Regioselective Electrophilic Substitution and Addition Reactions at an N-Coordinated Pyrrolyl Ligand in $(PMe_2Ph)_3Cl_2Re(NC_4H_4)$

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The reaction of excess pyrrolyllithium with *mer*-$(PMe_2Ph)_3ReCl_3$ leads to the formation of the air-stable product *mer*-$(PMe_2Ph)_3Cl_2Re(NC_4H_4)$ (**1**), which has been characterized by spectroscopic techniques and by an X-ray diffraction study. Complex **1** reacts with electrophiles to form new Re(III) complexes with regioselectively substituted pyrrolyl ligands. For example, reaction with 1 equiv of *N*-chlorosuccinimide forms the complex with a 3-chloropyrrolyl ligand, while reaction with excess reagent produces the 3,4-dichloropyrrolyl and 2,3,4-trichloropyrrolyl complexes. The regiochemistry of the reactions has been established from the ^1H NMR data, and the structure of the dibrominated product $(PMe_2Ph)_3Cl_2Re(3,4\text{-}NC_4H_2Br_2)$ (**5**) has been confirmed by X-ray diffraction. Reaction of **1** with methyl triflate produces after workup $(PMe_2Ph)_3Cl_2Re(3\text{-}NC_4H_3Me)$ (**6**), and further reaction of **6** with methyl triflate yields $(PMe_2Ph)_3Cl_2Re(3,4\text{-}NC_4H_2(Me)_2)$ (**7**). In contrast, triflic acid protonates the pyrrolyl ligand of **1** at the α-carbon to form $[(PMe_2Ph)_3Cl_2Re(NC_4H_5)]OTf$ (**8**), which has been isolated and identified by an X-ray diffraction study. The Michael addition of dimethyl acetylenedicarboxylate to the *β*-carbon of the pyrrolyl ligand in **1** has also been characterized. Methods for the removal of the substituted pyrrolyl ligands from the rhenium center are described.

Introduction

The pyrrole ring is incorporated into many biologically active molecules,[1] and various synthetic methods for the substitution and derivatization of the heterocycle have been studied. Electrophilic substitution reactions on the *π*-electron-rich pyrrole molecule usually occur at the α-positions of the ring.[2] However, several methods have been developed for enhancing and controlling an alternate regioselectivity in the reactions of pyrrole with electrophiles. For example, the use of *N*-(phenylsulfonyl)pyrrole in electrophilic substitution reactions has led to the selective substitution at the *β*-position of the ring for certain reagents.[3] The change in selectivity has been attributed to an electronic effect of the electron-withdrawing sulfonyl group. *N*-(triisopropylsilyl)pyrrole has also been developed as a reagent that promotes electrophilic substitution and metalation reactions of the ring at the *β*-position, because of the large steric bulk of the N-substituent.[4] After substitution by certain electrophiles, removal of the triisopropylsilyl group by Bu_4NF is facile, providing an efficient route to selected 3- and 3,4-substituted pyrroles.

The activation of pyrrole toward regioselective electrophilic attack has also been achieved by its interaction with transition-metal systems. For example, unusual activation of pyrrole has been characterized for the η^2-bonding mode of the ring to osmium(II) in $[(NH_3)_5Os(\eta^2\text{-pyrrole})]^{2+}$.[5] The η^2 coordination disrupts the delocalization of *π* electrons in the pyrrole ligand and induces enamine character for the heterocycle. The back-bonding ability of the osmium center enhances the electron-rich character of the ring, and regioselective electrophilic substitution at the 3-position of the pyrrole has been observed for a wide range of electrophiles. Many synthetic elaborations on this reactivity have been developed.[6]

Examples of transition-metal systems with a sterically hindered N-substituent are the pyrrolylimido

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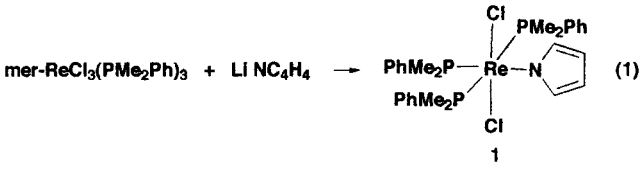
complexes of the formula $[C_4H_4N{=}NM(dppe)_2F]^+$ (M = Mo, W), which were derived from the corresponding dinitrogen complexes.[7] The phenyl groups of the diphosphine ligands created a steric pocket which prevented the electrophilic attack at the α-carbons of the pyrrolylimido ligand, and selective *β*-substitution was observed with a range of strong electrophiles. Further reaction of the substituted complex with hydride reagents in methanol produced a combination of substituted pyrroles and *N*-aminopyrroles.

In the complex $CpRe(PPh_3)(NO)(NC_4H_4)$, the *σ*-N-coordinated pyrrolyl ligand was initially protonated by strong acid at the α-carbon, but this derivative underwent an isomerization to form products containing a 2-C-coordinated ring protonated at the 2′- or 3-position.[8] Reactions of the parent rhenium pyrrolyl complex with other electrophiles were not reported, and in general the reactivity of *σ*-coordinated pyrrolyl ligands in metal complexes has not been well-studied. The use of a metal complex as an N-substituent of pyrrole has the potential for providing not only a steric influence but also an electronic control of the reactivity at the pyrrolyl ring, and this control may be varied as the redox state and auxiliary ligands of the metal complex are varied. To extend the chemistry of *σ*-coordinated pyrrolyl ligands, we have synthesized a new rhenium(III) N-bonded pyrrolyl complex of the formula $(PMe_2Ph)_3Cl_2Re(NC_4H_4)$ (**1**). We report here a study of the structure and reactivity of this complex, which has proven to be a versatile reagent for the activation of pyrrole to regioselective reactions with electrophiles.

Results and Discussion

Synthesis of $(PMe_2Ph)_3Cl_2Re(NC_4H_4)$ (1). The reaction of $(PMe_2Ph)_3ReCl_3$ with excess pyrrolyllithium proceeded in diethyl ether at room temperature to form the product $(PMe_2Ph)_3Cl_2Re(NC_4H_4)$ (**1**), which was isolated in 94% yield as a brown crystalline solid after hydrolysis of the excess lithium reagent (eq 1). The



1

formulation of **1** was confirmed by elemental analysis and by the electrospray mass spectrum, which showed a parent ion centered at *m*/*z* 738. The effective magnetic moment for **1** was found to be 1.9 μ_B at 300 K. Similar magnetic moments have been reported previously for the starting Re complex and for related octahedral d^4 Re(III) and Os(IV) complexes.[9,10] The moments have been explained on the basis of a second-order paramagnetism of the octahedral d^4 metal centers.[11] The ^1H NMR spectra for these complexes show resonances with narrow line widths and paramagnetic shifts.[10−14]

In the ^1H NMR spectrum of **1**, two methyl resonances are observed for inequivalent sets of dimethylphenylphosphine ligands at 1.38 and −3.65 ppm in a ratio of 12:6. Phosphorus coupling is not observed, and the resonances are sharp singlets. Two doublets for the ortho hydrogens and four triplets (meta and para hydrogens) are also observed for the phenyl rings in the two types of phosphine ligands. These multiplets occur in the range of 14−8 ppm (see assignments in Table 1). Two additional singlets which are integrated for two hydrogens each are observed at 10.56 and −2.53 ppm and are assigned to the coordinated pyrrolyl ligand. The upfield resonance is assigned to the α-hydrogens of the ring, which are in closest proximity to the rhenium ion, and the downfield resonance is assigned to the *β*-hydrogens. These assignments are supported by comparisons with spectra of substituted pyrrolyl derivatives of **1**, which are described below. In previous NMR studies of Tc(III) and Re(III) pyridine complexes,[10,15] the ortho and para protons of the ring have shown upfield shifts, while the meta protons are shifted downfield. However, this pattern of alternating upfield and downfield shifts was not consistently observed in the Re(III) derivatives with the five-membered imidazole ligand.[10]

