}	73.8	65.4	53.4	61.9
temp, K	298	298	296	299
T(max)/*T*(min)	6.623	1.589	1.762	
		(b) Data Collection		
diffractometer	Nicolet R3m	Nicolet R3m	Nicolet R3m	Siemens P4
monochromator	graphite	graphite	graphite	graphite
radiation (λ)	Mo Kα (0.710 73 Å)	Mo Kα (0.710 73 Å)	Mo Kα (0.710 73 Å)	Mo Kα (0.710 73 Å)
2θ scan rnge, deg	4–50	4–48	4–52	4–56
data (*h*,*k*,*l*)	+26,+35,+14	±10,+24,+14	±13,+14,+14	±12,±13,+15
no. of rflns coll	6965	3893	4926	4969
no. of indpt rflns	6193	3833	4752	4741
no. of indpt obsd rflns	3322 ($F_o \geq 5\sigma(F_o)$)	1803 ($F_o \geq 5\sigma(F_o)$)	3917 ($F_o \geq 5\sigma(F_o)$)	4229 ($F_o \geq 4\sigma(F_o)$)
std rflns	3 std/197	3 std/197	3 std/197	3 std/197
var in stds, %	<2	<2	<2	<2
		(c) Refinement		
R(*F*), %	8.48	3.39	3.74	4.18
R(w*F*), %	8.91	3.37	3.80	5.29
Δ/σ(max)	0.055	0.001	0.08	0.004
$\Delta(\rho)$, e Å^{-3}	3.77	0.56	1.56	2.62
N_o/N_v	8.54	7.6	12.7	16.6
GOF	1.33	1.12	1.124	1.32

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

when chloride was provided by the BCl_4^- anion, CO underwent insertion into the Re–C bond of the metallacycle in **5** to give complex **8** (eq 3), but as suggested here, the delivery of chloride via [PPN]Cl or [Et_4N]Cl induced insertion of CO into the Re–N bond of the metallacycle. The difference in the reactions shown in eqs 3 and 5 may be due to the presence of the Lewis acid BCl_3 in the former. Indeed, it was observed by IR that the addition of BCl_3 to a solution of the BPh_4^- salt of **5a** gave a new species which showed two ν_{CO} bands at 2092 and 2018 cm^{-1}, indicating the formation of a dicarbonyl complex. These bands are at higher energy than those of **5a** (ν_{CO} = 2058, 1999 cm^{-1}), indicating the loss of electron density from the metal center upon interaction with the Lewis acid BCl_3. The most basic site in **5a** is presumably the "amido" nitrogen atom of the metallacycle, and we thus suggest that this new complex has the structure **D** drawn below.



D

It was further observed that the addition of 1 equiv of [PPN]Cl to the solution of the **5a**·BCl_3 adduct gave the immediate formation of **8a** (by IR) but not **10a** which forms in the absence of BCl_3 (eq 5), confirming the importance of the Lewis acid BCl_3 in directing the outcome of the chloride-induced CO insertion reaction. It is of course well known that Lewis acids promote the insertion of CO into metal–alkyl bonds, although it is generally assumed that this occurs by complexation with the carbonyl oxygen and not through complexation with a nitrogen atom as in **D**.[6]

Crystal and Molecular Structure of 10a. The molecule crystallizes in the orthorhombic space group *Pccn* with two crystallographically independent but chemically similar molecules in the asymmetric unit. An ORTEP drawing of the molecule with unprimed labels is shown in Figure 1, and important crystallographic data are set out in Tables I and II. The hydrogen atom attached to the ring nitrogen atom was not located, but its presence on the nitrogen was inferred from the ^{1}H NMR spectrum of **10a** which showed a broad NH resonance at δ 11.72. The molecule has a distorted four-legged piano stool geometry, with the bond angles between the "legs" ranging from 72.1-(11) to 82.7(8)°. The five-membered metallacycle is essentially coplanar with the four carbon atoms of the metallated phenyl group (unprimed molecule, maximum deviation of 0.043 Å associated with C(7); primed molecule, maximum deviation of 0.009 Å associated with C(7′)), and

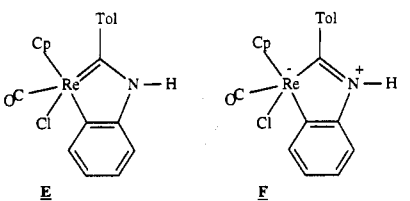
(6) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 6.

Table II. Selected Bond Distances and Angles for 10a[a]

molecule 1		molecule 2	
	(a) Bond Distances (Å)		
Re(1)–C(1)	1.97(3)	Re(1′)–C(1′)	1.89(3)
Re(1)–Cl	2.499(7)	Re(1′)–Cl′	2.488(9)
Re(1)–C(13)	2.11(3)	Re(1′)–C(13′)	2.07(3)
Re(1)–C(7)	2.11(3)	Re(1′)–C(7′)	2.12(3)
C(1)–O(1)	1.09(4)	C(1′)–O(1′)	1.17(3)
C(13)–C(14)	1.53(4)	C(13′)–C(14′)	1.46(4)
C(13)–N(1)	1.28(3)	C(13′)–N(1′)	1.39(3)
C(7)–C(8)	1.42(4)	C(7′)–C(8′)	1.41(4)
C(7)–C(12)	1.38(4)	C(7′)–C(12′)	1.40(4)
N(1)–C(12)	1.34(4)	N(1′)–C(12′)	1.41(4)
C(9)–C(10)	1.40(4)	C(9′)–C(10′)	1.47(5)
C(11)–C(12)	1.49(4)	C(11′)–C(12′)	1.35(4)
C(8)–C(9)	1.46(4)	C(8′)–C(9′)	1.33(4)
C(10)–C(11)	1.35(4)	C(10′)–C(11′)	1.35(4)
Re(1)–CNT	1.92(3)	Re(1′)–CNT	1.98(4)
	(b) Bond Angles (deg)		
Cl–Re(1)–CNT	109(1)	Cl–Re(1′)–CNT	107.7(8)
C(10)–Re(1)–CNT	124(1)	C(1′)–Re(1′)–CNT	128(1)
C(13)–Re(1)–CNT	111(1)	C(13′)–Re(1′)–CNT	109(1)
C(7)–Re(1)–CNT	126(1)	C(7′)–Re(1′)–CNT	128(1)
Cl–Re(1)–C(1)	78.0(11)	Cl′–Re(1′)–C(1′)	79.5(9)
Cl–Re(1)–C(13)	140.0(7)	Cl′–Re(1′)–C(13′)	142.9(8)
Cl–Re(1)–C(7)	82.7(8)	Cl′–Re(1′)–C(7′)	80.6(7)
C(1)–Re(1)–C(13)	82.4(13)	C(1′)–Re(1′)–C(13′)	78.3(12)
C(13)–Re(1)–C(7)	72.1(11)	C(13′)–Re(1′)–C(7′)	76.5(11)
Re(1)–C(1)–O(1)	178(3)	Re(1′)–C(1′)–O(1′)	173(2)
Re(1)–C(13)–N(1)	119(2)	Re(1′)–C(13′)–N(1′)	117(2)
Re(1)–C(13)–C(14)	126(2)	Re(1′)–C(13′)–C(14′)	130(2)
Re(1)–C(7)–C(8)	128(2)	Re(1′)–C(7′)–C(8′)	130(2)
Re(1)–C(7)–C(12)	118(2)	Re(1′)–C(7′)–C(12′)	113(3)
C(7)–C(12)–N(1)	113(3)	C(7′)–C(12′)–N(1′)	121(3)
C(13)–N(1)–C(12)	118(3)	C(13′)–N(1′)–C(12′)	116(2)
N(1)–C(12)–C11	123(3)	N(1′)–C(12′)–C(11′)	121(3)
N(1)–C(13)–C(14)	115(3)	N(1′)–C(13′)–C(14′)	114(2)

[a] CNT = centroid of atoms C(2)–C(6).

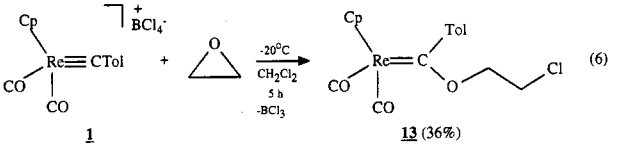
the molecule is best formulated as a hybrid of the two resonance forms **E** and **F**, but with the crystallographic



E **F**

data indicating that **F** is dominant. This is indicated mainly by the N(1)–C(13) distance of 1.28(3) Å which is characteristic of C=N double bond values in organic compounds (N=C(sp^2), 1.279 Å)[7] but is significantly shorter than typical N–C(sp^2) single bond distances (1.339 Å).[7] Similarly, the Re–C(13) bond length of 2.113(28) Å is longer than typical rhenium–carbon double bonds in carbene complexes (e.g., $Cp(NO)(PPh_3)Re{=}CHPh$, Re=C = 1.949(6) Å;[8] $Cp(CO)_2Re{=}CH(SiPh_3)$, Re=C = 1.92(2) Å;[9] $Cp(CO)_2Re{=}C(Tol)OCH_2CMe_2CH_2Cl$, **17** (see below), 1.973(11) Å). The Re–C(7) bond distance of 2.109(28) Å compares well to that found in other Re–aryl complexes (e.g., $RePh_3(PEt_2Ph)_3$, Re–C = 2.029(10) Å).[10]

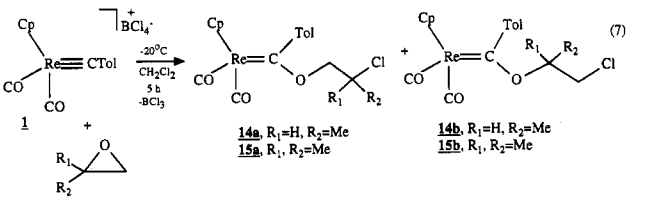
Reaction of $[Cp(CO)_2Re{\equiv}CTol]^+$ with Epoxides To Form Carbene Complexes. Reaction of epoxides with the BCl_4^- salt of the cationic carbyne complex **1** led to the formation of alkoxy–carbene complexes, as illustrated by the slow reaction with excess ethylene oxide to give complex **13**, eq 6. This product forms by ring opening of the epoxide



(6)

1 **13** (36%)

and abstraction of chloride from the BCl_4^- counterion. In contrast, no reaction occurred when the BPh_4^- salt of **1** was treated with ethylene oxide. Complex **13** was isolated as a spectroscopically characterized yellow microcrystalline solid (see Experimental Section). Carbyne complex **1** also reacts with propylene oxide and isobutylene oxide to form mixtures of isomeric carbene complexes that result from ring-opening of the epoxide in the two different directions, eq 7. As above, no reaction occurred when the BPh_4^- salt

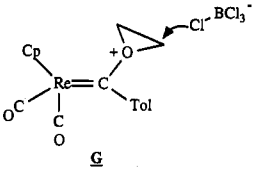


(7)

1

of **1** was treated with these epoxides. ^1H NMR data indicated that the reactions gave a 1:1.6 ratio of **14a/14b** and a 1:2.5 ratio of **15a/15b**, and chromatography led to the separation of the major regioisomer from the mixture, although the minor isomer could not be obtained pure.

We suggest that the reactions shown in eqs 6 and 7 proceed via the intermediacy of a species like **G**. It is well



G

known that ring opening of epoxides is assisted by the coordination of Lewis acids to the epoxide oxygen,[12] and the carbyne complex **1** has been demonstrated to have an electrophilic carbyne carbon atom and is Lewis acidic.[2] In further support of this suggestion, we note that the analogous manganese carbyne complex has been shown to form similar pyridine (**H**)[13] and THF (**I**)[14] adducts, and we have independently observed that $[Cp(CO)_2Mn{\equiv}C\text{-}Me]^+$ reacts with propylene oxide to give an unstable complex for which spectroscopic evidence indicates the formulation **J**.[14]

(7) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1987**, S1.
(8) 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.
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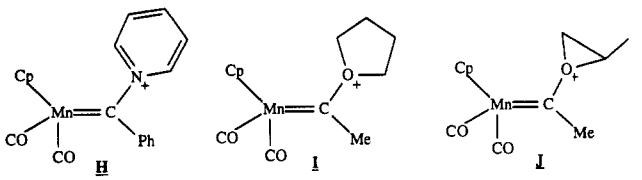
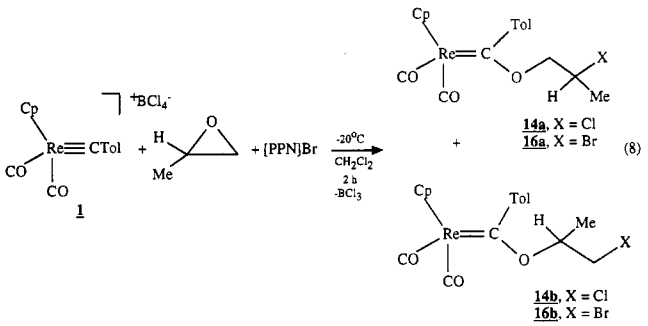
(10) Carroll, W. E.; Bau, R. *J. Chem. Soc., Chem. Commun.* **1978**, 825.
(11) Fischer, E. O.; Rustemeyer, P.; Ackermann, K. *Chem. Ber.* **1982**, *115*, 3851.
(12) (a) Smith, J. G. *Synthesis* **1984**, 629. (b) Winstein, S.; Henderson, R. B.; *Heterocyclic Compounds*; Elderfield, R. C., Ed.; John Wiley and Sons: New York, 1950; Vol. 1, pp 1–60. (c) Parker, R. E.; Isaacs, N. S. *Chem. Rev.* **1959**, 737. (d) Rosowsky, A. *Heterocyclic Compounds with Three- and Four-Membered Rings, Part I*; Weissberger, A., Ed.; John Wiley and Sons: New York, 1964; pp 1–523.
(13) (a) Meineke, E. W. Dissertation Technische Universität München, 1975. (b) See also: Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schrock, R. R.; Schubert, U.; Weiss, K. *Carbyne Complexes*; VCH Publishers: New York, 1988; p 115.
(14) Terry, M. R.; Geoffroy, G. L. unpublished results. For **J**: IR-(CH_2Cl_2), ν_{CO} = 1991 (s), 1926 (s) cm^{-1}.