In the ^{13}C NMR spectrum of **1**, weak resonances are observed between 45 and 145 ppm. Because the paramagnetic nature of the complex gives unusual chemical shifts, the carbon resonances were assigned by two-dimensional $^1H-^{13}C$ correlation techniques. Using a heteronuclear multiple quantum coherence (HMQC) experiment, we were able to correlate heteronuclei while detecting high-sensitivity protons. Singlets at 49.5 and 86.2 ppm in the ^{13}C spectrum were found to correspond to the α- and *β*-hydrogens in the pyrrolyl ligand, respectively. Broadened singlets at 93.3 and 72.6 ppm in the carbon spectrum were assigned to the methyl groups in the phosphine ligands that are trans and cis to the pyrrolyl ligand, respectively. The resonances for the phenyl groups in the phosphine ligands have also been assigned, and data are included in Table 1. Complex **1** is stable toward air and moisture and can be stored on the benchtop without decomposition. The cyclic voltammogram of **1** in 0.1 M n-Bu_4NPF_6/acetonitrile solution at a Pt electrode showed a quasi-reversible oxidation at +0.016 V vs Fc (ΔE = 80 mV, $i_{p,a}/i_{p,c}$ = 1.6) and a reversible reduction at −1.42 V (ΔE = 76 mV, $i_{p,a}/i_{p,c}$ = 1). These electron transfers are likely to correspond to the Re(III)/Re(IV) and Re(III)/Re(II) couples, respectively.

In an earlier metathesis reaction of $(PMe_2Ph)_3ReCl_3$ with excess PhLi under conditions similar to those employed here, all the chloride ligands were substituted and the five-coordinate product $(PMe_2Ph)_2RePh_3$ was formed.[16] However, using the present solvent and temperature conditions, we were not able to identify prod-

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Table 1. ^{1}H and ^{13}C NMR Data for $(PMe_2Ph)_3Cl_2Re-L$[a]

	pyrrole						PPh					
	α		β		PMe		unique		trans		other	
compd (L)	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
1	−2.53	49.47	10.56	86.20	−3.65 (6H)	93.32	8.17 t, *m*	133.40	8.95 t, *m*	136.10		
(C_4H_4N)					1.38 (12H)	72.61	10.14 t, *p*	121.75	10.02 t, *p*	124.58		
							9.98 d, *o*	133.22	13.67 d, *o*	140.26		
2 (3-Cl-pyr)	−2.70	49.54	9.45	88.32	−3.51 (6H)	98.75	8.21 t, *m*	133.66	8.87 t, *m*	136.25		
	−1.46	58.62			1.07 (6H)	72.38	10.24 t, *p*	121.67	10.06 t, *p*	124.26		
					1.14 (6H)	72.38	10.19 d, *o*	133.72	13.48 d, *o*	140.26		
3 (3,4-Cl_2-pyr)	−1.86	51.71			−3.43 (6H)	104.64	8.23 t, *m*	134.07	8.78 t, *m*	136.18		
					0.74 (12H)	81.22	10.41 t, *p*	121.43	10.14 t, *p*	124.26		
							10.46 d, *o*	136.95	13.32 d, *o*	139.83		
4 (2,3,4-Cl_3-pyr)	−6.49				−5.03 (6H)		8.45 t, *m*		8.85 t, *m*			
					0.71 (6H)		10.94 t, *p*		10.30 t, *p*			
					0.97 (6H)		12.49 d, *o*		13.89 d, *o*			
(3-Br-pyr)	−2.68		9.75		−3.57 (6H)		8.16 t, *m*		8.81 t, *m*			
	−1.40				1.00 (6H)		10.16 d, *o*		10.02 t, *p*			
					1.03 (6H)		10.22 t, *p*		13.42 d, *o*			
(2,3,4-Br_3-pyr)	−6.88	196.86			−5.04 (6H)	14.67	8.50 t, *m*	134.94	8.82 t, *m*	137.25		
					0.88 (6H)	78.20	11.00 t, *p*	121.32	10.28 t, *p*	124.56		
					0.93 (6H)	75.09	12.69 d *o*	137.95	13.92 d, *o*	144.38		
5 (3,4-Br_2-pyr)	−1.48	63.29			−3.41 (6H)	105.30	8.26 t, *m*	134.95	8.79 t, *m*	136.78		
					0.73 (12H)	76.53	10.47 t, *p*	122.19	10.18 t, *p*	124.81		
							10.53 d, *o*	135.12	13.34 d, *o*	140.48		
6 (3-Me-pyr)	−3.24	50.95	8.22	94.30	−3.78 (6H)	94.52	8.07 t, *m*	133.88	8.93 t, *m*	136.60	10.55	16.98
	−3.37	54.54			1.42 (12H)	73.50	9.63 d, *o*	133.40	10.00 t, *p*	125.25	(Me)	
						76.48	9.95 t, *p*	122.25	13.72 d, *o*	140.25		
7 (3,4-Me_2-pyr)	−4.11 (2H)	41.88			−3.96 (6H)	96.96	7.97 t, *m*	133.48	8.93 t, *m*	136.00	11.98	4.81
					1.47 (12H)	77.81	9.77 t, *p*	122.35	9.97 t, *p*	125.09	(6H,	
							9.19 d, *o*	133.06	13.80 d, *o*	140.18	2 Me)	
8 ($C_4H_5N^+$)	0.65 (2H)	216.15	10.74 d (1H)	106.46	−2.26 (6H)	124.96	8.65 t, *m*	138.06	8.91 t, *m*	138.49		
	6.05 (1H)	223.53	23.30 d (1H)	105.30	−1.70 (6H)	61.99	11.49 t, *p*	122.28	11.21 t, *p*	122.75		
					−0.21 (6H)	131.49	12.25 d, *o*	140.89	13.33 d, *o*	135.49		
9 (3-C(C-O_2Me)-CH(C-O_2Me))	−1.11	42.30	12.29	83.90	−3.46 (6H)	100.82	8.22 t, *m*	134.62	8.79 t, *m*	136.81	6.53 (vinyl H)	114.81
	−1.21	24.34			0.81 (6H)	74.54	10.41 t, *p*	122.01	10.01 t, *p*	124.70	2.96 (CO_2-Me)	51.11
					0.93 (6H)	71.77	10.44 d, *o*	135.09	13.43 d, *o*	140.25	4.20 (CO_2-Me)	51.30

[a] Spectra were recorded in $CDCl_3$, except for **8**, which was recorded in CD_3CN. Resonances of quaternary carbons have not been assigned.

ucts containing more than one pyrrolyl ligand, even in reactions with a 9−10-fold excess of pyrrolyllithium. Other examples of Re(III) derivatives with amide ligands are quite rare, but complexes with an anilide ligand with the formulas $[(PMe_3)_4Re(NHPh)(I)]I$ and $[(PMe_3)_4Re(NHPh)(H)_2]$ have been reported previously.[17,18]

X-ray Diffraction Study of 1. Single crystals of **1** were grown from an ether/hexane solution and were characterized by an X-ray diffraction study. Two independent molecules were identified in the unit cell, and the Ortep plots for each of the structures are shown in Figure 1. Selected bond distances and angles are given in Table 2. The complex is an octahedral derivative with a meridional arrangement of phosphine ligands and with trans chloride ligands. The pyrrolyl ring is trans to the unique phosphine, and the plane of the ring is aligned with the Cl−Re−Cl vector. In one conformer the phenyl rings in both trans phosphine ligands are oriented away from the pyrrolyl ligand, while in the second conformer, the phenyl ring of one phosphine is directed toward and is roughly parallel with the pyrrolyl ligand. The trans phosphine ligands, P1 and P2, are displaced slightly away from the central phosphine and toward the pyrrolyl ring, and this results in a P1−Re−P2 angle of 166.17(6)°. Other angles about the rhenium ion are closer to the expected octahedral values.