H **I** **J**

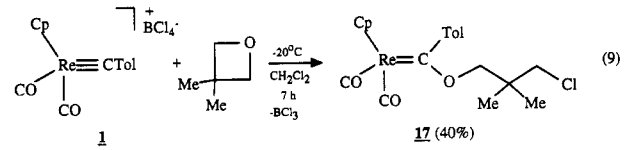
Reaction of $[Cp(CO)_2Re{\equiv}CTol]BCl_4$ with Propylene Oxide in the Presence of [PPN]X (X = Cl, Br). Since halides are known to promote the ring opening of epoxides,[15] it was of interest to explore the effect of added halide ion on these epoxide reactions. These reactions were conducted by preparing a solution of propylene oxide and [PPN]X and then transferring it to a −20 °C solution of carbyne complex 1. Although the addition of [PPN]Cl had little or no effect, [PPN]Br gave a near-instantaneous reaction, in contrast to the 5 h required in the absence of [PPN]Br. This reaction gave a mixture of the complexes **14a,b** and **16a,b** resulting from competitive incorporation of Br^- and Cl^- and ring opening of the epoxide in the two different directions, eq 8. Mass spectroscopic analysis



1 **14a**, X = Cl; **16a**, X = Br (8) **14b**, X = Cl; **16b**, X = Br

indicated that complexes **14** and **16** were formed in an approximate 1:2 ratio, and ^1H NMR analysis showed the formation of all four isomers and indicated a **14a/14b/16a/16b** ratio of 1:0.5:2.2:0.7. As suggested above, this reaction likely proceeds via addition of propylene oxide to the carbyne carbon to give a species like **G** which is then competitively attacked by Br^- and Cl^- (from BCl_4^-).

Ring Opening of 3,3-Dimethyloxetane with $[Cp(CO)_2Re{\equiv}CTol]BCl_4$. The cationic carbyne complex **1** also slowly reacts with excess 3,3-dimethyloxetane to form the carbene complex **17** shown in eq 9 which arises by ring



1 **17** (40%) (9)

opening of the oxetane and abstraction of chloride from the BCl_4^- counterion. As with the epoxide reactions, no reaction occurred when the BPh_4^- salt of **1** was used in the reaction. Complex **17** was isolated as a yellow microcrystalline solid and has been characterized spectroscopically (see Experimental Section) and by an X-ray diffraction study. An ORTEP drawing of **17** is shown in Figure 2, and the important crystallographic data are set out in Tables I and III. Two chemically similar chlorine locations were found on adjacent methyl groups C(13) and C(14) and refined at 62% [Cl(a)] and 38% [Cl(b)]

(15) (a) Rao, A. S.; Paknikar, S. K.; Kirtane, J. G. *Tetrahedron* **1983**, *39*, 2323. (b) Michelin, R. A.; Bertani, R.; Mozzon, M.; Bombieri, G.; Benetollo, F.; Angelici, R. J. *Organometallics* **1991**, *10*, 1751.

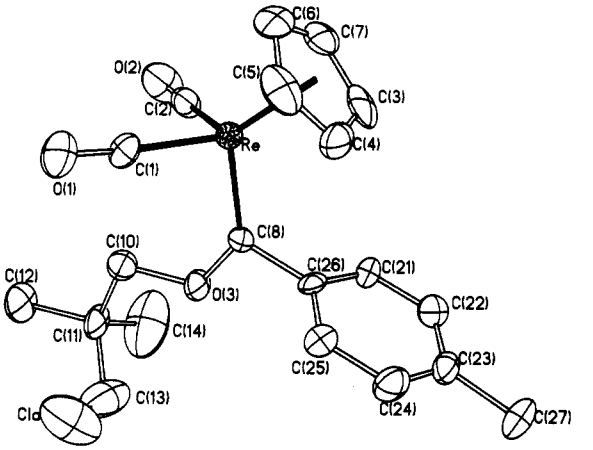


Figure 2. ORTEP drawing for **17**. Thermal ellipsoids are drawn at the 35% probability level.

Table III. Selected Bond Distances and Angles for 17[a]

(a) Bond Distances (Å)

Re–C(1)	1.889(12)	Re–C(2)	1.874(13)
Re–CNT	1.99(2)	Re–C(8)	1.973(11)
C(1)–O(1)	1.154(16)	C(2)–O(2)	1.149(16)
C(8)–O(3)	1.340(13)	C(8)–C(26)	1.488(15)
O(3)–C(10)	1.470(13)	Cl(a)–C(13)	1.58(3)
Cl(b)–C(14)	1.073(31)	C(10)–C(11)	1.490(18)
C(11)–C(13)	1.486(19)	C(11)–C(12)	1.546(16)
C(11)–C(14)	1.63(4)		

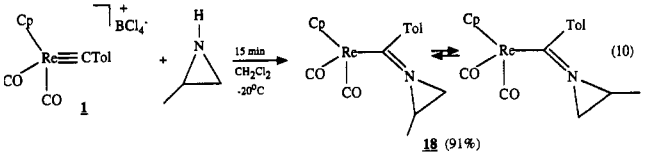
(b) Bond Angles (deg)

C(1)–Re–CNT	124.6(6)	C(2)–Re–CNT	125.9(6)
C(8)–Re–CNT	122.1(6)	C(1)–Re–C(2)	85.7(5)
C(1)–Re–C(8)	94.7(5)	C(2)–Re–C(8)	94.1(5)
C(8)–O(3)–C(10)	121.5(9)	C(8)–C(26)–C(21)	123.1(7)
Re–C(8)–O(3)	134.7(8)	Re–C(8)–C(26)	122.1(7)
C(26)–C(8)–O(3)	103.2(8)	O(3)–C(10)–C(11)	106.9(9)
Cl(a)–C(13)–C(11)	112.0(17)	Cl(b)–C(14)–C(11)	117(3)

[a] CNT = centroid of atoms C(3)–C(7).

occupancies, respectively. Anomalous bond distances within the neopentyl group are due to the observed chlorine disorder. The molecule has the usual pseudooctahedral geometry of CpL_3M complexes, as evidenced by the C(1)–Re–C(2) (87.7(5)°), C(1)–Re–C(8) (94.7(5)°), and C(2)–Re–C(8) (94.1(5)°) bond angles. The carbene carbon and its attached substituents are coplanar (maximum deviation of 0.001 Å associated with C(8)), and this plane bisects the OC–Re–CO bond angle. This is the typical orientation of carbene complexes within the $Cp(CO)_2M{=}CRR'$ (M = Mn, Re) family, although examples of other orientations are known.[4] The Re=C(8) distance of 1.973(11) Å is a typical rhenium–carbene value (e.g., $Cp(NO)(PPh_3)$-Re=CHPh, Re=C = 1.949(6) Å;[8] $Cp(CO)_2Re{=}CH(SiPh_3)$, Re=C = 1.92(2) Å).[9]

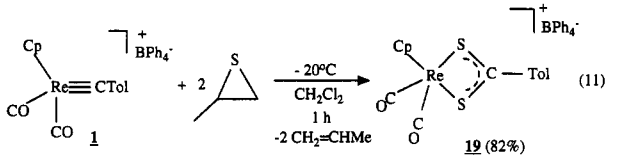
Formation of an Aziridinocarbene Complex from the Addition of 2-Methylaziridine to $[Cp(CO)_2Re{\equiv}CTol]^+$. In view of the above ring-opening reactions of carbyne complex **1** with epoxides and 3,3-dimethyloxetane, we considered the possibility of inducing a similar ring-opening of 2-methylaziridine. Complex **1**, either as the BCl_4^- or BPh_4^- salt, rapidly reacted with this reagent, but the product formed was the neutral aziridinocarbene complex **18**, eq 10, rather than a ring-opened product. This species forms by addition of the aziridine nitrogen atom to the electrophilic carbyne carbon followed by loss of H^+, analogous to the reported formation of aminocarbene complexes from the addition of amines to $[(\eta^6\text{-}C_6H_6)(CO)_2Cr{=}CPh]^+$.[16] Like most aminocarbene com-



plexes, **18** is best formulated as having partial double-bond character between the carbene carbon and the nitrogen atom, giving rise to restricted rotation about the C–N bond. Indeed, ^{1}H NMR data indicate that the complex forms as a 1.4:1 mixture of the two rotamers shown in eq 10 with a rotational barrier of 10.9 kcal/mol. At −40 °C, the ^{1}H NMR spectrum of **18** was clearly resolved and showed the presence of both rotamers. As illustrated in Figure 3, the spectrum showed two Cp resonances at δ 5.05 and 5.10, two doublets (J_{HH} = 5.5 Hz) at δ 1.01 and 1.58 assigned to the aziridine methyl groups, a single tolyl-CH_3 resonance at δ 2.30 for both rotamers, two doublets (J_{HH} = 3.1 Hz) at δ 2.17 and 2.51 assigned to one of the diastereotopic methylene protons, two doublets (J_{HH} = 5.4 Hz) at δ 2.25 and 2.82 assigned to the other diastereotopic methylene proton, and two multiplets at 2.66 and 2.94 for the methylene protons of the aziridine ring. Upon warming, these resonances broadened, coalesced around room temperature, and sharpened to average signals at 50 °C. Noteworthy in the ^{13}C NMR spectrum of **18** is a resonance at δ 256.0 assigned to the carbene carbon.

Rudler et al. reported that upon heating analogous chromium- and tungsten-aziridinocarbene complexes undergo a ring opening rearrangement to give nitrile complexes.[17] In contrast, complex **18** was thermally stable and gave no rearrangement or decomposition upon refluxing in toluene for 4 h.

Formation of an η^2-Dithiocarboxylate Complex from the Reaction of [Cp(CO)$_2$Re≡CTol]$^+$ with Propylene Sulfide. The reaction of carbyne complex **1** with propylene sulfide did not follow any of the reaction paths exhibited by the reactions of **1** with epoxides, 3,3-dimethyloxetane, or 2-methylaziridine. Instead, the BPh_4^- salt of **1** reacts with propylene sulfide to form complex **19** (eq 11) which possesses an η^2-dithiocarboxylate ligand



resulting from the transfer of two sulfur atoms from the propylene sulfide to the carbyne carbon. This reaction is analogous to the reported formation of η^2-dithiocarboxylate ligands from the reaction of cyclohexene sulfide with Cp(CO)$_2$W≡CMe[18a] and the reaction of the carbyne complexes Cp(CO)$_2$Mo≡CCH$_2$^{t}Bu, Cp{P(OMe)$_3$}$_2$Mo≡CCH$_2$^{t}Bu, and Cp(CO)$_2$W≡CTol with elemental sulfur.[18b] Like these earlier reactions, we suggest that **19** forms by the mechanism shown in Scheme III involving the coordination of propylene sulfide to the electrophilic carbyne carbon,

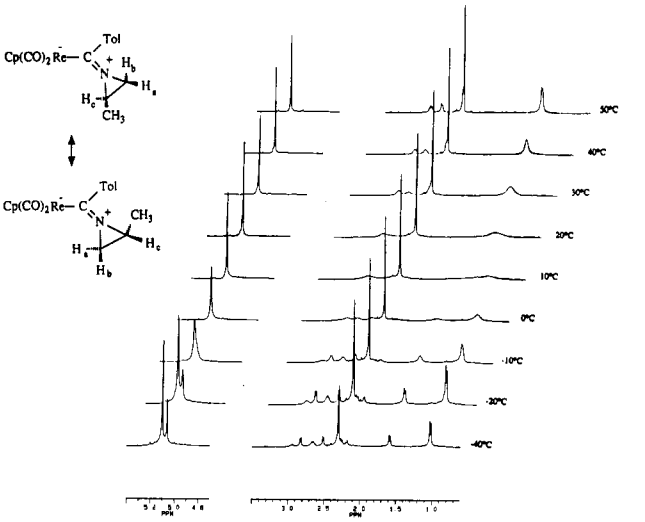
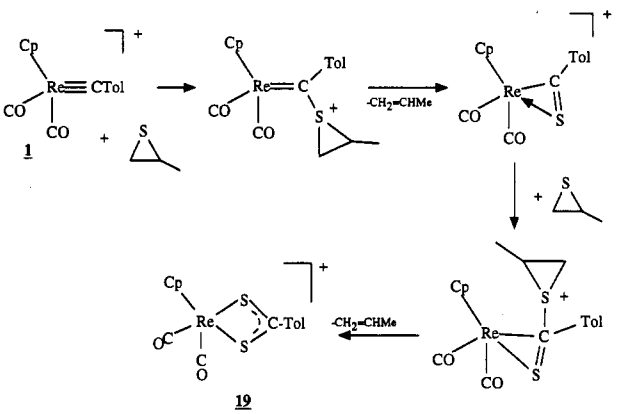


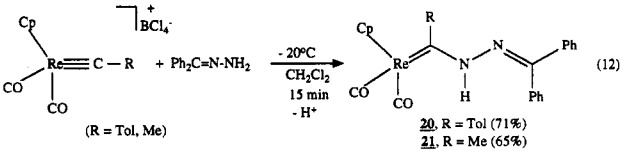
Figure 3. Variable-temperature ^{1}H NMR study of complex **18**.

Scheme III



loss of propylene to give an η^2-thioacyl complex, addition of a second equivalent of propylene sulfide to the acyl carbon, and then loss of propylene to give **19**. Consistent with this mechanism is Roper's isolation of an η^2-thioacyl complex from the reaction of (CO)(PPh$_3$)ClOs≡CTol with elemental sulfur.[19] Complex **19** was isolated in good yield as a yellow microcrystalline solid, and notable among its spectroscopic data is a ^{13}C NMR resonance at δ 246.3 assigned to the carbon atom of the dithiocarboxylate ligand which compares well to the similar resonance reported for the compound Cp(CO)$_2$W(η^2-S$_2$CTol) (δ 228.9).[18b]

Formation of Hydrazonyl Carbene Complexes from the Reaction of [Cp(CO)$_2$Re≡CTol]$^+$ and [Cp(CO)$_2$Re≡CCH$_3$]$^+$ with Benzophenone Hydrazone. Carbyne complex **1** and its ethylidyne analogue rapidly react with benzophenone hydrazone to form the hydrazonyl carbene complexes **20** and **21** shown in eq 12. The proton lost



from the hydrazone is presumably taken up by a second equivalent of benzophenone hydrazone, as evidenced by

(16) Fischer, E. O.; Stückler, P.; Beck, H.-J.; Kreissl, F. R. *Chem. Ber.* **1976**, *109*, 3089.
(17) Denise, B.; Parlier, A.; Rudler, H. *J. Organomet. Chem.* **1988**, *354*, C23.
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(19) Clark, G. R.; Marsden, K.; Roper, W. R.; Wright, L. J. *J. Am. Chem. Soc.* **1980**, *102*, 6570.

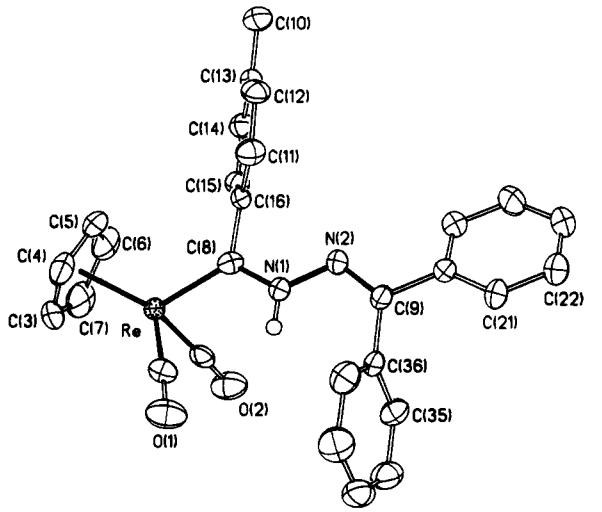


Figure 4. ORTEP drawing for **20**. Thermal ellipsoids are drawn at the 35% probability level.

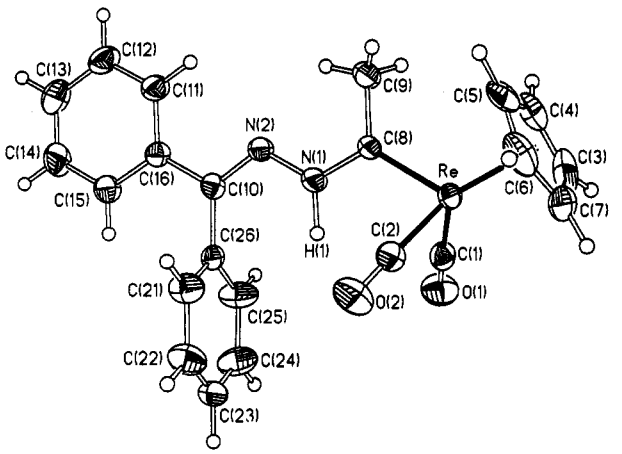


Figure 5. ORTEP drawing for **21**. Thermal ellipsoids are drawn at the 35% probability level.

the observation that 2 equiv of the latter reagent are required for complete reaction. These reactions are analogous to the formation of aminocarbene complexes from the reaction of $[(\eta\text{-}C_6H_6)(CO)_2Cr{=}CPh]^+$ with amines[16] and the above-described reaction of **1** with 2-methylaziridine, but we can find no evidence that hydrazonylcarbene complexes have been previously prepared by this route.

Both of these new complexes were isolated in good yield and have been spectroscopically characterized (see Experimental Section) and have been further defined by X-ray crystallographic studies. Although a few hydrazonyl carbene complexes are known,[20] to our knowledge none have been structurally characterized. ORTEP drawings of **20** and **21** are shown respectively, in Figures 4 and 5, and the important crystallographic data are set out in Tables I, IV, and V. For both molecules, the Re–carbene carbon distances (**20**, Re–C(8) = 2.021(6) Å; **21**, Re–C(8) = 2.029(7) Å) are slightly longer than a typical Re=C double bond value (1.92–1.95 Å; see data cited above for comparison[8,9]), and the C(8)–N(1) distances (**20**, 1.366(8) Å; **21**, 1.342(9) Å) are shorter than typical C–N single bond

Table IV. Selected Bond Distances and Angles for 20

(a) Bond Distances (Å)

Re–C(8)	2.021(6)	Re–C(1)	1.868(7)
Re–C(2)	1.888(8)	N(1)–N(2)	1.394(7)
C(8)–N(1)	1.366(8)	N(2)–C(9)	1.285(8)
C(9)–C(26)	1.484(8)	C(9)–C(36)	1.490(8)
C(8)–C(16)	1.502(7)		

(b) Bond Angles (deg)

C(1)–Re–C(2)	86.0(3)	C(1)–Re–C(8)	94.7(3)
C(2)–Re–C(8)	87.9(3)	Re–C(8)–N(1)	122.9(4)
Re–C(8)–C(16)	123.9(4)	C(16)–C(8)–N(1)	113.2(5)
C(8)–N(1)–N(2)	123.8(5)	N(1)–N(2)–C(9)	115.4(5)
N(2)–C(9)–C(26)	115.8(5)	N(2)–C(9)–C(36)	125.0(5)
C(26)–C(9)–C(36)	119.2(5)		

Table V. Selected Bond Distances and Angles for 21[a]

(a) Bond Distances (Å)

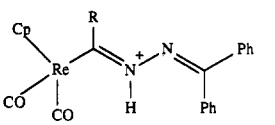
Re–CNT	1.988(13)	Re–C(8)	2.029(7)
Re–C(1)	1.892(8)	N(1)–N(2)	1.384(9)
Re–C(2)	1.866(6)	C(8)–N(1)	1.342(9)
N(2)–C(10)	1.286(9)	C(10)–C(26)	1.493(7)
C(10)–C(16)	1.473(10)		

(b) Bond Angles (deg)

CNT–Re–C(1)	127.4(4)	CNT–Re–C(2)	127.5(3)
CNT–Re–C(8)	123.7(4)	C(1)–Re–C(2)	87.2(3)
C(1)–Re–C(8)	88.2(3)	C(2)–Re–C(8)	90.5(3)
Re–C(1)–O(1)	178.8(8)	Re–C(2)–O(2)	177.8(7)
Re–C(8)–C(9)	125.3(5)	C(8)–N(1)–N(2)	124.0(4)
N(1)–N(2)–C(10)	116.2(5)	C(16)–C(10)–N(2)	116.4(5)
Re–C(8)–N(1)	122.3(4)	N(1)–C(8)–C(9)	112.4(6)
C(16)–C(10)–C(26)	120.3(6)	N(2)–C(10)–C(26)	123.2(7)

[a] CNT = centroid of atoms C(3)–C(7).

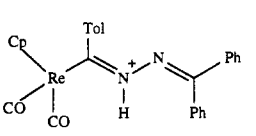
values (1.469 Å)[7] in organic molecules, indicating the importance of the resonance form **K** shown below. The



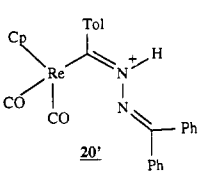
K

entire $Re{=}C(C_R)N(H)N{=}C(C_{Ph})_2$ unit of both molecules is essentially planar (**20**, maximum deviation of 0.106 Å associated with C(8); **21**, maximum deviation of 0.035 Å associated with N(1)) which also implies electron delocalization across this ligand system, and this plane bisects the CO–Re–CO bond angle. The N(1)–N(2) distances (**20**, 1.394(7) Å; **21**, 1.384(9) Å) are closer to typical N–N single (1.425 Å)[7] than to double (1.25 Å)[7] bond values in organic molecules. The C–N distances of the terminal $Ph_2C{=}N$ group (**20**, C(9)–N(2) = 1.285(8) Å; **21**, C(10)–N(2) = 1.286(9) Å) correspond to typical organic C=N double bonds (1.279 Å)[7] and imply a localized double bond between these latter atoms.

The spectroscopic data for **20** indicate that the complex forms as a 1:1 mixture of two isomers which do not readily interconvert. These are presumably the isomer which was crystallographically characterized and its rotomer **20′** that



20



20′

results from restricted rotation about the C–N bond (see **K** and the above discussion of restricted rotation in

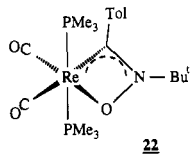
(20) (a) Connor, J. A.; Rose, P. D. *J. Organomet. Chem.* **1972**, *46*, 329. (b) Alt, H. G.; Engelhardt, H. E.; Steinlein, E.; Rogers, R. D. *J. Organomet. Chem.* **1987**, *344*, 321.

(21) Albano, V. G.; Bellon, P. L.; Ciani, G. *J. Organomet. Chem.* **1971**, *31*, 75.

complex **18**). Analytically pure samples of complex **20** showed a single parent ion at m/z = 606 in its mass spectrum, but these samples showed *four* IR ν_{CO} bands at 1954, 1944, 1890, and 1877 cm^{-1}, whereas two bands are expected for a CpRe(CO)$_2$L complex. The energy separation indicates that the 1954 and 1890 cm^{-1} IR bands are due to one isomer and the 1944 and 1877 cm^{-1} bands are due to the second (compare to Cp(CO)$_2$Re=C(OEt)-(SiPh$_3$), ν_{CO} = 1957, 1880 cm^{-1}).[11] The ^{1}H and ^{13}C NMR spectra of **20** also showed a doubling of all expected resonances. Upon heating, complex **20** decomposed to unidentified compounds, but no evidence was obtained for interconversion of the two rotamers.

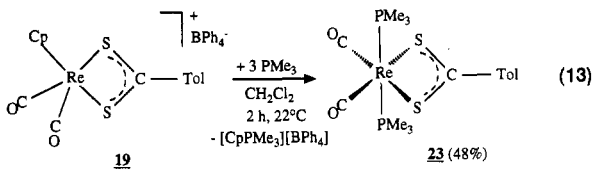
In contrast to the two rotamers observed for **20**, the NMR data for **21** indicate that this is the only species present in solution, and broadening of the ^{1}H NMR resonances was not observed even down to −80 °C. This difference between **20** and **21** must be due to the differing steric influence of the substituents on the carbene carbon, with the tolyl group hindering rotation in **20** and with the methyl group permitting less restricted rotation of this ligand in **21**.

PMe$_3$ Induced Displacement of the Cp Ring from 5, 7, and 19. In earlier work we showed that addition of PMe$_3$ to the metallacyclic complex **4** (see Scheme I) induced displacement of the Cp ligand as the phosphonium salt [CpPMe$_3$][BPh$_4$] and formed complex **22**.[1] We have



22

since found that similar reactions occur with the metallacyclic complexes described herein, but with some important differences. The η^2-dithiocarboxylate complex **19** behaved similarly to **4** and reacted with excess PMe$_3$ to form complex **23**, eq 13. This latter species is similar to



19 **23** (48%) (13)

the complex Re(CO)$_2$(PPh$_3$)$_2$(S$_2$CH) reported by Albano et al.[22] to result from the addition of CS$_2$ to HRe(CO)$_2$-(PPh$_3$)$_3$. It was isolated as a microcrystalline solid and was spectroscopically characterized (see Experimental Section). An X-ray diffraction study confirmed the connectivity in the complex (see Figure A of the supplementary material), but the overall poor quality of the crystal and the resulting data set precluded a complete structural refinement. Of particular interest in the ^{13}C NMR spectrum of **23** is the tolyl-substituted carbon resonance at δ 249.3 which appears as a triplet (J_{PC} = 9.9 Hz) due to coupling to the two equivalent phosphorus atoms. IR monitoring of reaction 13 showed the formation of an intermediate species in the **19** to **23** conversion with ν_{CO} bands at 1886 and 1990 cm^{-1}, but all attempts to isolate this species or characterize it by ^{1}H NMR failed due to its facile conversion into **23**.

(22) Mason, R.; Thomas, K. M.; Zubieta, J. A.; Douglas, P. G.; Galbraith, A. R.; Shaw, B. L. *J. Am. Chem. Soc.* **1974**, *96*, 260.

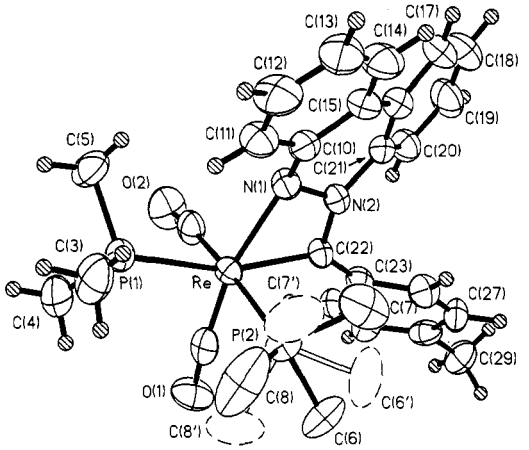


Figure 6. ORTEP drawing for **24**. Thermal ellipsoids are drawn at the 35% probability level.

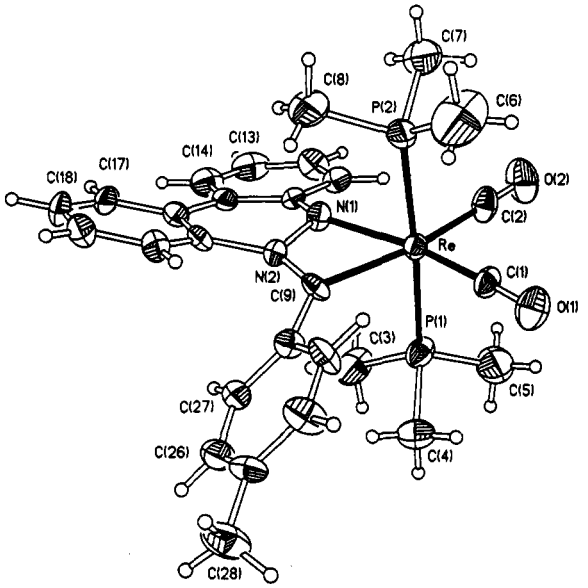
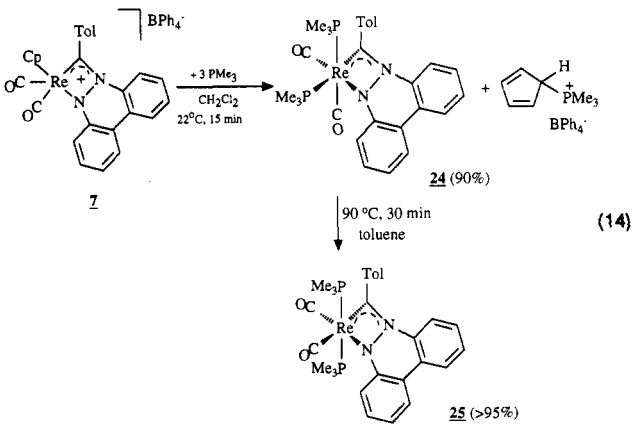


Figure 7. ORTEP drawing for **25**. Thermal ellipsoids are drawn at the 35% probability level.