Related octahedral Re(III) complexes with nitrogen donor ligands which have been structurally characterized[19−22] include the nitrile complex $(PPh_3)_2Cl_3Re(NCMe)$,[19] heterocyclic derivatives $(PPh_3)Cl_3ReL_2$ (where L = pyridine, picoline or imidazole),[10a] and a complex containing both ammonia and a protonated azo ligand, $[(PMe_2Ph)_2Cl_2Re(NH_3)(N{=}N(H)Ph)]Br$.[20] The Re−N distances reported for these derivatives were 2.05(3) Å for the nitrile ligand, 2.178(12) Å for the pyridine ligand, and 2.200(13) Å for the ammonia ligand, each trans to a chloride. These distances appear to define a typical range for a single Re(III)−N bond for neutral ligands.

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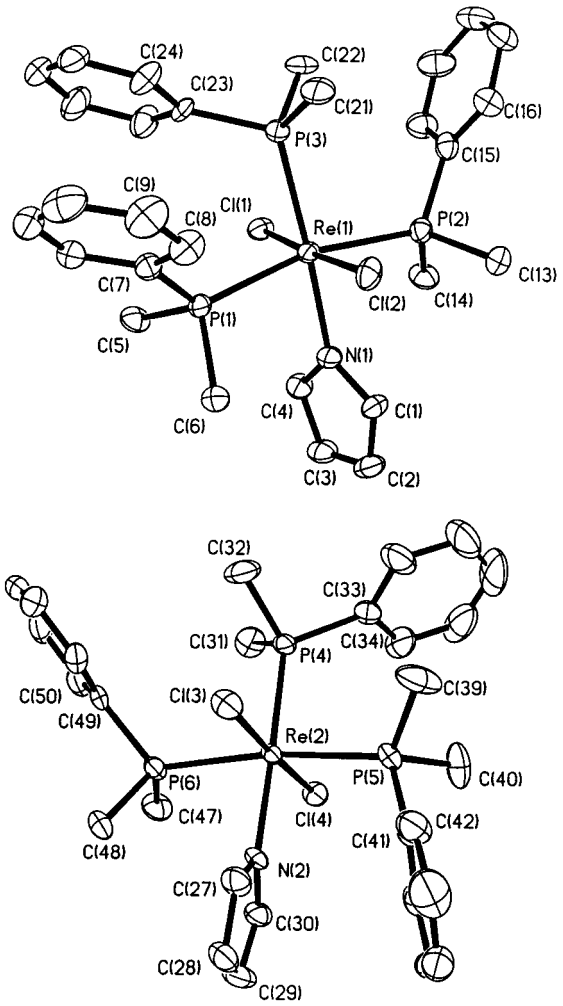


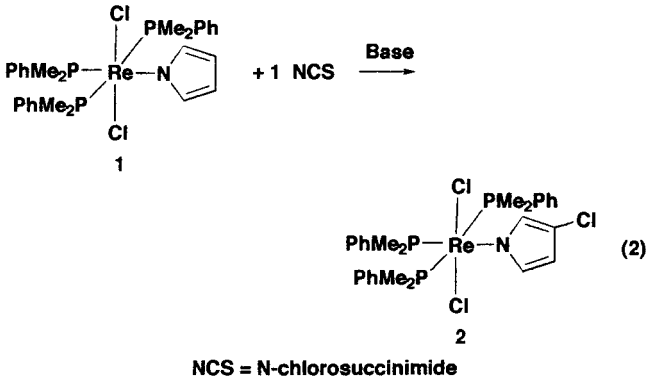
Figure 1. Perspective drawing and numbering scheme for conformers of $(PMe_2Ph)_3Cl_2Re(NC_4H_4)$ (**1**).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $(PMe_2Ph)_3Cl_2Re(NC_4H_4)$ (1)

Bond Lengths			
Re(1)−N(1)	2.171(6)	Re(2)−N(2)	2.168(5)
Re(1)−Cl(1)	2.3546(16)	Re(2)−Cl(3)	2.3406(16)
Re(1)−Cl(2)	2.3511(16)	Re(2)−Cl(4)	2.3551(16)
Re(1)−P(1)	2.4656(18)	Re(2)−P(4)	2.4323(17)
Re(1)−P(2)	2.4659(18)	Re(2)−P(5)	2.4608(18)
Re(1)−P(3)	2.4383(18)	Re(2)−P(6)	2.4677(18)
N(1)−C(1)	1.385(8)	N(2)−C(29)	1.360(9)
N(1)−C(4)	1.376(9)	N(2)−C(32)	1.373(8)
C(1)−C(2)	1.392(10)	C(29)−C(30)	1.385(10)
C(2)−C(3)	1.401(10)	C(30)−C(31)	1.399(12)
C(3)−C(4)	1.383(10)	C(31)−C(32)	1.387(10)
Bond Angles			
N(1)−Re(1)−P(1)	83.75(16)	N(2)−Re(2)−P(6)	82.91(15)
N(1)−Re(1)−P(2)	82.70(16)	N(2)−Re(2)−P(5)	87.63 (15)
N(1)−Re(1)−P(3)	175.98(15)	N(2)−Re(2)−P(4)	175.65(14)
P(1)−Re(1)−P(2)	166.17(6)	P(5)−Re(2)−P(6)	170.19(6)
Cl(1)−Re(1)−Cl(2)	176.53(6)	Cl(3)−Re(2)−Cl(4)	177.36(6)
Re(1)−N(1)−C(1)	127.4(5)	Re(2)−N(2)−C(27)	126.5(5)
Re(1)−N(1)−C(4)	126.4(4)	Re(2)−N(2)−C(30)	126.2(4)
C(1)−N(1)−C(4)	106.3(6)	C(27)−N(2)−C(30)	107.1(6)

In contrast, the protonated azo ligand in the above complex, for which multiple Re−N bond character was proposed, had a Re−N distance of 1.750(12) Å. The mean Re−N bond distance for the conformers of **1** of 2.170(6) Å appears to be consistent with a single-bond distance of an anionic ligand, and suggests there is little multiple-bond character arising from π donation from the formal amide nitrogen of the pyrrolyl ring. This is consistent with the electron-rich character of the pyrrolyl ligand, which is reflected in its reactivity with electrophiles described below.

Reactions of 1 with Electrophiles. Halogenating Agents. The reactivity of the N-coordinated pyrrolyl ligand in **1** toward electrophilic reagents has been studied. The Re(III) −N bond has proven to be quite kinetically inert, and new Re complexes with substituted pyrrolyl ligands have been isolated and characterized. The $(PMe_2Ph)_3ReCl_2$ moiety coordinated to the pyrrolyl nitrogen provides a steric, and perhaps an electronic, influence which promotes electrophilic substitution at the β-carbons of the pyrrolyl ligand. For example, the reaction of **1** with 1−2 equiv of *N*-chlorosuccinimide in THF followed by hydrolysis with an aqueous sodium bicarbonate solution gave a single major product (88%). This was isolated after column chromatography and identified as a derivative with a monochloro-substituted pyrrolyl ligand, $(PMe_2Ph)_3ReCl_2(3\text{-}NC_4H_3Cl)$ (**2**) (eq 2). The synthesis of the 3-chloro-



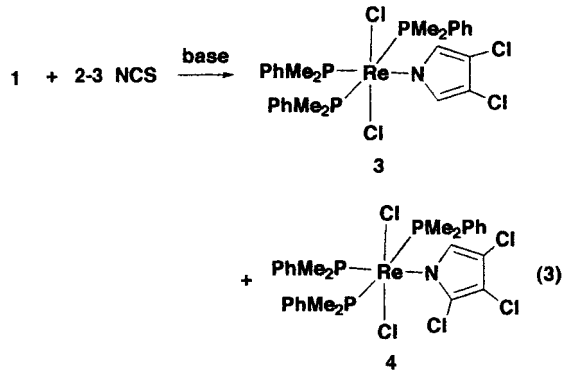
pyrrolyl ligand appeared to be quite regioselective. In contrast, the reaction of *N*-chlorosuccinimide with previously studied N-substituted pyrrole systems resulted in the formation of primarily α-substituted products.[4b,7]

The electrospray mass spectrum of **2** showed a parent ion at *m*/*z* 772 and fragments at *m*/*z* 666 and 628 which corresponded to the stepwise loss of chloropyrrolyl and dimethylphenylphosphine ligands. In the ^{1}H NMR spectrum of **2**, three singlets for the pyrrolyl hydrogens were observed at −2.70, −1.46, and 9.45 ppm. The two upfield resonances are assigned to inequivalent α-hydrogens, and the chloro substituent is assigned to a β-position on the ring. (These chemical shift assignments are consistent with those of a related structure identified by an X-ray diffraction study, which is discussed below.) In the HMQC spectrum the α-hydrogens (−2.70 and −1.46 ppm) on the pyrrolyl ligand are correlated with carbon resonances at 49.54 and 58.62 ppm, respectively, while the unsubstituted β-carbon is assigned to a resonance at 88.32 ppm. Other ^{13}C data are given in Table 1.