However, an intermediate species was isolated in the reaction of the benzo[*c*]cinnoline adduct **7** with PMe$_3$. The initial reaction gave rapid displacement of the Cp ligand as [CpPMe$_3$][BPh$_4$] and formation of the *cis*-bis-(phosphine) complex **24**, but upon heating this species underwent isomerization to give the *trans*-bis(phosphine) complex **25**, eq 14. Both of these complexes were isolated



7 **24** (90%) (14) **25** (>95%)

as microcrystalline solids and were spectroscopically (see Experimental Section) and crystallographically charac-

Table VI. Crystallographic Parameters for 24, 25, and 26a[a]

	24	25	26a
	(a) Crystal Parameters		
formula	$C_{28}H_{24}N_2O_2P_2Re$	$C_{28}H_{33}N_2O_2P_2Re$	$C_{28}H_{35}N_2O_2P_2Re$
formula wt	668.6	677.7	679.7
cryst sys	monoclinic	monoclinic	orthorhombic
space gp	$C2/c$	$P2_1/c$	$Pca2_1$
a, Å	12.539(3)	10.282(2)	27.639(6)
b, Å	12.669(3)	32.288(6)	10.047(2)
c, Å	36.460(7)	8.777(2)	21.632(4)
β, deg	91.35(3)	103.90(3)	
V, Å	5823(2)	2828.5(10)	6007(2)
Z	8	4	8
cryst dimens, mm	0.16 × 0.36 × 0.36	0.08 × 0.30 × 0.35	0.32 × 0.41 × 0.46
cryst color	dark red	dark red	yellow
D(calcd), g/cm^3	1.525	1.591	1.503
μ(Mo Kα) cm^{-1}	43.6	44.4	41.8
F(000)	2616	1344	2704
temp, K	298	298	298
T(max)/T(min)	2.656	1.976	1.429
	(b) Data Collection		
diffractometer	Siemens P4	Siemens P4	Siemens P4
monochromator	graphite	graphite	graphite
radiation	Mo Kα (λ = 0.710 73 Å)	Mo Kα (λ = 0.710 73 Å)	Mo Kα (λ = 0.710 73 Å)
2θ scan rnge, deg	4–48	4–50	4–45
data (h,k,l)	±14,±14,+41	±12,+38,–10	+29,+10,+23
no. of rflns coll	4636	5446	4429
no. of indpt rflns	4554	4988	4048
no. of indpt obsd rflns	3262 ($F_o \geq 5\sigma(F_o)$)	3099 ($F_o \geq 5\sigma(F_o)$)	3136 ($F_o \geq 4\sigma(F_o)$)
std rflns	3 std/197	3 std/197	3 std/197
var in stds, %	<2	<1	<1
	(c) Refinement		
$R(F)$, %	5.43	4.43	4.18
R(wF), %	7.05	5.12	5.08
Δ/σ(max)	0.015	0.107	0.059
$\Delta(\rho)$, e Å^{-3}	1.75	1.20	0.72
N_o/N_v	9.4	9.8	7.1
GOF	1.61	1.04	0.95

[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 = $[\sum w||F_o| - |F_c||/(N_o - N_v)]^{1/2}$.

Table VII. Selected Bond Distances and Angles for 24

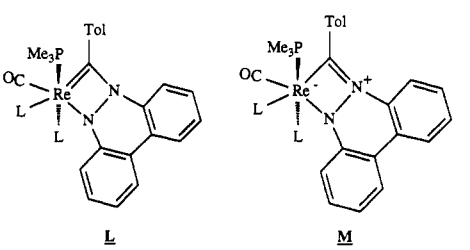
	(a) Bond Distances (Å)		
Re–C(1)	1.845(13)	Re–C(2)	1.934(14)
Re–P(1)	2.421(4)	Re–P(2)	2.445(4)
C(1)–O(1)	1.205(17)	C(2)–O(2)	1.139(18)
Re–N(1)	2.215(10)	Re–C(22)	2.109(11)
C(22)–N(2)	1.327(14)	N(2)–N(1)	1.425(14)
N(2)–C(21)	1.431(15)	N(1)–C(10)	1.330(16)
C(15)–C(16)	1.452(21)		
	(b) Bond Angles (deg)		
P(1)–Re–P(2)	99.4(1)	P(1)–Re–N(1)	102.4(3)
P(2)–Re–N(1)	89.8(3)	P(1)–Re–C(1)	93.1(4)
P(2)–Re–C(1)	85.9(4)	N(1)–Re–C(1)	164.5(5)
P(1)–Re–C(2)	84.5(4)	P(2)–Re–C(2)	171.6(4)
N(1)–Re–C(2)	96.6(5)	C(1)–Re–C(2)	86.4(6)
P(1)–Re–C(22)	162.6(3)	P(2)–Re–C(22)	87.9(3)
N(1)–Re–C(22)	61.6(4)	C(1)–Re–C(22)	103.2(5)
C(2)–Re–C(22)	90.4(5)	Re–N(1)–C(10)	145.1(8)
Re–N(1)–N(2)	91.6(6)	C(10)–N(1)–N(2)	115.4(10)
N(1)–N(2)–C(21)	117.9(9)	N(1)–N(2)–C(22)	107.3(9)
C(21)–N(2)–C(22)	133.2(10)	N(2)–C(22)–C(23)	122.5(10)
N(2)–C(22)–Re	99.3(7)	Re–C(22)–C(23)	138.2(8)

terized. ORTEP drawings are shown in Figures 6 and 7, and important crystallographic data are set out in Tables VI, VII, and VIII. Both molecules have an octahedral geometry with cis PMe_3 ligands and cis carbonyls in **24** and with trans PMe_3 ligands and cis carbonyls in **25**. As illustrated in Figure 6, one of the PMe_3 ligands in **24** is

Table VIII. Selected Bond Distances and Angles for 25

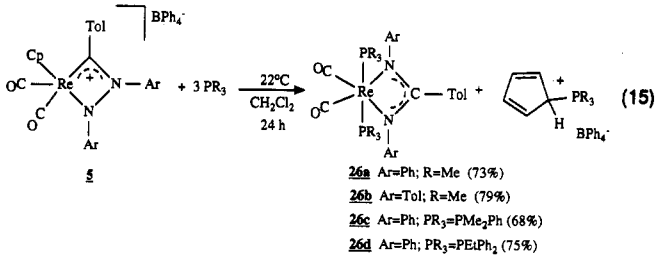
	(a) Bond Distances (Å)		
Re–C(1)	1.877(10)	Re–C(2)	1.938(13)
Re–P(1)	2.383(4)	Re–P(2)	2.406(4)
Re–N(1)	2.170(8)	Re–C(9)	2.146(10)
C(9)–N(2)	1.323(13)	N(2)–N(1)	1.395(13)
	(b) Bond Angles (deg)		
P(1)–Re–P(2)	176.3(1)	P(1)–Re–N(1)	92.7(2)
P(2)–Re–N(1)	84.2(2)	P(1)–Re–C(1)	89.5(4)
P(2)–Re–C(1)	93.0(4)	N(1)–Re–C(1)	165.1(4)
P(1)–Re–C(2)	92.1(4)	P(2)–Re–C(2)	90.6(4)
N(1)–Re–C(2)	103.8(4)	C(1)–Re–C(2)	90.8(5)
P(1)–Re–C(9)	85.7(3)	P(2)–Re–C(9)	91.0(3)
N(1)–Re–C(9)	60.7(4)	C(1)–Re–C(9)	104.9(5)
C(2)–Re–C(9)	164.1(4)	Re–N(1)–N(2)	94.7(5)
Re–N(1)–C(10)	143.5(7)	N(2)–N(1)–C(10)	117.5(8)
N(1)–N(2)–C(9)	106.6(8)	N(1)–N(2)–C(21)	119.3(8)
C(9)–N(2)–C(21)	133.0(9)	Re–C(9)–N(2)	98.0(7)
Re–C(9)–C(22)	137.7(7)	N(2)–C(9)–C(22)	123.8(9)

disordered by a 60° rotation. The bond parameters within the $Re(CO)_2(PMe_3)_2$ fragment of each molecule appear normal, and we discuss here only the structural features associated with the metallacycles. In each case, the metallacycle and its biphenyl substituent are nearly coplanar (**24**, maximum deviation of 0.160 Å associated with C(22); **25**, maximum deviation of 0.186 Å associated with C(9)). The Re–N(1) bond lengths (**24**, 2.215(10) Å; **25**, 2.170(8) Å) are similar to the dative Re–NH_3 bond value found in $[ReCl_2(NH_3)(N{=}NHPh)(PMe_2Ph)_2]Br$ (Re–NH_3 = 2.200(13) Å) but are considerably longer than the ReN=NHPh bond length (Re–N = 1.750(12) Å) found in the same compound.[22] The rhenium–carbene carbon bond lengths (**24**, Re–C(22) = 2.109(11) Å; **25**, 2.146(10) Å) are longer than found in typical $Re{=}CR_2$ carbene complexes (1.92–1.95 Å; see **17** and data cited above for comparison[8,9]). The C–N bond length in the metallacycle (**24**, C(22)–N(2) = 1.327(14) Å; **25**, C(9)–N(2) = 1.323 (13) Å) falls between typical values for C–N single (1.469 Å)[7] and double bond (1.279 Å)[7] values in organic molecules, and overall both molecules are best represented as a hybrid of the resonance forms **L** and **M**. The N(1)–N(2) bond lengths (**24**, 1.425(14) Å; **25**, 1.395(13) Å) are typical of N–N single bonds in organic molecules (1.425 Å).[7]



L M

The reaction of complexes **5a** and **5b** with PR_3 differs in a significant fashion from the reactions described above. As with **7** and **19**, treatment of **5a** with excess PMe_3, PMe_2Ph, and $PEtPh_2$ (but not PPh_3!) and treatment of **5b** with excess PMe_3 led to displacement of the Cp ligand as a phosphonium salt and formation of the pseudooctahedral complexes **26a–d** *in which the metallacycle has rearranged to form a benzamidinato ligand*, eq 15. These complexes were isolated as spectroscopically characterized microcrystalline solids, and complex **26a** was further characterized by an X-ray diffraction study which clearly showed the rearranged metallacycle (see below). The $[CpPMe_3][BPh_4]$ salt was also isolated from the reactions of **5a,b** with PMe_3 and was spectroscopically characterized (see



Experimental Section). It was also observed that the Cp* (η^5-C_5Me_5) analogue of **5a** reacted with PMe_3 to give **26a** via phosphine-induced displacement of the Cp* ligand (see Experimental Section), but no attempt was made to characterize the resultant phosphonium salt.

The important crystallographic data for **26a** are set out in Tables II and IX. The asymmetric unit contains two chemically similar but crystallographically independent molecules, and an ORTEP drawing of the unprimed molecule is shown in Figure 8. The molecule has an octahedral coordination geometry with trans phosphines and cis carbonyls. The bond parameters within the Re-$(CO)_2(PMe_3)_2$ fragment are normal, and the ReNCN core of the metallacycle is essentially planar, with a maximum deviation of 0.006(8) Å associated with C(9). The Re–N(1) (2.219(14) Å) and Re–N(2) (2.206(16) Å) bond lengths are similar to the dative Re–NH_3 bond value found in $[ReCl_2(NH_3)(N{=}NHPh)(PMe_2Ph)_2]Br$ (Re–NH_3 = 2.200 (13) Å).[22] The N(1)–C(9) (1.369(29) Å) and the N(2)–C(9) (1.302(29) Å) bond lengths are slightly longer than typical organic N=C double-bond distances (1.279 Å)[7] but shorter than typical C–N single-bond values (1.469 Å)[7], indicating delocalized π-bonding within the benzamidinato ligand.

The PMe_3-induced Cp ligand displacement reactions described above likely proceed via the steps outlined in Scheme IV which involve coordination of one and then two PMe_3 ligands as the Cp ligand slips from η^5 to η^3 to η^1 coordination and finally addition of PMe_3 to the η^1-Cp ligand to induce its displacement from the metal. These Cp displacement reactions are reminiscent of similar reactions studied by Casey and co-workers who showed that $CpRe(PMe_3)(NO)(CH_3)$ reacts with excess PMe_3 to form the salt $[Re(PMe_3)_4(NO)(CH_3)]^+Cp^-$ by reactions involving a similar η^5 to η^3 to η^1 slippage of the Cp ligand upon addition of PMe_3.[23] As described above, the initial product of displacement of the Cp ligand from the benzo[*c*]cinnoline complex **7** is a *cis*-bis(phosphine) complex **27** in Scheme IV) which isomerizes to the *trans*-bis(phosphine) product (**28** in Scheme IV) upon heating. A similar step may be involved in the reaction of the dithiocarboxylate complex **19** with PMe_3 where the final product is the *trans*-bis(phosphine) complex **23** but where an unstable intermediate was observed by IR and which may be a *cis*-bis(phosphine) complex analogous to **25**.

It is still necessary to account for the rearrangement of the metallacycles of **5a,b** to form benzamidinato ligands in the products **26a,b** upon reaction with excess PMe_3. Intermediates were also observed in these latter reactions, and these complexes (**29a,b**) could be isolated in impure form by stopping the reaction when IR analysis indicated their maximum concentration. These complexes rapidly transformed into **26a,b** upon attempted chromatographic purification and more slowly upon standing in solution.

(23) (a) Casey, C. P.; O'Conner, J. M.; Haller, K. J. *J. Am. Chem. Soc.* **1985**, *107*, 1241. (b) O'Conner, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307.