Three phosphine methyl singlets (6 H each) were observed in the ^{1}H NMR spectrum of **2** at −3.51, 1.07, and 1.14 ppm, suggesting a restricted rotation about the Re−N bond of the pyrrolyl ligand. Although the trans phosphine ligands are related by a plane of symmetry, the two methyls on each trans phosphine ligand are diastereotopic and are resolved with slow rotation of the monosubstituted ligand. A high-temperature NMR study

of **2** showed coalescence of the two methyl singlets near 1 ppm at 52 °C.[23] The restricted rotation appears to arise primarily from steric effects rather than from multiple-bond character in the Re−N bond.

The reaction of **1** with 2−3 equiv of *N*-chlorosuccinimide gave a mixture of products which could be partially separated by column chromatography and which were identified as the derivatives with dichloro- and trichloro-substituted pyrrolyl ligands, $(PMe_2Ph)_3ReCl_2(3,4\text{-}NC_4H_2Cl_2)$ (**3**) and $(PMe_2Ph)_3ReCl_2(2,3,4\text{-}NC_4HCl_3)$ (**4**) (eq 3). The relative yields of these products



varied depending on reaction conditions (see Experimental Section). When 3 equiv of the chlorinating reagent was used, **4** was the major product (52%), but some displacement of the pyrrolyl ligand was also observed to form $(PMe_2Ph)_3ReCl_3$. No evidence was observed in the NMR spectra for the formation of the tetrachloropyrrole product.

The electrospray mass spectra showed the expected parent ions for **3** and **4,** and the formulation of **4** was also supported by elemental analyses. The ^{1}H NMR spectrum of **3** indicates that the complex maintains planes of symmetry along the Cl−Re−Cl axis as well as along the P1−Re−P2 axis. Two phosphine methyl signals (12:6 ratio) are observed at 0.74 and −3.43 ppm, and a single resonance for the equivalent pyrrolyl hydrogens is present at −1.86 ppm. This upfield resonance is assigned to the α-hydrogens on the ring, and **3** is formulated as the 3,4-dichloropyrrolyl derivative. This assignment is confirmed by an X-ray diffraction study of the analogous dibromopyrrolyl derivative, which is discussed below.

The spectroscopic data and elemental analyses for **4** are consistent with the formulation $(PMe_2Ph)_3ReCl_2(2,3,4\text{-}NC_4HCl_3)$. In the ^{1}H NMR spectrum a resonance for a single pyrrolyl α-hydrogen is observed in the spectrum at −6.49 ppm. Three singlets for inequivalent phosphine methyls are observed, and, as was discussed for the monochloropyrrolyl derivative, this indicates a restricted rotation about the Re−N bond. Coalescence of the two Me signals on the trans phosphine ligands was not observed in NMR spectra in d_8-toluene at temperatures up to 100 °C. There appears to be a significant activation energy for rotation of the bulky trisubstituted ligand.

The reactions of **1** with *N*-bromosuccinimide in varying ratios were also carried out. The electrophilic addition products were deprotonated with aqueous sodium bicarbonate solution and then separated by column chromatography. Derivatives with 3-bromo-, 3,4-dibromo-, and 2,3,4-tribromo-substituted pyrrolyl ligands were isolated and characterized by spectroscopic data and in some cases by elemental analyses. The electrospray mass spectra show the expected parent ions for the mono and disubstituted products, and the NMR data for all three products are very similar to those described for the chloro analogues.

(23) In the low-temperature spectra of these rhenium complexes, we observed that the chemical shift difference between the two trans Me resonances continued to increase and a limiting value for $\delta\nu$ was not observed. As a result, values for $\Delta G^{\ddagger}$ were not calculated.

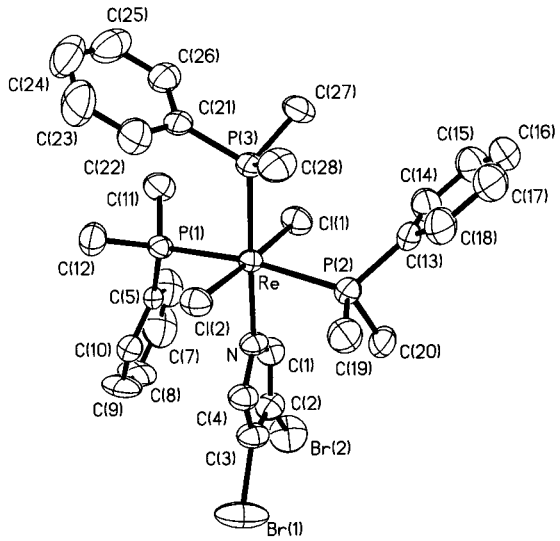


Figure 2. Perspective drawing and numbering scheme for $(PMe_2Ph)_3Cl_2Re(3,4\text{-}NC_4H_2Br_2)$ (**5**).

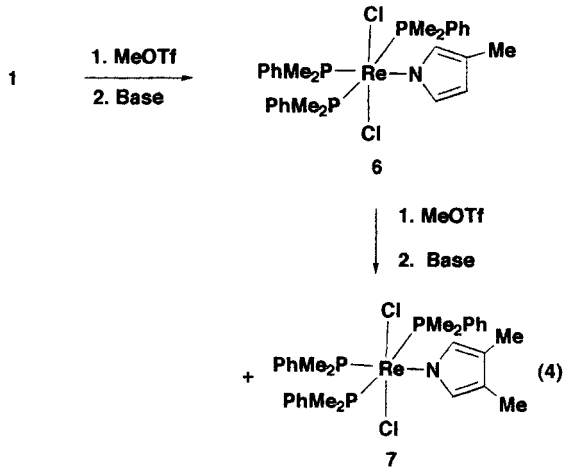
Table 3. Selected Bond Lengths (Å) and Angles (deg) for $(PMe_2Ph)_3Cl_2Re(NC_4H_2Br_2)$ (5)

Bond Lengths			
Re−N	2.170(4)	N−C(1)	1.367(6)
Re−Cl(1)	2.3381(12)	N−C(4)	1.370(6)
Re−Cl(2)	2.3524(11)	C(1)−C(2)	1.375(7)
Re−P(1)	2.4662(12)	C(2)−C(3)	1.377(7)
Re−P(2)	2.4734(12)	C(3)−C(4)	1.371(7)
Re−P(3)	2.4338(12)	C(2)−Br(2)	1.867(5)
C(3)−Br(1)	1.892(5)		
Bond Angles			
N−Re−P(1)	86.75(11)	Cl(1)−Re−Cl(2)	177.75(4)
N−Re−P(2)	83.45(11)	Re−N−C(1)	126.1(3)
N−Re−P(3)	176.04(10)	Re−N−C(4)	127.3(3)
P(1)−Re−P(2)	170.06(4)	C(1)−N−C(4)	106.4(4)
N−Re−Cl(1)	90.60(11)	N−Re−Cl (2)	90.85(11)