Table IX. Selected Bond Distances and Angles for 26a

molecule 1		molecule 2	
	(a) Bond Distances (Å)		
Re(1)–P(1)	2.409(6)	Re(1′)–P(1′)	2.396(6)
Re(1)–P(2)	2.405(6)	Re(1′)–P(2′)	2.384(6)
Re(1)–C(1)	1.922(27)	Re(1′)–C(1′)	1.865(26)
Re(1)–C(2)	1.925(26)	Re(1′)–C(2′)	1.869(29)
Re(1)–N(1)	2.219(14)	Re(1′)–N(1′)	2.205(16)
Re(1)–N(2)	2.206(16)	Re(1′)–N(2′)	2.199(19)
N(1)–C(9)	1.396(29)	N(1′)–C(9′)	1.375(26)
N(2)–C(9)	1.302(29)	N(2′)–C(9′)	1.292(28)
N(1)–C(16)	1.413(27)	N(1′)–C(16′)	1.36(3)
N(2)–C(36)	1.39(3)	N(2′)–C(36′)	1.467(29)
C(9)–C(26)	1.52(3)	C(9′)–C(26′)	1.439(28)
	(b) Bond Angles (deg)		
C(1)–Re(1)–C(2)	92.1(10)	C(1′)–Re(1′)–C(2′)	86.9(11)
C(1)–Re(1)–P(1)	92.3(7)	C(1′)–Re(1′)–P(1′)	93.7(8)
C(1)–Re(1)–P(2)	91.8(7)	C(1′)–Re(1′)–P(2′)	93.3(8)
C(1)–Re(1)–N(1)	163.4(9)	C(1′)–Re(1′)–N(1′)	163.9(9)
C(1)–Re(1)–N(2)	104.4(9)	C(1′)–Re(1′)–N(2′)	105.2(9)
C(2)–Re(1)–P(1)	91.0(7)	C(2′)–Re(1′)–P(1′)	90.8(8)
C(2)–Re(1)–P(2)	91.1(7)	C(2′)–Re(1′)–P(2′)	90.9(8)
C(2)–Re(1)–N(1)	104.4(9)	C(2′)–Re(1′)–N(1′)	109.1(9)
C(2)–Re(1)–N(2)	163.5(8)	C(2′)–Re(1′)–N(2′)	167.9(10)
P(1)–Re(1)–P(2)	175.3(2)	P(1′)–Re(1′)–P(2′)	172.9(2)
P(1)–Re(1)–N(1)	88.9(4)	P(1′)–Re(1′)–N(1′)	85.6(4)
P(1)–Re(1)–N(2)	88.1(4)	P(1′)–Re(1′)–N(2′)	88.9(5)
P(2)–Re(1)–N(1)	86.5(4)	P(2′)–Re(1′)–N(1′)	87.3(4)
P(2)–Re(1)–N(2)	88.7(4)	P(2′)–Re(1′)–N(2′)	88.0(5)
N(1)–Re(1)–N(2)	59.1(6)	N(1′)–Re(1′)–N(2′)	58.8(7)
Re(1)–C(1)–O(1)	176.1(24)	Re(1′)–C(1′)–O(1′)	178.0(21)
Re(1)–C(2)–O(2)	175.5(22)	Re(1′)–C(2′)–O(2′)	176.5(23)
Re(1)–N(1)–C(9)	94.3(13)	Re(1′)–N(1′)–C(9′)	95.0(13)
Re(1)–N(2)–C(9)	97.0(13)	Re(1′)–N(2′)–C(9′)	97.9(13)
N(1)–C(9)–N(2)	109.6(19)	N(1′)–C(9′)–N(2′)	108.2(18)
C(9)–N(1)–C(16)	130.8(17)	C(9′)–N(1′)–C(16′)	128.1(19)
C(9)–N(2)–C(36)	127.9(18)	C(9′)–N(2′)–C(36′)	126.3(19)
N(1)–C(9)–C(26)	124.1(20)	N(1′)–C(9′)–C(26′)	124.7(18)
Re(1)–N(1)–C(16)	133.6(13)	Re(1′)–N(1′)–C(16′)	135.0(15)
Re(1)–N(2)–C(36)	133.5(14)	Re(1′)–N(2′)–C(36′)	135.0(14)

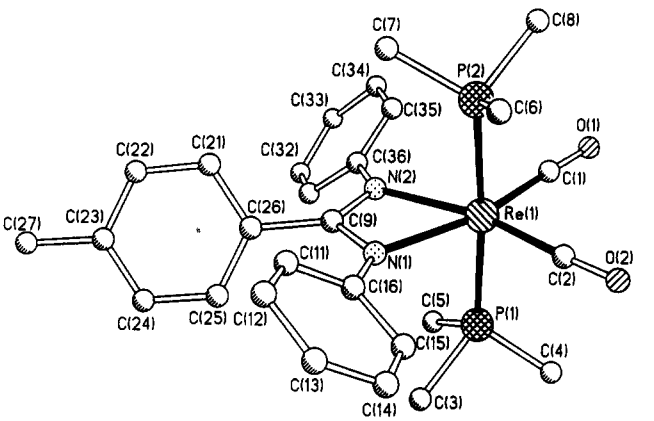
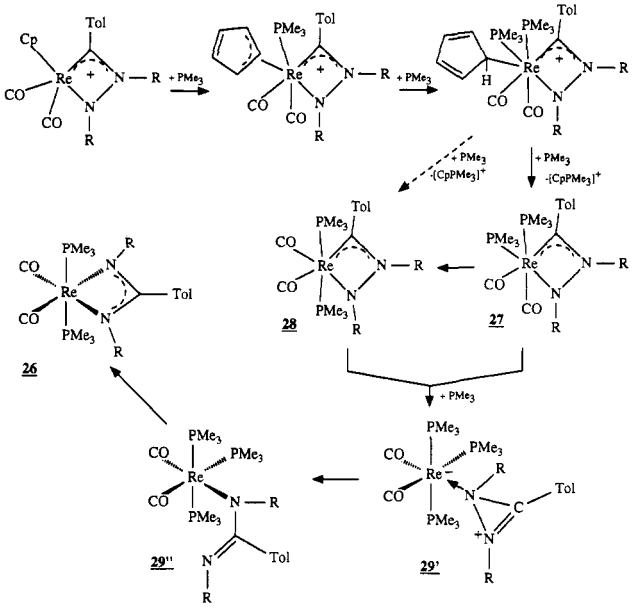


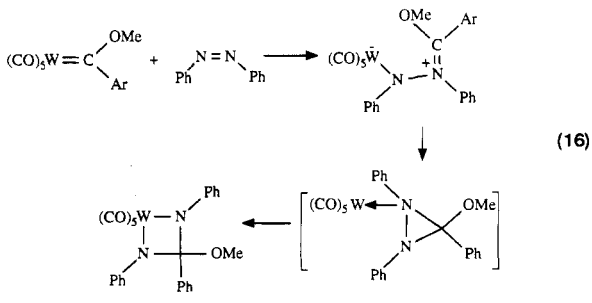
Figure 8. ORTEP drawing for **26a**. Thermal ellipsoids are drawn at the 35% probability level.

This latter reaction is at least partially reversible since it was observed by IR that the addition of 1.2 equiv of PMe_3 to a solution of **26a** induced the formation of a small amount of **29a**, although most of the **26a** remained unchanged. Both complexes showed two ν_{CO} bands in their IR spectra (e.g., **29a**, ν_{CO} = 1933, 1837 cm^{-1}) in a 1:1 intensity ratio which implies two carbonyl ligands in a cis arrangement. The ^{31}P NMR spectrum of **29a** showed a doublet at δ −35.2 (J_{PH} = 27 Hz) and a triplet at δ −38.0 (J_{PH} = 27 Hz) in a 2:1 intensity ratio, implying the presence of two equivalent PMe_3 ligands which couple to a third PMe_3 ligand. The ^1H NMR spectrum of **29a** showed aryl and tolyl methyl resonances, but no resonances were present

Scheme IV



which could be assigned to a Cp ligand, indicating that it has already been displaced in this intermediate. Also present in the ^{1}H NMR spectrum was a triplet at δ 1.63 (J_{PH} = 3.5 Hz) for the methyl groups of the trans PMe_3 ligands[24] and a doublet at δ 1.51 (J_{PH} = 7.4 Hz) for the methyl substituents of the third PMe_3 ligand, with these PMe_3 resonances integrating in a 2:1 ratio. This intermediate complex is soluble in hexane and is thus likely a neutral species. While we do not know the further details of its structure, its facile transformation into **26** and its spectroscopic data are consistent with either of the proposed structures **29′** or **29″** illustrated in Scheme IV. Complex **29′** could form by coordination of a third PMe_3 ligand to either **27** or **28** with extrusion of the metal from the metallacycle to form a diaziridinyl ligand. Ring opening of this ligand would give **29″** which possesses an η^1-benzamidinato ligand, and loss of PMe_3 from this species concomitant with coordination of the second nitrogen atom would give the observed product **26**. The final steps in this mechanism are similar to the mechanistic steps recently proposed by McElwee-White and co-workers to explain the formation of 2,4-diazametallacycles from the reaction of *cis*-PhN=NPh with the carbene complexes $(CO)_5W{=}C(OMe)(p\text{-}C_6H_4X)$ (X = H, OMe, CF_3), eq 16.[5e]



(16)

Concluding Remarks

The results described herein significantly extend the known chemistry of the carbyne complex $[Cp(CO)_2Re{\equiv}CTol]^+$ (1) and also give important new insight into the reactivity properties of carbyne complexes in general. The cycloaddition reactions of 1 with azobenzene, azotoluene, and benzo[*c*]cinnoline represent the first examples of such [2 + 2] cycloadditions with carbyne complexes of which we are aware, and the resultant metallacycles **5a,b** and **7** appear to be new types of organometallic ring systems, as are the five-membered metallacycles in **8a,b**. Similarly, the chloride-induced ring opening and addition of epoxides and 3,3-dimethyloxetane to 1 to form carbene derivatives are previously unreported transformations for carbyne complexes, although they are somewhat related to known examples of halide-induced addition of epoxides to carbonyl ligands to form cyclic carbene complexes.[25] The high reactivity of $[Cp(CO)_2Re{\equiv}CTol]^+$ toward these substrates and those described earlier[1,2] is clearly a consequence of the high electrophilicity of the carbyne carbon which permits it to coordinate and then activate weak organic nucleophiles. Since few carbyne complexes are as electrophilic as 1, the reactions described herein are not likely to prove characteristic of carbyne complexes in general, but it is also true that because of its unique electrophilicity there are likely many more nucleophiles yet to be examined that will give fundamentally new and interesting chemistry with 1.

Experimental Section

The complexes $[Cp(CO)_2Re{\equiv}CTol]BCl_4$ and $[Cp(CO)_2Re{\equiv}CTol]BPh_4$ were prepared using previously described[1] modifications of the original literature synthesis.[2d] Solvents were dried by refluxing over CaH_2 (CH_2Cl_2, $CHCl_3$, pentane, hexane) or Na/benzophenone (THF) and were freshly distilled prior to use. The silica gel chromatography support (Baker 3405, 60–200 mesh) was purchased from Thomas Scientific, and neutral alumina (Brockmann I, 150 mesh) was purchased from Aldrich Chemical Co. and adjusted to Brockmann II by addition of 3% H_2O prior to use. The reagents $Re_2(CO)_{10}$, PMe_2Ph, $PEtPh_2$ (Strem Chemicals), isobutylene oxide (TCI American Chemical Co.), 1.5 M ethylene oxide in Et_2O (Alfa), $SnCl_2{\cdot}2H_2O$, NaOH (Baker Chemical Co.), azobenzene, benzo[*c*]cinnoline, PMe_3, PPh_3, propylene oxide, propylene sulfide, [PPN]Cl, $Na[BPh_4]$, BCl_3, 3,3-dimethyloxetane, 2-methylaziridine, benzophenone hydrazone, $[Et_4N]Cl$, and 4-nitrotoluene (Aldrich Chemical Co.) were purchased and used as received. 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 Bruker AM 300 FT NMR spectrometer, and electron impact (EI) and fast atom bombardment (FAB) mass spectra were recorded on an AEI-MS9 mass spectrometer. Elemental analyses were obtained from Schwarzkopf Microanalytical Laboratories, Woodside, NY, or Galbraith Laboratories, Inc., Knoxville, TN.

Formation of *cis*-ArN=NAr. A pentane (200 mL) solution of azobenzene (2.5 g, 13.7 mmol) in a sealed 250-mL Schlenk flask was irradiated for 1 h by placing it next to a Hanovia 450-W medium-pressure Hg discharge lamp (Ace Glass, Inc.; catalog no. 7825-35) in a Pyrex water-cooled immersion well. This solution was concentrated and chromatographed on neutral grade II alumina. An orange band of *trans*-PhN=NPh eluted with pentane, and then an orange band of *cis*-PhN=NPh came off the column with 1:1 CH_2Cl_2/pentane as eluent. Solvent evaporation from the latter left *cis*-PhN=NPh in 37% yield (0.92 g, 5.1 mmol). This solid was stored at −20 °C in a flask wrapped in Al foil to exclude light. Azotoluene was prepared by the method of Cook,[26] and its cis isomer was obtained and stored as above.

(24) The triplet arises through virtual coupling of the methyl hydrogens with the both phosphorus atoms: Silverstein, P. M.; Bassler, G. C.; Morrill, T. C. *Spectroscopic Identification of Organic Compounds*; John Wiley & Sons: New York, 1981; p 207.

(25) (a) Motschi, H.; Angelici, R. J. *Organometallics* **1982**, *1*, 343. (b) Singh, M. M.; Angelici, R. J. *Inorg. Chem.* **1984**, *23*, 2691; (c) *Ibid.* **1984**, *23*, 2699.

Reaction of [Cp(CO)$_2$Re≡CTol]BPh$_4$ with *cis*-ArN=NAr. The salt [Cp(CO)$_2$Re≡CTol]BPh$_4$ (147 mg, 0.201 mmol) was dissolved in CH_2Cl_2 (20 mL) at −20 °C. *cis*-Azobenzene (40 mg, 0.220 mmol) was added, and the reaction mixture was allowed to stir for 15 min. The solvent was reduced in vacuo to 10 mL, and sufficient hexane was added to induce crystallization of **5a**. The supernatant was removed by cannula, and the solid was washed with hexane (3 × 10 mL) to leave **5a** as an orange microcrystalline solid in 90% yield (165 mg, 0.181 mmol). A similar reaction with *cis*-azotoluene gave **5b** in 93% yield.

5a. IR (CH_2Cl_2): ν_{CO} = 2058(s), 1999(s) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 2.40 (s, 3 H, Tol-C*H*$_3$), 5.44 (s, 5 H, Cp), 6.61–7.36 (m, 14 H, aryl). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 21.5 (Tol-*C*H$_3$), 94.9 (Cp), 120.6–153.0 (aryl), 173.2 (Re*C*), 196.6, 198.4 (*C*O). MS (FAB, 18-crown-6 mtarix): *m*/*z* = 593 (M$^+$). Anal. Calcd for $C_{51}H_{42}BN_2O_2Re$: C, 67.17; H, 4.64. Found: C, 67.23; H, 4.78.

5b. IR (CH_2Cl_2): ν_{CO} = 2057(s), 1996(s) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 2.26 (s, 3 H, NTol-C*H*$_3$), 2.29 (s, 3 H, NTol-C*H*$_3$), 2.40 (s, 3 H, CTol-C*H*$_3$), 5.64 (s, 5 H, Cp), 6.57–8.30 (m, 36 H, aryl). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 20.5, 21.1 (NTol-*C*H$_3$), 21.3 (CTol-*C*H$_3$), 94.8 (Cp), 120.6–150.4 (aryl), 170.9 (Re*C*), 196.6, 198.6 (*C*O). MS (FAB, 18-crown-6 matrix): *m*/*z* = 621 (M$^+$). Anal. Calcd for $C_{53}H_{46}BN_2O_2Re$: C, 67.72; H, 4.93. Found: C, 67.60; H, 4.94.

Reaction of [Cp(CO)$_2$Re≡CTol]BPh$_4$ with Benzo[*c*]cinnoline. The salt [Cp(CO)$_2$Re≡CTol]BPh$_4$ (153 mg, 0.209 mmol) was dissolved in CH_2Cl_2 (20 mL) at −20 °C. Benzo[*c*]cinnoline (38 mg, 0.210 mmol) was added, and the reaction mixture was allowed to stir for 15 min. The solvent was reduced in vacuo to 10 mL, and sufficient hexane was added to induce crystallization of complex **7**. The supernatant was removed by cannula, and the product was washed with hexane (3 × 10 mL) to give **7** as an orange microcrystalline solid in 85% yield (162 mg, 0.178 mmol).