X-ray Diffraction Study of $(PMe_2Ph)_3ReCl_2(3,4\text{-}NC_4H_2Br_2)$ (5). To confirm the NMR assignments for the pyrrolyl hydrogens in these halogenated derivatives, an X-ray diffraction study was carried out. Single crystals of $(PMe_2Ph)_3ReCl_2(3,4\text{-}NC_4H_2Br_2)$ **(5)** were obtained by slow evaporation of an ether/hexane solution. The structure determined by X-ray diffraction is shown in Figure 2. Selected bond distances and angles are shown in Table 3. The structure shows that the rhenium complex maintains an octahedral geometry with the same stereochemistry of the ligands as observed in the parent pyrrolyl complex **1**. The structure also confirms that the bromo substitution of the pyrrolyl ligand occurs at the 3- and 4-positions of the ring. A disorder was observed in the bromine positions with bromines observed at the 2-, 3-, and 4-positions of the ring. This was modeled as partial contamination by the

triply brominated product, which was observed in the NMR spectrum of the crystallized dibromo product in trace amounts (<5%). In the final structure solution the tribromo derivative had a site occupancy of 0.033(2). All of the rhenium ligand distances in **5** as well as the C−N and C−C distances within the pyrrolyl ligand are very similar to those of **1**. The P1−Re−P2 angle in this complex was 170.06(4)°, slightly larger than the corresponding angle of **1**.

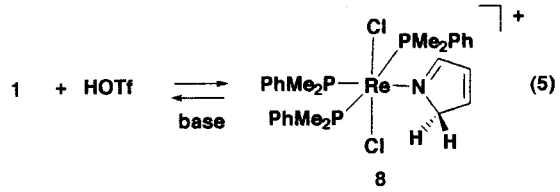
Reactions of 1 with Carbon Electrophiles. The reactions of **1** with alkylating agents have also led to the formation of new substituted pyrrole products. For example, reaction with methyl triflate followed by deprotonation with base resulted in the formation of a complex with a β-substituted methylpyrrolyl ligand, $(PMe_2Ph)_3ReCl_2(3\text{-}NC_4H_3Me)$ (**6**), which was isolated in pure form by column chromatography (eq 4). The ^1H



NMR spectrum for this product shows the characteristic pattern of one low-field (8.22 ppm) and two high-field (−3.24 and −3.37 ppm) resonances for the pyrrolyl hydrogens. A singlet at 10.55 ppm (3 H) is assigned to the methyl group on the pyrrole ring. In the room-temperature ^1H spectrum, only two phosphine methyl singlets are observed at δ 1.42 (12 H) and δ −3.78 (6 H), but the former resonance is broadened. In the low-temperature spectra of **6**, evidence for restricted rotation about the Re−N bond was observed with the splitting of the resonance at δ 1.42 into two singlets (T_c = 11 °C). The splitting ($\delta\nu$) for these signals continued to increase as the temperature was decreased to −60 °C, and a limiting value was not established. Other spectroscopic characterization data for **6** are included in the Experimental Section.

Complex **6** reacted readily with an additional 1 equiv of methyl triflate to form a complex with a 3,4-dimethylpyrrolyl ligand, $(PMe_2Ph)_3ReCl_2(3,4\text{-}NC_4H_2Me_2)$ (**7**), which was also isolated and characterized by spectroscopic data (see Experimental data). Further reactions to free the substituted pyrrole rings from the rhenium center can be achieved with certain acidic reagents and are described below. The alkylation of a β-carbon of the *N*-methylpyrrole ring with MeOTf has been accomplished previously with the Os−η^2-*N*-methylpyrrole complex,[5] but this system was not useful for the synthesis of the NH analogue or of the dialkylated rings. Other reagents designed to promote the electrophilic substitution of pyrrole in the β-positions have not been reported to react directly with carbocations. However, 3,4-dimethylpyrrole has been synthesized previously by the monolithiation of *i*-$Pr_3Si{-}NC_4H_2Br_2$ and its reaction with methyl iodide, followed by a second lithiation/alkylation step.[4c]

Reaction of 1 with Protic Acid. The reactions of **1** with electrophiles studied so far involved regioselective attack on the β-carbons of the heterocycle. We were interested in the regiochemistry displayed for the reaction of **1** with protic acid, since this is the least sterically demanding electrophile. Although **1** did not react with acetic acid, the reaction with triflic acid proceeded at room temperature to form a ring-protonated product which was isolated as a crystalline yellow solid. Both elemental analyses and FAB mass spectral data confirmed the formulation of the product as $[(PhMe_2P)_3Cl_2Re(NC_4H_5]OTf$ (**8**) (eq 5). The addition of sodium



carbonate to a solution of **8** resulted in deprotonation of the ligand and regeneration of the pyrrolyl complex **1**. The NMR spectrum of **8** in CD_3CN solution indicated that only one isomer was present over a period of 24−48 h, and within this time frame there was no evidence for a tautomerization of the ligand such as that reported previously for $[CpRe(NO)(PPh_3)(NC_4H_5)]^+$.[8]

The ^1H NMR spectrum of **8** in CD_2Cl_2 was invariant over a temperature range of −60 to +20 °C.[24] Two new doublets (each with intensity for 1 H) were observed at 23.30 and 10.74 ppm (J = 6.3 Hz), and additional singlets assigned to the protonated pyrrole ligand were observed at 6.05 (1 H) and 0.65 ppm (2 H). Three singlets for inequivalent phosphine methyls were also present, as well as the usual multiplets for the phenyl hydrogens. On the basis of the integration value of 2 for the upfield pyrrole resonance, the site of protonation was tentatively assigned to the α-position of the ring, and the two doublets were assigned to the β-protons. A similar coupling between β-hydrogens has been observed in the ^1H NMR spectrum of free pyrrole protonated at the α-position.[25] In the HMQC spectrum of **8**, the low-field proton doublets at 10.74 and 23.30 ppm were correlated with carbon resonances at 106.49 and 105.30 ppm, respectively, while the α-hydrogen resonance at 6.05 ppm was correlated with a carbon signal at 223.53 ppm. The ^{13}C resonance of the protonated α-carbon was also found to have a very large downfield shift of 216.15 ppm.

To confirm the site of the pyrrolyl ring protonation, single crystals of **8** were grown by vapor diffusion of diethyl ether into a concentrated CH_2Cl_2 solution of the

(24) The pattern of the spectrum did not change at lower temperatures, but changes in chemical shifts were observed and these were found to be proportional to temperature. Similar direct proportionalities have been observed for spectra of other octahedral Re(III) derivatives.

(25) Chiang, Y.; Whipple, E. B. *J. Am. Chem. Soc.* **1963**, *85*, 2763. Whipple, E. B.; Chiang, Y.; Hinman, R. L. *J. Am. Chem. Soc.* **1963**, *85*, 26.

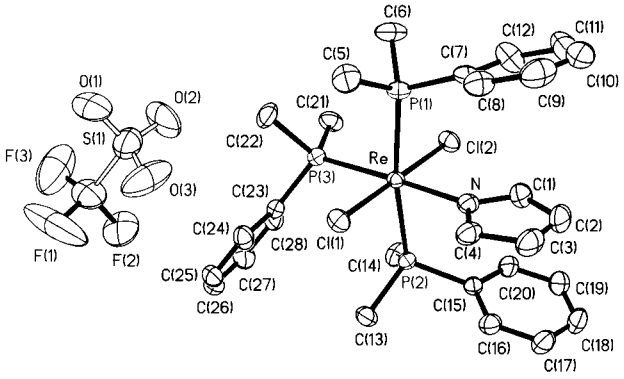


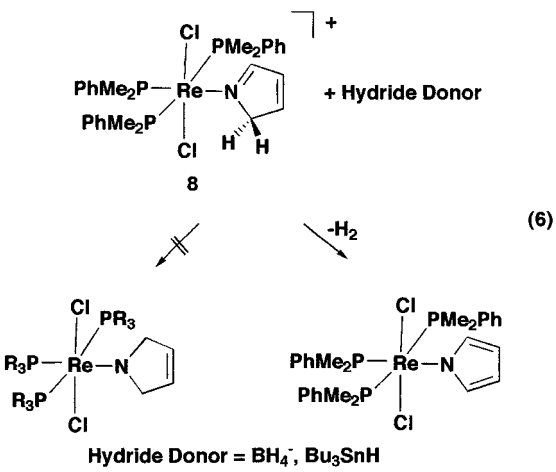
Figure 3. Perspective drawing and numbering scheme for $[(PMe_2Ph)_3Cl_2Re(NC_4H_5)]OTf$ (**8**).