7. IR (CH_2Cl_2): ν_{CO} = 2058(s), 1999(s) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 2.48 (s, 3 H, Tol-C*H*$_3$), 5.48 (s, 5 H, Cp), 6.22–7.63 (aryl). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 21.6 (Tol-*C*H$_3$), 91.2 (Cp), 112.8–146.6 (aryl), 163.6 (Re*C*), 195.2 (*C*O), 197.4 (*C*O). MS (FAB, 15-crown-5 matrix): *m*/*z* = 591 (M$^+$). Anal. Calcd for $C_{51}H_{40}BN_2O_2Re$: C, 67.32; H, 4.43. Found: C, 67.42; H, 4.79.

Reaction of [Cp(CO)$_2$Re≡CTol]BCl$_4$ with *cis*-ArN=NAr. The salt [Cp(CO)$_2$Re≡CTol]BCl$_4$ (144 mg, 0.256 mmol) was dissolved in CH_2Cl_2 (20 mL) at 0 °C. One equiv of PhN=NPh (46.6 mg, 0.256 mmol) was added, and this mixture was allowed to stir for 1 h. IR monitoring of the reaction showed the initial formation of the intermediate complex **5a** (ν_{CO} = 2058(s), 1999(s) cm^{-1}) and its conversion to complex **8a** over the course of 1 h. The solvent was reduced under vacuum to 10 mL, and hexane was added to induce crystallization of **8a**. The supernatant was removed by cannula, and the product was washed with hexane (3 × 10 mL) to yield **8a** as a light orange microcrystalline solid in 68% yield (109 mg, 0.173 mmol). A similar reaction with *cis*-TolN=NTol gave **8b** in 80% yield.

8a. IR (CH_2Cl_2): ν_{CO} = 1954(s) cm^{-1} {the ring acyl vibration was not resolved}. ^{1}H NMR (CD_2Cl_2): δ 2.23 (s, 3 H, Tol-C*H*$_3$), 5.51 (s, 5 H, Cp), 6.8–7.9 (m, 14 H, aryl). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 21.0 (Tol-*C*H$_3$), 92.0 (Cp), 123.0–152.9 (aryl), 194.1 (*C*-Tol), 201.2 (metal *C*O), 228.1 (ring *C*O). MS (FAB, 18-crown-6 matrix): *m*/*z* = 629 (MH$^+$). Anal. Calcd for $C_{27}H_{22}ClN_2O_2Re$: C, 51.63; H, 3.53. Found: C, 51.75; H, 3.77.

8b. IR (CH_2Cl_2): ν_{CO} = 1953 cm^{-1} (the ring acyl vibration was not resolved). ^{1}H NMR (CD_2Cl_2): δ 2.13 (s, 3 H, CTol-C*H*$_3$), 2.23 (s, 3 H, NTol-C*H*$_3$), 2.24 (s, 3 H, NTol-C*H*$_3$), 5.49 (s, 5 H, Cp), 6.77–8.20 (m, 12 H, aryl). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 20.9 (CTol-*C*H$_3$), 22.6, 31.5 (NTol-*C*H$_3$), 91.8 (Cp), 121.9–151.1 (aryl), 194.3 (*C*-Tol), 201.2 (metal *C*O), 227.2 (ring *C*O). MS (FAB, 18-crown-6 matrix): *m*/*z* = 657 (MH$^+$). Anal. Calcd for $C_{29}H_{26}ClN_2O_2Re$: C, 53.08; H, 3.99. Found: C, 53.33; H, 4.38.

Reaction of [Cp(CO)$_2$Re≡CTol]BCl$_4$ with Benzo[*c*]cinnoline. The BCl_4^- salt of complex **1** (103 mg, 0.183 mmol) was dissolved in CH_2Cl_2 (20 mL) at 0 °C. One equiv of benzo[*c*]-cinnoline (33.0 mg, 0.182 mmol) was added, and the reaction was allowed to stir for 2 h. IR and ^{1}H NMR monitoring of the reaction showed the formation of the chlorocarbene complex **9** [IR (CH_2Cl_2): ν_{CO} = 1985, 1905 cm^{-1}. ^{1}H NMR (acetone-d_6, −20 °C): δ 2.40 (s, 3 H, Tol-CH$_3$), 5.81 (s, 5 H, Cp), 7.21, 7.23, 7.64, 7.67 (Tol) (lit.[26] for Cp(CO)$_2$Re=C(Cl)Ph. IR (hexane): ν_{CO} = 1989, 1912 cm^{-1}. ^{1}H NMR (acetone-d_6): δ 5.98 (s, 5 H, Cp), 7.40 (m, 5 H, Ph)]. Chromatography of the reaction mixture on neutral grade II alumina with 1:1 CH_2Cl_2/hexane as eluent gave a yellow band of benzo[*c*]cinnoline, but the chlorocarbene complex **9** decomposed on the column.

Reaction of Complex 7 with [PPN]Cl. The BPh_4^- salt of complex **7** (88 mg, 0.097 mmol) was dissolved in CH_2Cl_2 (20 mL) at 22 °C, [PPN]Cl (66.8 mg, 0.116 mmol) was added, and the reaction mixture was allowed to stir for 1 h during which time IR monitoring showed the formation of the chlorocarbene complex **9**. The solvent was removed in vacuo, and the residue was chromatographed on neutral grade II alumina using 1:1 CH_2Cl_2/hexane as eluent to give a yellow band of benzo[*c*]cinnoline. Complex **9** decomposed on the column and failed to elute.

Reaction of 8a with AgBF$_4$ To Form 5a. Complex **8a** (80.0 mg, 0.127 mmol) was placed in a 50-mL Schlenk flask and dissolved in CH_2Cl_2 (20 mL) at room temperature. Solid $AgBF_4$ (33.6 mg, 0.172 mmol) was added, the mixture was stirred for 5 min, the solution was filtered through Celite to remove the precipitated AgCl, and the solvent was removed under vacuum to leave a bright yellow residue. Recrystallization from CH_2Cl_2/hexane gave complex **5a** (as its BF_4^- salt) in 62% yield (53.8 mg, 0.080 mmol) as a bright yellow microcrystalline solid.

Reaction of 8a with HBF$_4$·Et$_2$O To Form 5a. Complex **8a** (70.0 mg, 0.111 mmol) was placed in a 50-mL Schlenk flask and dissolved in CH_2Cl_2 (20 mL) at room temperature. HBF_4·Et_2O (0.01 mL, 8.5 mmol) was added, the mixture was stirred for 5 min, and the solvent was removed under vacuum to leave a bright yellow residue. Recrystallization from CH_2Cl_2/hexane gave complex **5a** (as its BF_4^- salt) in 78% yield (43.3 mg, 0.087 mmol) as a bright yellow microcrystalline solid.

Reaction of the [BPh$_4$]$^-$ Salts of 5a and 5b with [PPN]Cl To Form 10a,b. The BPh_4^- salt of complex **5a** (50.1 mg, 0.055 mmol) was dissolved in CH_2Cl_2 (20 mL) at 22 °C. One equiv of [PPN]Cl (31.5 mg, 0.055 mmol) was added, and the reaction mixture was stirred for 30 min. The solvent was removed under vacuum, $CHCl_3$ (10 mL) was added, the mixture was filtered, and hexane was added to induce crystallization of **10a**. The supernatant was removed by cannula, and the product was washed with hexane (3 × 10 mL) to give **10a** as a maroon microcrystalline solid in 95% yield (28.0 mg, 0.0521 mmol). A similar reaction of **5b** with [PPN]Cl gave **10b** in 89% yield.

10a. IR (CH_2Cl_2): ν_{CO} = 1881(s) cm^{-1}; ν_{CN} = 1680(br) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 2.42 (s, 3 H, Tol-C*H*$_3$), 5.61 (s, 5 H, Cp), 6.61–7.67 (m, 8 H, aryl), 11.72 (s, 1 H, N*H*). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 21.3 (Tol-*C*H$_3$), 92.6 (Cp), 118.0–144.9 (aryl), 156.3 (Re*C* aryl), 164.5 (*C*N=Ctol), 216.8 (*C*O), 221.6 (*C*-Tol). MS (FAB, 18-crown-6 matrix): *m*/*z* = 510 (MH$^+$). Anal. Calcd for $C_{20}H_{17}ClNORe$: C, 47.19; H, 3.37. Found: C, 46.69; H, 3.61.

10b. IR (CH_2Cl_2): ν_{CO} = 1877(s) cm^{-1}; ν_{CN} = 1684(br) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 2.38 (s, 3 H, NTol-C*H*$_3$), 2.40 (s, 3 H, CTol-C*H*$_3$), 5.23 (s, 5 H, Cp), 6.67–8.06 (m, 7 H, aryl), 10.43 (N*H*). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 21.0, 22.2 (Tol-*C*H$_3$), 92.5 (Cp), 121.4–146.7 (aryl), 150.7 (Re*C* aryl), 163.7 (*C*N=Ctol), 215.1 (*C*O), 222.1 (*C*-Tol). MS (FAB, 18-crown-6 matrix): *m*/*z* = 524 (MH$^+$). Anal. Calcd for $C_{21}H_{19}ClNORe$: C, 48.22; H, 3.66. Found: C, 48.59; H, 3.57.

Reaction of 5a with BCl$_3$/[PPN]Cl. Complex **5a** (71.1 mg, 0.0780 mmol) was dissolved in CH_2Cl_2 (20 mL) at room temperature, and BCl_3 (0.5 mL, 1.0 M) was added to the solution. IR monitoring indicated the formation of a new complex [ν_{CO} = 2092, 2018 cm^{-1}) within 5 min. One equiv of [PPN]Cl (44.7 mg, 0.0780 mmol) was then added to give instantaneous formation of **8a**.

Reaction of [Cp(CO)$_2$Re≡CTol]BCl$_4$ with Ethylene Oxide. The salt [Cp(CO)$_2$Re≡CTol]BCl$_4$ (150 mg, 0.266 mmol) was dissolved in CH_2Cl_2 (20 mL) at −20 °C. An excess of an Et_2O

(26) Cook, A. H. *J. Chem. Soc.* **1938**, *170*, 876.

solution of ethylene oxide (1.5 M) was added via syringe, and the reaction mixture was stirred for 5 h at 0 °C. The solvent was removed under vacuum, and the yellow residue was chromatographed on a silica gel column (0.5 in. × 1.5 ft) using 1:1 CH_2Cl_2/hexane as eluent. This gave one bright yellow band which upon removal of solvent left complex **13** (46.9 mg, 0.096 mmol) as a yellow microcrystalline solid in 36% yield.

13. IR (CH_2Cl_2): ν_{CO} = 1874(s), 1953(s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 2.34 (s, 3 H, Tol-CH_3), 3.95 (t, 2 H, J_{HH} = 5.3 Hz, CH_2Cl), 4.76 (t, 2 H, J_{HH} = 5.3 Hz, OCH_2), 5.22 (s, 5 H, Cp), 6.9–7.1 (m, 4 H, Tol). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 20.8 (Tol-CH_3), 42.3 (CH_2Cl), 77.5 (CH_2O), 89.6 (Cp), 123.0, 127.5, 137.4, 156.1 (Tol), 203.2 (CO), 286.4 (Re=C). MS (EI): m/z = 490 (M^+).

Reaction of [Cp(CO)$_2$Re≡CTol]BCl$_4$ with Propylene Oxide. This reaction was conducted as described above for the corresponding reaction with ethylene oxide using [Cp(CO)$_2$Re≡CTol]BCl_4 (200 mg, 0.36 mmol) and excess propylene oxide to give after chromatography complex **14** as a 1:1.6 mixture of **14a** and **14b** in 42% yield (76.0 mg, 0.151 mmol) as a yellow microcrystalline solid. The mixture was then chromatographed on neutral alumina using 1:4 CH_2Cl_2/hexane as eluent which gave two overlapping bands. The first band to elute gave a red/orange microcrystalline solid upon solvent removal and was shown by NMR analysis to be mainly **14a** contaminated with a small amount of **14b**. The second band to elute left a yellow/orange microcrystalline solid upon removal of solvent and was shown by NMR analysis to be a mixture of **14a** and **14b**.

14. IR (CH_2Cl_2): ν_{CO} = 1874(s), 1954(s) cm^{-1}. MS (EI): m/z = 504 (M^+). Anal. Calcd for $C_{18}H_{18}ClO_3Re{\cdot}0.5CH_2Cl_2$: C, 40.66; H, 3.50. Found: C, 40.96; H, 3.75.

14a. ^1H NMR (CD_2Cl_2): δ 1.53 (d, 3 H, J_{HH} = 6.2 Hz, CH_3), 2.34 (s, 3 H, Tol-CH_3), 3.78 (d, 2 H, J_{HH} = 5.6 Hz, CH_2), 5.50 (sextet, 1 H, J_{HH} = 6.1 Hz, CH), 5.21 (s, 5 H, Cp), 6.80–7.20 (m, 4 H, Tol). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 18.5 (CH_3), 21.2 (Tol-CH_3), 55.0 (CHCl), 82.4 (OCH_2), 89.9 (Cp), 123.8, 128.0, 137.9, 156.7 (Tol), 203.7 (CO), 287.9 (Re=C).

14b. ^1H NMR (CD_2Cl_2): δ 1.60 (d, 3 H, J_{HH} = 6.7 Hz, CH_3), 2.34 (s, 3 H, Tol-CH_3), 4.43 (sextet, 1 H, J_{HH} = 6.0 Hz, CH), 4.62 (d, 2 H, J_{HH} = 5.8 Hz, CH_2), 5.22 (s, 5 H, Cp), 6.80–7.20 (m, 4 H, Tol). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 18.5 (CH_3), 22.0 (Tol-CH_3), 47.6 (CH_2Cl), 85.1 (OCH), 89.8 (Cp), 123.6, 128.0, 137.7, 156.6 (Tol), 203.2 (CO), 287.2 (Re=C).

Reaction of [Cp(CO)$_2$Re≡CTol]BCl$_4$ with Isobutylene Oxide. This reaction was conducted as described above for the corresponding reaction with ethylene oxide using [Cp(CO)$_2$Re≡CTol]BCl_4 (124 mg, 0.220 mmol) and excess isobutylene oxide to give after chromatography **15** as a 1:2.5 mixture of **15a** and **15b** as a yellow microcrystalline solid in 84% yield (77.5 mg, 0.0149 mmol). The mixture was then chromatographed on neutral alumina using 1:4 CH_2Cl_2/hexane as eluent to give two overlapping bands of **15a** and **15b**. The first band to elute was the major product, **15b**, which upon removal of the solvent gave the compound as a spectroscopically pure red/orange microcrystalline solid. The second band to elute gave a yellow/orange solid upon removal of solvent which was shown by NMR analysis to be a mixture of **15a** and **15b**.

15. IR (CH_2Cl_2): ν_{CO} = 1871(s), 1951(s) cm^{-1}. MS (EI): m/z = 518 (M^+). Anal. Calcd for $C_{19}H_{20}ClO_3Re{\cdot}0.5$ mol hexane: C, 47.09; H, 4.85. Found: C, 46.84; H, 4.22.

15a. ^1H NMR (CD_2Cl_2): δ 1.46 (s, 6 H, CH_3), 2.35 (s, 3 H, Tol-CH_3), 4.29 (s, 2 H, CH_2), 5.18 (s, 5 H, Cp), 6.3–7.2 (m, 4 H, Tol). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 20.9 (Tol-CH_3), 29.4 (CH_3), 65.8 (CMe_2Cl), 81.0 (OCH_2), 89.2 (Cp), 123.3, 127.7, 137.4, 156.5 (Tol), 203.4 (CO), 284.9 (Re=C).

15b. ^1H NMR (CD_2Cl_2): δ 1.66 (s, 6 H, CH_3), 2.35 (s, 3 H, Tol-CH_3), 4.53 (s, 2 H, CH_2), 5.23 (s, 5 H, Cp), 6.7–7.2 (m, 4 H, Tol). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 21.0 (Tol-CH_3), 29.4 (CH_3), 66.7 (CH_2Cl), 85.6 ($OCMe_2$), 89.6 (Cp), 123.3, 127.7, 137.6, 156.2 (Tol), 203.4 (CO), 286.0 (Re=C).

Reaction of [Cp(CO)$_2$Re≡CTol]BCl$_4$ with Propylene Oxide in the Presence of [PPN]Br. A solution of [PPN]Br (60.6 mg, 0.0979 mmol) and propylene oxide (7.1 μL, 0.0979 mmol) in CH_2Cl_2 was allowed to stir for 2 h, and this solution was then transferred to a −20 °C CH_2Cl_2 (20 mL) solution of the salt [Cp(CO)$_2$Re≡CTol]BCl_4 (51 mg, 0.091 mmol). IR monitoring indicated that the reaction was complete upon mixing. The solvent was removed after the reaction mixture was stirred for an additional 2 h, and chromatography of the residue on silica gel (0.5 in × 1 ft column) using 1:1 CH_2Cl_2/hexane as eluent gave one bright yellow band which upon solvent removal left a mixture of **14a,b** and **16a,b** as a yellow microcrystalline solid. Electron impact mass spectral analysis of this solid showed a 2:1 ratio of parent ions at m/z = 548 (**16a**/**16b**) and m/z = 504 (**14a**/**14b**). ^1H NMR analysis (CH_2Cl_2, 22 °C) showed the presence of all four isomers in the ratios given in the text, and the resonance assignments for **16a** and **16b** are as follows.

16a. δ 1.51 (d, 3 H, J_{HH} = 6.8 Hz, CH_3), 2.34 (s, 3 H, Tol-CH_3), 3.64 (d, 2 H, J_{HH} = 5.3 Hz, CH_2), 5.19 (s, 5 H, Cp), 5.45 (m, 1 H, CH), 6.81–7.12 (m, 4 H, Tol).

16b: δ 1.77 (d, 3 H, J_{HH} = 6.9 Hz, CH_3), 2.34 (s, 3 H, Tol-CH_3), 4.44 (m, 1 H, CH), 4.59 (d, 2 H, CH_2), 5.20 (s, 5 H, Cp), 6.81–7.12 (m, 4 H, Tol).

Reaction of [Cp(CO)$_2$Re≡CTol]BCl$_4$ with 3,3-Dimethyloxetane. The salt [Cp(CO)$_2$Re≡CTol]BCl_4 (73 mg, 0.13 mmol) was dissolved in CH_2Cl_2 (20 mL) at −20 °C. Excess 3,3-dimethyloxetane was added via syringe, and the reaction was stirred for 7 h. The solvent was removed under vacuum, and the residue was chromatographed on silica gel (0.5 in. × 1.5 ft) using 1:1 CH_2Cl_2/hexane as eluent. This gave one bright yellow band which upon removal of solvent left complex **17** (28 mg, 0.052 mmol) as yellow microcrystals in 40% yield.

17. IR (CH_2Cl_2): ν_{CO} = 1871(s), 1952(s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 1.10 (s, 3 H, C(CH_3)$_2$), 2.34 (s, 3 H, Tol-CH_3), 3.48 (s, 2 H, CH_2O), 4.30 (s, 2 H, CH_2Cl), 5.20 (s, 5 H, Cp), 6.89 (d, 2 H, J_{HH} = 8.0 Hz), 7.07 (d, 2 H, J_{HH} = 8.0 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 20.9 (CH_3), 22.6 (Tol-CH_3), 36.2 (CMe_2), 65.4 (CH_2Cl), 83.1 (OCH_2), 89.5 (Cp), 123.1, 127.6, 137.2, 156.7 (Tol), 203.6 (CO), 288.8 (Re=C). MS (EI): m/z = 532 (M^+). Anal. Calcd for $C_{20}H_{22}ClO_3Re$: C, 45.15; H, 4.17. Found: C, 44.86; H, 4.09.

Reaction of [Cp(CO)$_2$Re≡CTol]BCl$_4$ with 2-Methylaziridine. The salt [Cp(CO)$_2$Re≡CTol]BCl_4 (512 mg, 0.911 mmol) was dissolved in CH_2Cl_2 (20 mL) at −20 °C. Excess 2-methylaziridine (0.6 mL, 8.49 mmol) was added via syringe, and the reaction mixture was stirred for 15 min. The solvent was removed under vacuum, and the residue was chromatographed on silica gel (0.5 in. × 1.5 ft column) using 1:1 CH_2Cl_2/hexane as eluent. This gave one bright yellow band which upon removal of solvent left complex **18** as a yellow oil in 91% yield (386 mg, 0.827 mmol).

18. IR (CH_2Cl_2): ν_{CO} = 1847(s), 1923(s) cm^{-1}. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 22 °C): δ 18.0 (CHCH_3), 21.1 (Tol-CH_3), 37.0 (CH_2), 39.0 (CH), 87.6 (Cp), 124.3, 128.2, 137.6, 155.0 (aryl), 205.0 (CO), 256.4 (Re=C). MS (EI): m/z = 467 (M^+). ^1H NMR (CD_2Cl_2, −40 °C, major rotamer): δ 1.01 (d, 3 H, J_{HH} = 5.5 Hz, CH_3), 2.30 (s, 3 H, Tol-CH_3), 2.51 (d, 1 H, J_{HH} = 3.1 Hz, CH_2), 2.66 (m, 1 H, CH), 2.82 (d, 1 H, J_{HH} = 5.4 Hz, CH_2), 5.10 (s, 5 H, Cp), 6.96–7.11 (m, 4 H, Tol). ^1H NMR (CD_2Cl_2, −40 °C, minor rotamer): δ 1.58 (d, 3 H, J_{HH} = 5.5 Hz, CH_3), 2.17 (d, 1 H, J_{HH} = 3.1 Hz, CH_2), 2.25 (d, 1 H, J_{HH} = 5.4 Hz, CH_2), 2.30 (s, 3 H, Tol-CH_3), 2.94 (m, 1 H, CH), 5.05 (s, 5 H, Cp), 6.96–7.11 (m, 4 H, Tol). Anal. Calcd for $C_{18}H_{15}NO_2Re.0.5CH_2Cl_2$: C, 43.92; H, 3.19. Found: C, 43.76; H, 3.91.

Reaction of [Cp(CO)$_2$Re≡CTol]BPh$_4$ with Propylene Sulfide. The salt [Cp(CO)$_2$Re≡CTol]BPh_4 (159 mg, 0.22 mmol) was dissolved in CH_2Cl_2 (20 mL) at −20 °C. Propylene sulfide (0.09 mL, 1.1 mmol) was added, and the reaction mixture was stirred for 1 h. The solvent was removed under vacuum, and the residue was taken up in 20 mL of CH_2Cl_2 and filtered through Celite. Hexane was added until crystals of [Cp(CO)$_2$Re{η^2-S$_2$-CTol}]BPh_4 (**19**) precipitated. The supernatant was removed via cannula, and the crystals were washed with hexane (3 × 10 mL) to leave **19** (139 mg, 0.18 mmol) as yellow microcrystals in 82% yield.

19. IR (CH_2Cl_2): ν(CO) = 2066, 2004 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 2.43 (s, 3 H, Tol-CH_3), 5.53 (s, 5 H, Cp), 6.84–7.75 (m, 24

H, Ar). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 22.2 (Tol-CH_3), 95.6 (Cp), 122.6, 129.8, 143.2, 149.0 (Tol), 194.2 (*C*O), 246.3 (*C*S$_2$). MS (FAB): *m/z* = 475 (M$^+$). Anal. Calcd for $C_{39}H_{32}BO_2S_2Re$: C, 59.01; H, 4.06. Found: C, 59.10; H, 4.21.

Reaction of [Cp(CO)$_2$Re≡CTol]BCl$_4$ with Benzophenone Hydrazone. Benzophenone hydrazone (126 mg, 0.06 mmol) was added to a −20 °C CH_2Cl_2 (30 mL) solution of [Cp(CO)$_2$Re≡CTol]-BCl_4 (180 mg, 0.03 mmol) which induced an immediate color change from yellow to bright yellow-orange. The solution was stirred for 15 min, and the solvent was then removed under vacuum. The residue was chromatographed on alumina (activity III) using 30% CH_2Cl_2/hexane as eluent. A single orange band eluted which gave 137 mg (71%) of **20** as an orange, microcrystalline soild upon solvent evaporation.

20. ^1H NMR (toluene-d_8): δ 1.93 (s, 3 H, Tol-CH_3), 2.14 (s, 3 H, Tol-CH_3), 4.67 (s, 5 H, Cp), 4.85 (s, 5 H, Cp), 6.67–7.41 (m, 28 H, aryl), 9.51 (s, 1 H, N*H*), 10.62 (s, 1 H, N*H*.) $^{13}C\{H\}$ NMR ($CDCl_3$): δ 21.0 (Tol-CH_3), 21.2 (Tol-CH_3), 87.5 (Cp), 87.8 (Cp), 123.1–136.6 (aryl), 152.1, 153.0 (N=*C*Ph$_2$), 203.2 (*C*O), 205.2 (*C*O), 241.0 (Re=*C*), 242.8 (Re=*C*). IR(pentane): ν_{CO} = 1877 (s), 1890 (vs), 1944 (vs), 1954 (s) cm^{-1}. MS (EI): *m/z* = 606 (M$^+$). Anal. Calcd for $C_{28}H_{23}N_2O_2Re{\cdot}0.5CH_2Cl_2$: C, 52.81; H, 3.73. Found: C, 53.10; H, 3.67.

Reaction of [Cp(CO)$_2$Re≡CCH$_3$]BCl$_4$ with Benzophenone Hydrazone. This reaction was conducted as above using benzophenone hydrazone (71 mg, 0.36 mmol) and [Cp(CO)$_2$-Re≡CCH$_3$]BCl_4 (88 mg, 0.18 mmol) to give complex **21** as a yellow microcrystalline solid in 65% yield (62 mg).

21. IR (CH_2Cl_2): ν_{CO} = 1928(s), 1853(s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 2.81 (s, 3 H, CH_3), 5.21 (s, 5 H, Cp), 6.85–7.64 (m, 10 H, aryl), 10.1 (s, 1 H, N*H*). ^{13}C NMR (CD_2Cl_2, proton coupled): δ 38.7 (q, *C*H$_3$, J_{CH} = 133.0), 86.9 (d, Cp, J_{CH} = 177.9), 126.9–137.1 (m, Ph), 152.4 (s, *C*Ph$_2$), 204.3 (s, *C*O), 241.5 (s, Re=*C*). MS (EI): *m/z* = 530 (M$^+$). Anal. Calcd for $C_{20}H_{22}ClO_3Re{\cdot}0.25$ mol hexane: C, 51.21; H, 4.11. Found: C, 51.08; H, 3.47.

Reaction of [Cp(CO)$_2$Re{η^2-S$_2$CTol}]BPh$_4$ with PMe$_3$. The salt [Cp(CO)$_2$Re{η^2-S$_2$CTol}]BPh_4 (139 mg, 0.17 mmol) was dissolved in CH_2Cl_2 (30 mL) at room temperature, PMe_3 (0.05 mL, 0.52 mmol) was added via syringe, and the reaction mixture was stirred for 2 h. IR monitoring showed the initial formation of an intermediate complex (ν_{CO} = 1990(s), 1886(s) cm^{-1}) and then complete conversion to complex **23**. The solvent was removed under vacuum, and the residue was chromatographed on silica gel (0.5 in. × 1.5 ft column) using 1:1 CH_2Cl_2/hexane as eluent. This gave one orange-red band which upon removal of solvent left complex **23** (47.1 mg, 0.084 mmol) as orange-red microcrystals in 48% yield.

23. IR (CH_2Cl_2): ν_{CO} = 1845(s), 1918(s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 1.60 (t,[24] 18 H, P(CH_3)$_3$, J_{PH} = 3.7 Hz), 2.33 (s, 3 H, Tol-CH_3), 7.17 (d, 2 H, J_{HH} = 8.2 Hz, Tol), 7.86 (d, 2 H, *J* = 8.2 Hz, Tol). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 18.3 (t, P(CH$_3$)$_3$, J_{PC} = 63.7 Hz), 21.6 (Tol-*C*H$_3$), 122.7, 128.7, 143.6, 145.8 (Tol), 200.0 (t, *C*O, J_{PC} = 6.9 Hz), 200.1 (t, *C*O, J_{PC} = 7.6 Hz), 249.4 (t, *C*S$_2$, J_{PC} = 9.9 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −27.0 (*P*(CH$_3$)$_3$). MS (EI): *m/z* = 562 (M$^+$). Anal. Calcd for $C_{16}H_{25}O_2P_2S_2Re$: C, 34.22; H, 4.49. Found: C, 33.86; H, 4.75.

Addition of PMe$_3$ to Complex 7 To Form 24. Complex **7** (88.0 mg, 0.097 mmol) was dissolved in CH_2Cl_2 (20 mL) at 22 °C, PMe_3 (0.1 mL, 1.04 mmol) was added via syringe, and the reaction mixture was stirred for 15 min. The solvent was removed under vacuum, and the residue was chromatographed on neutral alumina using 1:1 CH_2Cl_2/hexane as eluent. This gave one dark maroon band which upon removal of the solvent left complex **24** (59.0 mg, 0.087 mmol) as a dark maroon solid in 90% yield.