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $[(PMe_2Ph)_3Cl_2Re(NC_4H_5)]OTf$ (8)

Bond Lengths			
Re−N	2.20(2)	N−C(1)	1.348(4)
Re−Cl(1)	2.3537(6)	N−C(4)	1.436(4)
Re−Cl(2)	2.33638(6)	C(1)−C(2)	1.465(5)
Re−P(1)	2.4847(7)	C(2)−C(3)	1.332(5)
Re−P(2)	2.4860(6)	C(3)−C(4)	1.475(4)
Re−P(3)	2.4435(7)		
Bond Angles			
N−Re−P(1)	87.26(6)	Cl(1)−Re−Cl(2)	179.21(2)
N(1)−Re−P(2)	87.36(6)	Re−N−C(1)	128.8(2)
N(1)−Re−P(3)	175.88(6)	Re−N−C(4)	125.17(19)
P(1)−Re−P(2)	171.27(2)	C(1)−N−C(4)	106.1(2)
N−Re−Cl(1)	88.85(6)	N−Re−Cl (2)	90.46(6)

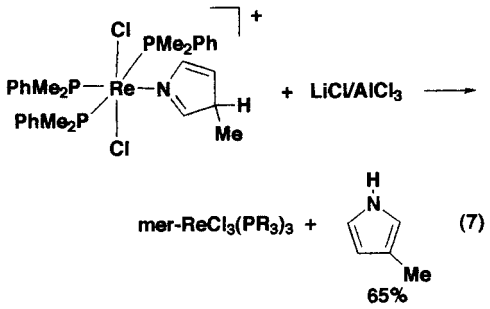
compound, and a structural study was carried out. The complex crystallized with eight formula units per unit cell in the orthorhombic space group *Pbca*. A perspective drawing of the cation is shown in Figure 3, and selected bond distances and angles are given in Table 4. The structure confirmed that the protonation occurs on an α-carbon (C4) of the pyrrolyl ligand. The N−C4 distance is 1.436(4) Å, while the N−C1 distance is 1.348(4) Å. Alternating C−C lengths in the ring are also observed with the C4−C3 distance of 1.475(4) Å, the C3−C2 distance of 1.332(5) Å, and the C2−C1 distance of 1.465-(5) Å. The ring retains its planar structure with the plane parallel to the Cl−Re−Cl vector. The Re−N bond distance for the protonated ligand is lengthened slightly relative to that of the pyrrolyl complex to a value of 2.201 Å, and the Re−P distances in **7** are found to be about 0.02 Å longer than those of the starting pyrrolyl derivative.

Although larger electrophiles preferentially attacked the 3- and 4-positions of the pyrrolyl ligand in **1**, the protonation product indicates that the coordinated ring retains significant electron density at the α-carbon atoms. The alternate regioselectivity for the larger electrophiles therefore appears to be driven primarily by steric factors. Several attempts were made to further reduce the ligand in **8** to an N-coordinated pyrrolinyl ring by the addition of $NaBH_4$ or other hydride donors. In a previous report, stepwise diastereoselective additions of electrophiles and nucleophiles to $\sigma(N)$-indole ligands in chiral complexes of rhenium have been carried out to form indoline derivatives.[26] However, in the reactions of **8** with $NaBH_4$ as well as with other nucleophilic reagents, the deprotonation of the ligand was observed, and **1** was regenerated in high yield (eq 6). Partial deprotonation of **8** was also observed in the



reaction with Bu_3SnH, while no reaction was observed when the nonbasic hydride donor Et_3SiH was used.

The addition of $HCl/AlCl_3$ to **1**, **6**, or **7** resulted in the dissociation of the pyrrole ligands and the quantitative formation of $(PMe_2Ph)_3ReCl_3$. When the reactions of **6** and **7** with excess $HCl/AlCl_3$ were monitored by NMR spectroscopy, the corresponding rhenium complexes with α-protonated pyrrolyl ligands were observed as the initial products, which underwent pyrrole ligand dissociation (see Experimental for NMR data). It was not necessary to use an isolated sample of **6** for the preparation of methylpyrrole. For example, **1** was reacted with MeOTf to form the cationic addition product. When this cation was stirred at room temperature with $LiCl/AlCl_3$ in acetonitrile solution, free 3-methylpyrrole was displaced (eq 7). The free pyrrole was vacuum-transferred and identified by NMR and mass spectroscopy.

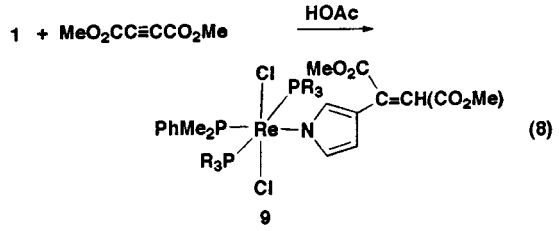


Michael Addition Reactions. Free pyrrole has been found to react with the activated alkyne dimethyl acetylenedicarboxylate (DMAD) to give several products that result either from Michael addition at the 2-position or from cycloaddition of one or two molecules of DMAD.[27] The η^2-pyrrole complex $[(NH_3)_5Os(\eta^2\text{-pyrrole})]^{2+}$ has been found to undergo Michael addition

(26) (a) Johnson, T. J.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1994**, *13*, 3182. For related stepwise additions of nucleophiles and then electrophiles to $\sigma(N)$-quinoline and $\sigma(N)$-isoquinoline complexes of Re, see: (b) Stark, G. A.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1994**, *13*, 4523. (c) Richter-Addo, G. B.; Knight, A. D.; Dewey, M. A.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 11863.

(27) (a) Kotsuki, H.; Mori, Y.; Nishizawa, H.; Ochi, M.; Matsuoka, K. *Heterocycles* **1982**, *19*, 1915. (b) Lee, C. K.; Hahn, C. S.; Noland, W. E. *J. Org. Chem.* **1978**, *43*, 3727. (c) Acheson, R. M.; Vernon, J. M. *J. Chem. Soc.* **1962**, 1148.

reactions at the 3-position of the ring,[5] but this type of reactivity has not been observed previously for N-bonded pyrrolyl complexes. The reaction of **1** with DMAD proceeds at room temperature in the presence of a catalytic amount of acetic acid to form the addition product $(PMe_2Ph)_3Cl_2Re(NC_4H_3C(CO_2Me)CH(CO_2Me))$ (**9**) (eq 8). After 3 days the NMR spectrum of the crude



reaction mixture indicated a mixture of **9** and **1** in a 85/15% ratio. The cycloaddition product was not identified in this reaction. After chromatography on a neutral alumina column the product ratio decreased to about 50/50, and significant amounts of **1** were recovered under these conditions. The factors that promoted the loss of the substituent were not studied further.

The product **9** has been isolated in pure form after column chromatography and recrystallization. The electrospray mass spectrum, which shows a parent ion at *m*/*e* 880, confirms the formulation of the addition product. Once again the ^{1}H NMR data indicate that the addition reaction occurs at the 3-position of the heterocycle. The resonance for the unique β-hydrogen of the ring is observed at 12.29 ppm, while the inequivalent α-hydrogens occur as singlets at −1.11 and −1.21 ppm. As is noted for other β-substituted ligands in this system, three singlets are observed for the methyls in the phosphine ligands. The methyls of the dicarboxylate groups occur as singlets at 2.96 and 4.20 ppm, and the vinyl hydrogen is assigned to a singlet at 6.53 ppm.