24. IR (CH_2Cl_2): ν_{CO} = 1920, 1831 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 1.30 (d, 9 H, P(CH_3)$_3$, J_{PH} = 7.9 Hz), 1.83 (d, 9 H, P(CH_3)$_3$, J_{PH} = 7.3 Hz), 2.37 (s, 3 H, Tol-CH_3), 6.81–7.72 (aryl). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 18.1 (d, P(*C*H$_3$)$_3$, J_{PC} = 27.0 Hz), 21.2 (Tol-*C*H$_3$), 23.5 (d, P(CH$_3$)$_3$, J_{PC} = 27.0 Hz), 111.4–139.4 (aryl), 194.5 (dd, *C*Tol, J_{PC} = 8.0, 50.6 Hz), 204.5 (d, *C*O, J_{PC} = 9.3 Hz), 206.1 (dd, *C*O, J_{PC} = 8.0, 41.4 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −33.5 (d, *P*Me$_3$, J_{PP} = 26.8 Hz), −36.2 (d, *P*Me$_3$, J_{PP} = 26.8 Hz). MS (EI): *m/z* = 678 (M$^+$). Anal. Calcd for $C_{28}H_{33}N_2O_2P_2Re$: C, 49.62; H, 4.91. Found: C, 51.65; H, 5.59.

Thermally-Induced Transformation of 24 into 25. Complex **24** was dissolved in toluene-d_8, and the solution was heated in an NMR tube to 90 °C for 30 min during which time ^1H NMR monitoring indicated complete conversion to complex **25**. This species was isolated as a purple microcrystalline solid by evaporation of solvent from this solution.

25. IR (CH_2Cl_2): ν_{CO} = 1907, 1828 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 1.42 (t,[24] 18 H, P(CH_3)$_3$, J_{PH} = 3.4 Hz), 2.37 (s, 3 H, Tol-CH_3), 6.93–7.80 (m, 12 H, aryl). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 19.1 (t, P(*C*H$_3$)$_3$, J_{PC} = 15.3 Hz), 21.3 (Tol-*C*H$_3$), 112.0–149.7 (aryl), 205.0 (t, *C*-Tol, J_{PC} = 9.3 Hz), 205.7 (t, *C*O, J_{PC} = 8.0 Hz), 206.6 (t, *C*O, J_{PC} = 8.0 Hz). $^{31}P\{^1H\}$ NMR (toluene-d_8): δ −30.1 (*P*Me$_3$). MS (EI): *m/z* = 678. Anal. Calcd for $C_{28}H_{33N2}O_2P_2Re$: C, 49.62; H, 4.91. Found, C, 49.59; H, 5.00.

Reaction of Complexes 5a,b with PMe$_3$ To Form 26a,b. The BPh_4^- salt of **5a** (94.5 mg, 0.104 mmol) was dissolved in CH_2Cl_2 (20 mL) at 22 °C, and the flask was wrapped in aluminum foil to exclude light. Trimethylphosphine (0.1 mL, 1.04 mmol) was added via syringe, and the reaction mixture was stirred for 5 h. Infrared monitoring showed the initial formation of an intermediate complex (**29a**, ν_{CO} = 1929(s), 1834(s) cm^{-1}) followed by complete conversion to complex **26a**. The solvent was removed under vacuum, and the residue was chromatographed on silica gel (0.5 in. × 1.5 ft column) using 1:1 CH_2Cl_2/hexane as eluent. This gave one bright yellow band which upon removal of solvent left **26a** (56.3 mg, 0.076 mmol) as a bright yellow microcrystalline solid in 73% yield. A similar reaction of **5b** with PMe_3 gave **26b** in 79% yield as a bright yellow microcrystalline solid. Complexes **26c** and **26d** were similarly obtained in 68% and 75% yields, respectively, from the reactions of **5a** with PMe_2Ph and $PEtPh_2$. From the reaction of **5a** with PMe_3, the byproduct phosphonium salt [CpPMe$_3$][BPh_4] was isolated by adding sufficient hexane to the original reaction mixture to induce its crystallization. The supernatant was removed by cannula, and the phosphonium salt was then washed with hexane (3 × 10 mL) to give a white microcrystalline solid in 83% yield. The above-mentioned intermediate complexes **29a,b** were isolated by stopping the reaction when IR analysis indicated their presence at maximum concentration. The solvent was then removed under vacuum, the intermediate complex was extracted with hexane (2 × 10 mL), and the extract was filtered through Celite. A yellow microcrystalline solid was obtained upon removal of the solvent by evaporation under vacuum. These complexes transformed into **26a,b** rapidly upon attempts at chromatographic purification and more slowly when allowed to stir in solution. In a separate experiment, IR monitoring indicated the formation of a small amount of the above-mentioned intermediate upon addition of 1.2 equiv of PMe_3 (0.010 mL, 0.0966 mmol) to a CH_2Cl_2 (15 mL) solution of **26a** (55.7 mg; 0.0819 mmol).

[CpPMe$_3$][BPh_4]. ^1H NMR (CD_2Cl_2): δ 1.32 (d, 9 H, J_{PH} = 13.8 Hz, CH_3), 1.33 (d, 1 H, J_{PH} = 13.8 Hz, α-proton to P), 3.06 (t, 4 H, J_{PH} = 1.5 Hz, Cp), 6.85–7.40 (m, 24 H, aryl). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −27.4 (Cp*P*Me$_3$). MS (FAB, 18-crown-6 matrix): *m/z* = 141 (CpPMe$_3^+$).

26a. IR (CH_2Cl_2): ν_{CO} = 1903(s), 1821(s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 1.43 (t, 18 H, P(CH_3)$_3$, J_{PH} = 3.5 Hz), 2.36 (s, 3 H, Tol-CH_3), 6.49–7.03 (m, 14 H, aryl). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 17.4 (t, P(*C*H$_3$)$_3$, J_{PC} = 15.8 Hz), 21.5 (Tol-*C*H$_3$), 121.2–151.6 (aryl), 164.0 (*C*Tol), 204.2 (t, *C*O, J_{PC} = 8.7 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −22.2 (*P*Me$_3$). MS (EI): *m/z* = 680 (M$^+$). Anal. Calcd for $C_{28}H_{35}N_2O_2P_2Re{\cdot}0.5$ mol hexane: C, 51.51; H, 5.86. Found: C, 51.01; H, 5.56.

26b. IR (CH_2Cl_2): ν_{CO} = 1904(s), 1824(s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 1.43 (t, 18 H, P(CH_3)$_3$, J_{PH} = 3.4 Hz), 2.18 (s, 3 H, NTol-CH_3), 2.20 (s, 3 H, NTol-CH_3), 2.42 (s, 3 H, CTol-CH_3), 6.38–7.70 (m, 12 H, Tol). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 17.3 (t, P(*C*H$_3$)$_3$, J_{PC} = 14.7 Hz), 20.6 (NTol-*C*H$_3$), 21.5 (CTol-*C*H$_3$), 122.2–144.9 (aryl), 163.0 (*C*Tol), 204.4 (*C*O). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −22.1 (*P*(CH$_3$)$_3$. MS (EI): *m/z* = 708 (M$^+$). Anal. Calcd for $C_{30}H_{39}N_2O_2P_2Re$: C, 50.91; H, 5.55. Found: C, 50.69; H, 5.89.

26c. IR (CH_2Cl_2): ν_{CO} = 1905(s), 1829(s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 1.86 (t, 12 H, $P(CH_3)_3$, J_{PH} = 3.1 Hz), 2.25 (s, 3 H, Tol-CH_3), 6.23–7.53 (m, 24 H, Tol). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 14.2 (t, $P(CH_3)_3$, J_{PC} = 15.2 Hz), 22.8 (Tol-CH_3), 121.0–146.5 (aryl), 165.0 (*C*Tol), 203.9 (*C*O, J_{PC} = 8.7 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 6.31 (PMe_2Ph). Anal. Calcd for $C_{38}H_{39}N_2O_2P_2Re$·0.5 mol hexane: C, 58.14; H, 5.47. Found: C, 57.94; H, 5.17.

26d. IR (CH_2Cl_2): ν_{CO} = 1904(s), 1826(s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 0.65 (quintet, 6 H, CH_3, J_{PH} = 7.9 Hz), 2.24 (s, 3 H, Tol-CH_3), 2.34 (m, 4 H, CH_2, J_{HH} = 2.6 Hz, J_{PH} = 7.4 Hz), 5.99–7.56 (m, 34 H, aryl). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 20.6 (d, CH_2, J_{PC} = 10.9 Hz), 21.4 (Tol-CH_3), 24.0 (t, $P(CH_2CH_3)$, J_{PC} = 14.4 Hz), 120.9–145.8 (aryl), 165.0 (*C*Tol), 204.2 (t, *C*O, J_{PC} = 7.6 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 18.9 (PPh_2Et). MS (EI): m/z = 956 (M^+). Anal. Calcd for $C_{40}H_{47}N_2O_2P_2Re$·1.0 mol CH_2Cl_2: C, 58.84; H, 4.74. Found: C, 58.51; H, 5.51.

29a. IR (CH_2Cl_2): ν_{CO} = 1929(s), 1834(s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 1.51 (d, 9 H, $P(CH_3)_3$, J_{PH} = 7.4 Hz), 1.63 (t, 18 H, $P(CH_3)_3$, J_{PH} = 3.5 Hz), 2.31 (s, 3 H, Tol-CH_3), 6.43–7.70 (m, 14 H, aryl). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −35.2 (t, $P(CH_3)_3$, J_{PH} = 27 Hz), −38.0 (d, $P(CH_3)_3$, J_{PH} = 27 Hz).

29b. IR (CH_2Cl_2): ν_{CO} = 1933(s), 1837(s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 1.51 (d, 9 H, $P(CH_3)_3$, J_{PH} = 7.4 Hz), 1.62 (t, 18 H, $P(CH_3)_3$, J_{PH} = 3.5 Hz), 2.19 (s, 3 H, NTol-CH_3), 2.29 (s, 3 H, NTol-CH_3), 6.40–7.80 (m, 14 H, aryl). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −35.1 (d, $P(CH_3)_3$, J_{PP} = 27 Hz), −37.9 (t, $P(CH_3)_3$, J_{PP} = 27 Hz). MS (FAB$^+$, 15-crown-5-matrix): m/z = 784.

Addition of PMe_3 to [Cp*(CO)$_2$Re-η^2-{C(Tol)N(Ph)N(Ph)}][BPh_4]. The salt [Cp*(CO)$_2$Re-η^2-{C(Tol)N(Ph)N(Ph)}][BPh_4] (90.2 mg, 0.092 mmol), prepared from [Cp*(CO)$_2$Re≡CTol]BPh_4 and *cis*-PhN=NPh as described above for **5a**, was dissolved in CH_2Cl_2 (20 mL) at 22 °C, and the flask was wrapped in aluminum foil to exclude light. Trimethylphosphine (0.1 mL, 1.04 mmol) was added via syringe, and the reaction mixture was stirred for 5 h. Infrared monitoring showed the initial formation of an intermediate complex (ν_{CO} = 1929(s), 1834(s) cm^{-1}) followed by complete conversion to complex **26a**. The solvent was removed under vacuum, and the residue was chromatographed on silica gel (0.5-in. × 1.5-ft column) using 1:1 CH_2Cl_2/hexane as eluent. This gave one bright yellow band which upon removal of solvent left **26a** (42.5 mg, 0.076 mmol) as a bright yellow microcrystalline solid in 68% yield.

Crystallographic Characterization of Complexes 10a, 17, 20, 21, 24, 25, and 26a. Crystal, data collection, and refinement parameters are collected in Tables I and VI. For each compound, a crystal suitable for X-ray structural determination was mounted on a glass fiber with epoxy cement, and the unit-cell parameters were obtained from the least-squares fit of 25 reflections (20° ≤ 2θ ≤ 25°). For **10a**, **17**, and **25** the systematic absences in the diffraction data uniquely established the space groups as *Pccn*, $P2_1/c$, and $P2_1/c$, respectively. For **26a**, the systematic absences in the diffraction data established the space group as either $Pca2_1$ or *Pcam* (nonstandard *Pbcm*). *E*-statistics suggested the non-centrosymmetric alternative, and the chemically sensible results of refinement established the space group as $Pca2_1$. For **20** and **21**, no evidence for symmetry higher than triclinic was found in either the photographic or diffraction data. The centrosymmetric alternative *P*1(bar) was initially assumed and was subsequently confirmed by the results of refinement. For similar reasons *C*2/*c* was preferred over *Cc* for **24**. A semiempirical correction factor for absorption was applied to the data sets of **10a**, **17**, **20**, **21**, **24**, **25**, and **26a** (216 ψ-scans).

The structures of **10a**, **17**, **21**, **24**, **25**, and **26a** were solved by direct methods which located the Re atoms (and the Cl atom of **10a**). The remaining non-hydrogen atoms were located through subsequent difference Fourier syntheses. The structure of **20** was solved by heavy-atom methods and completed from difference maps. For **17**, two chemically similar chlorine locations were found on adjacent methyl groups C(13) and C(14) and refined at 62% [Cl(a)] and 38% [Cl(b)] occupancies, respectively. Anomalous bond distances within the neopentyl group are due to the observed chlorine disorder. For **24** and **25**, the P(2) phosphine unit was also disordered.

For **10a**, **17**, **21**, **24**, **25**, and **26a**, all hydrogen atoms were included as idealized isotropic contributions (d_{CH} = 0.960 Å, U = 1.2U for attached C). All non-hydrogen atoms were refined with anisotropic thermal parameters, except for the aromatic carbons in **26a**. For **20**, non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were located and refined isotropically, except for those of the Cp ring and the methyl group which were treated as idealized contributions (dCH = 0.960 Å). For **20** and **26a**, the aromatic rings were treated as rigid hexagonal bodies (dCC = 1.395 Å). For **21**, an empirical isotropic extinction parameter was refined [χ = 0.001 18(16)]. The method used is similar to that described in *Crystallographic Computing* (Ahm, F. R., Ed.; Munksgaard: Copenhagen, 1970) except for the exclusion of polarization factors.

All software and the sources of the scattering factors are contained in either the SHELXTL (5.1) (**10a**, **17**, **20**, **24**, **25**) or the SHELXTL PLUS (4.2) (**21**, **26a**) program libraries (G. Sheldrick, Siemens XRD, Madison, WI).

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Supplementary Material Available: Figure A, an ORTEP drawing of **23**, and tables of atomic coordinates and isotropic parameters, anisotropic thermal parameters, bond lengths, bond angles, and hydrogen-atom coordinates for **10**, **17**, **20**, **21**, **24**, **25**, and **26a** (44 pages). Ordering information is given on any current masthead page.

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