We were unable to isolate Michael addition products from reactions of **1** with other less activated reagents such as methyl propionate and dimethyl fumarate. Nor did **1** undergo a Diels−Alder reaction with malonic anhydride. These observations indicate that the η^1-pyrrole ligand in **1** is significantly less activated toward electrophilic attack than the η^2-ligand in $[(NH_3)_5Os(\eta^2$-pyrrole$)]^{2+}$, which reacted readily with all of the above reagents.[5] In general, the range of reactivity of the heterocycle in **1** is similar to that of free pyrrole, and the $(PMe_2Ph)_3Cl_2Re^{III}$ substituent on the pyrrole nitrogen appears to exert primarily a steric rather than an electronic effect on the ring. It will be interesting to determine to what extent a change in auxiliary ligands and/or in metal oxidation state might alter the electronic influence of the σ-metal complex on the pyrrolyl ligand, and further studies are in progress to address this question.

Experimental Section

General Procedures. Reactions were carried out under nitrogen using Schlenk-line and vacuum-line techniques. Dichloromethane and acetonitrile were distilled from CaH_2 prior to use. Tetrahydrofuran, toluene, and diethyl ether were distilled from sodium/benzophenone. ^{1}H NMR spectra were recorded at 300 and 400.13 MHz on Varian VXR-300 and Bruker AM-400 spectrometers, respectively. HMQC data were collected on a Varian Inova 500 MHz instrument. All chemical shifts are reported in ppm relative to tetramethylsilane. Mass spectra were obtained on a HB5989A mass spectrometer with ES ionization, on a VG Analytical 7070 EQ-HF mass spectrometer, or on a Finnigan MATR LCQ ion-trap mass spectrometer. Elemental analyses were performed by Desert Analytical Laboratory, Tucson, AZ. The complex $(PMe_2Ph)_3ReCl_3$ was prepared according to the literature procedure.[13,28] $KReO_4$ and PMe_2Ph were obtained from Strem Chemicals. Dimethyl acetylenedicarboxylate was obtained from Aldrich and vacuum-distilled prior to use.

Synthesis of *mer*-$(PMe_2Ph)_3Cl_2Re(NC_4H_4)$ (1). Diethyl ether (40 mL) was added to a flask containing *mer*-$(PMe_2Ph)_3ReCl_3$ (0.938 g, 1.33 mmol) and pyrrolyllithium (0.891 g, 8.03 mmol). The yellow solution immediately turned green and then slowly changed to brown. After the reaction mixture was stirred for 21 h at room remperature, the diethyl ether was removed in vacuo. Dichloromethane was then added to the reaction flask, and salts were extracted with a saturated aqueous solution of NaCl. The organic layer was dried over Na_2SO_4, filtered, and dried in vacuo to give a brown solid. Yield: 0.978 g (94.5%). The complex could be recrystallized from ether/hexanes or chloroform/hexanes solvent mixtures. Mp: 150−151 °C. See Table 1 for ^{1}H and ^{13}C NMR data. MS (ESI): *m*/*z* 738 (P^+); 671 ($P^+ - C_4H_4N$). Anal. Calcd for $C_{28}H_{37}Cl_2NP_3Re$: C, 45.59; H, 5.06; N, 1.90. Found: C, 45.58; H, 5.10; N, 2.20.

X-ray Diffraction Study of 1. A suitable crystal was selected and mounted with silicone grease into the 153 K N_2 cold stream of a Siemens SMART three-circle goniometer. Indexing was determined after collection of 3 sets of 20 0.3° (ω) scans. Least-squares refinement of final cell dimensions was performed using all reflections harvested during data collection. An arbitrary sphere of data was collected. Equivalent reflections were merged, and all data were corrected for Lorentz and polarization effects as well as for absorption. Friedel opposites were merged.

Structure solution by direct methods in the centrosymmetric space group $P\bar{1}$ revealed the complete non-hydrogen structure. All other hydrogens were placed at calculated positions and then refined using a riding model. Hydrogen thermal motion was modeled as isotropic; thermal parameters for hydrogen were calculated as 1.2 times the U_{eq} value for the parent atom.

The asymmetric unit contains two crystallographically independent molecules. The space group choice was verified using LePage's MISSYM algorithm as incorporated in Spek's Platon package.[29] No disorder is present. The largest peak in the final difference map is 5.13 e/Å^3, located 0.95 Å from Re(2). Details of data collection and refinement are given in Table 5.

Reactions of 1 With Halogenating Agents. Synthesis of $(PMe_2Ph)_3ReCl_2(3\text{-}NC_4H_3Cl)$ (2). Complex **1** (0.190 g, 0.257 mmol) and *N*-chlorosuccinimide (NCS; 0.0566 g, 0.424 mmol) were dissolved in 70 mL of tetrahydrofuran. The yellow solution was stirred for 20 h at room temperature. The tetrahydrofuran was removed, and the product was redissolved in dichloromethane and extracted with a saturated aqueous solution of $NaHCO_3$. The organic layer was dried over $MgSO_4$, filtered, and dried in vacuo. The ^{1}H NMR spectrum showed one major product in about 88% yield. The crude product mixture was dissolved in dichloromethane and loaded on an alumina/toluene chromatography column. A yellow fraction was eluted with dichloromethane. Evaporation of solvent gave the desired product, which could be recrystallized by vapor diffusion of hexanes into a concentrated dichoromethane solution. Mp: 167−169 °C. See Table 1 for ^{1}H and ^{13}C NMR data. MS (ESI): *m*/*z* 772 (P). Anal. Calcd for $C_{28}H_{37}Cl_3NP_3Re$: C, 43.49; H, 4.79; N, 1.81. Found: C, 43.40; H, 4.56; N, 1.73.

(28) Parshall, G. W. *Inorg. Synth.* **1977**, *17*, 110.
(29) Spek, A. L. PLATON, A Multipurpose Crystallographic Tool; Utrecht University: Utrecht, The Netherlands, 1995.

Table 5. Crystal Data for Compounds 1, 5, and 8

	1	5	8
formula	$C_{28}H_{37}Cl_2NP_3Re$	$C_{28}H_{35}Br_2Cl_2NP_3Re$	$C_{29}H_{38}Cl_2F_3NO_3P_3SRe$
fw	737.60	895.40	887.67
cryst syst	triclinic	monoclinic	orthorhombic
unit cell dimens			
a (Å)	13.5873(5)	12.0709(2)	21.6796(1)
b (Å)	14.9088(6)	20.6838(3)	14.3429(2)
c (Å)	15.2916(6)	14.0166(1)	23.2750(3)
α (deg)	83.5610(10)	90	90
β (deg)	86.5230(10)	104.7220(10)	90
γ (deg)	80.6980(10)	90	90
V (Å^3)	3034.8(2)	3384.66(8)	7237.32(14)
space group	$P\bar{1}$	$P2_1/c$	$Pbca$
Z	4	4	8
calcd density (g/cm^3)	1.614	1.757	1.629
λ(Mo Kα) (Å)	0.710 73	0.710 73	0.710 73
temp (K)	153(2)	297(2)	171(2)
scan type	ω scans	ω scans	ω scans
θ range (deg)	1.34−25.00	1.97−28.29	1.75−30.00
no. of unique rflns	10 382 (R(int) = 0.0312)	8110 (R(int) = 0.0435)	10 534 (R(int) = 0.0768)
no. of rflns obsd	8719	6239	8152
abs coeff (mm^{-1})	4.356	6.269	empirical from equivalents[d]
R^a	0.0583	0.0577	0.0283
$R_w{}^b$	0.1304	0.0915	0.0549
GOF[c]	1.039	1.009	1.047
largest peak in final diff map (e/Å^3)	5.133 and −2.528	1.201 and −1.994	1.002 and −0.776

[a] $R = \mathrm{R1} = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = \mathrm{wR2} = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. [c] $\mathrm{GOF} = S = [\sum[w(F_o^2 - F_c^2)^2]/(M - N)]^{1/2}$ where M is the number of reflections and N is the number of parameters refined. [d] Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *A51*, 33−38.

Synthesis of $(PMe_2Ph)_3ReCl_2(3,4\text{-}NC_4H_2Cl_2)$ (3). Complex **1** (0.062 g, 0.083 mmol) and NCS (0.025 g, 0.19 mmol) were dissolved in 50 mL of tetrahydrofuran. The solution was stirred at room temperature for 19.5 h before the solvent was evaporated. The residue was redissolved in dichloromethane, extracted with saturated aqueous $NaHCO_3$, dried over $MgSO_4$, filtered over Celite, and dried in vacuo. The ^{1}H NMR spectrum of the crude reaction mixture showed that complexes **3**, **4**, and $(PMe_2Ph)_3ReCl_3$ were present in approximately 27%, 35%, and 37% yield, respectively. The mixture was eluted on a silica gel column with dichloromethane. The second fraction was enriched in **3** but still contaminated with **4**. See Table 1 for ^{1}H and ^{13}C NMR data for **3**. MS (ESI): *m*/*z* 807 (M); 671 (M − Cl_2pyrr).

Synthesis of $(PMe_2Ph)_3ReCl_2(2,3,4\text{-}NC_4HCl_3)$ (4). Complex **1** (0.089 g, 0.121 mmol) and NCS (0.0470 g, 0.352 mmol) were dissolved in 20 mL of tetrahydrofuran. The solution was stirred at room temperature for appoximately 1 day. After a similar workup procedure, the ^{1}H NMR spectrum of the crude product mixture showed approximately 52% **4**, 27% $(PMe_2Ph)_3ReCl_3$, and 21% **3**. The brown residue was dissolved in dichoromethane and the solution eluted on a silica gel column. Complex **4** was eluted with dichloromethane and isolated in the first yellow fraction. The product was recrystallized by vapor diffusion of hexanes into a dichloromethane solution of **4**. See Table 1 for ^{1}H NMR data. MS (ESI): *m*/*z* 841 (P); 807 (P − Cl); 671 (P − Cl_3pyrr). Anal. Calcd for $C_{28}H_{34}Cl_5NP_3Re$: C, 39.99; H, 4.08; N, 1.67. Found: C, 40.02, H, 4.34; N, 1.69.

Synthesis of $(PMe_2Ph)_3ReCl_2(3,4\text{-}NC_4H_2Br_2)$ (5) and Other Brominated Products. Complex **1** (0.233 g, 0.316 mmol) and *N*-bromosuccinimide (NBS) (0.119 g, 0.668 mmol) were combined in 20 mL of tetrahydrofuran, and the solution was stirred at room temperature. After 1 day the reaction was quenched with a saturated aqueous solution of $NaHCO_3$ (30 mL) and extracted with CH_2Cl_2 (40 mL). The extract was washed with $NaHCO_3$ solution, dried over $MgSO_4$, and evaporated to give a brown solid. This solid was eluted on a silica gel column with CH_2Cl_2 to give an orange-brown band which was evaporated and identified as $(PMe_2Ph)_3ReCl_2(3,4\text{-}NC_4H_2Br_2)$ (**5**). Yield: 0.012 g, 19%. Mp: 147−150 °C. See Table 1 for ^{1}H NMR data. MS (ESI): *m*/*z* 896 (P^+); 757 (P − PMe_2Ph); 671 (P − PMe_2Ph − Br_2pyrr); 619 (P − 2 PMe_2Ph). Anal. Calcd for $C_{28}H_{35}Br_2Cl_2NP_3Re$: C, 37.67; H, 3.92; N, 1.56. Found: C, 37.49; H, 3.69; N, 1.27.

Further elution of the silica gel column with dichloromethane gave a second yellow-green band that was then eluted on a neutral alumina column with CH_2Cl_2. The resulting band contained $(PMe_2Ph)_3ReCl_2(3\text{-}NC_4H_3Br)$ and some starting material. Yield: 19%. See Table 1 for ^{1}H NMR data. MS (ESI): *m*/*z* 818 (P^+); 671 (P − Br − pyrr); 533 (P − Br − pyrr − PMe_2Ph). Relative yields are as follows. When 1.3 equiv of NBS was added in portions at room temperature and the reaction mixture was stirred for 1 or 2 days, about 50% mono-Br and 25% di-Br products were formed. When 2.3 equiv of NBS was added at room temperatue and the reaction mixture was stirred for 3 h, 10% mono-Br and 40% di-Br products were formed.

A similar reaction with **1** (0.045 g, 0.061 mmol) and NBS (0.034 g, 0.189 mmol) was carried out at room temperature for 1 day. The workup procedure was similar to that described above. The NMR spectrum of the resulting product showed that the major product was $(PMe_2Ph)_3ReCl_2(2,3,4\text{-}NC_4HBr_3)$. The product was further purified by recrystallization from CH_2Cl_2/hexane. Mp: 138−142 °C. See Table 1 for ^{1}H and ^{13}C NMR data.

X-ray Diffraction Study of 5. A suitable crystal was selected and mounted with 5-min epoxy into a Siemens SMART three-circle goniometer. Indexing was determined after collection of 3 sets of 20 0.3° (ω) scans. Least-squares refinement of final cell dimensions was performed using all reflections harvested during data collection. A hemisphere of data was collected. Equivalent reflections were merged, and all data were corrected for Lorentz and polarization effects. Friedel opposites were merged.

Structure solution by direct methods in the centrosymmetric space group $P2_1/c$ revealed the complete non-hydrogen structure. All hydrogens were placed at calculated positions and then refined using a riding model. Hydrogen thermal motion was modeled as isotropic; thermal parameters for hydrogen were calculated as 1.2 times the U_{eq} value for the parent atom. The largest feature in the final difference map is 1.2 e/Å^3, located 1.10 Å from Re, and likely is an artifact of absorption.

Disorder was observed in phenyl ring C(5)−C(10) as well

as in the bromine positions. The phenyl ring is slipped across two positions. The site occupancy of each group was refined dependent upon the other. Final refined occupancies were 0.31(3)/0.69(3). Three positions were observed for Br. This was modeled as partial contamination by the triply brominated product, consistent with NMR data. This triply brominated species has a site occupancy of 0.033(2). Details of data collection and refinement are given in Table 5.

Synthesis of $(PMe_2Ph)_3ReCl_2(3\text{-}NC_4H_3Me)$ (6). Complex **1** (0.200 g, 0.271 mmol) was dissolved in 20 mL of diethyl ether, and methyl triflate (100 μL, 0.88 mmol) was syringed into the solution. Within hours, a yellow precipitate had formed. After it was stirred at room temperature for 3 days, the green solution was removed by cannula. The solvent was removed from this portion, and the remaining complex was identified as **1** (0.030 g). The yellow-brown precitipate was redissolved in dichloromethane and extracted with a saturated aqueous solution of $NaHCO_3$. The solution was then dried over Na_2SO_4, filtered, and dried in vacuo to give a dark yellow-brown solid. Chromatography on a neutral Al_2O_3 column, with dichloromethane as eluent, gave a yellow band which was evaporated to give **6**. Yield: 0.088 g, 51%. See Table 1 for NMR data. MS (ESI): *m*/*z* 752 (P); 671 (P − Mepyrr); 614 (P − PMe_2Ph). The analytical data were calculated for 1 mol of H_2O included with the complex. Evidence for the water molecule was observed in the NMR spectrum (s, 2 H, 1.51 ppm). Anal. Calcd for $C_{31}H_{39}Cl_2NOP_3Re$: C, 45.25; H, 5.37; N, 1.82. Found: C, 45.21; H, 4.99; N, 1.88.

Synthesis of $(PMe_2Ph)_3ReCl_2(3,4\text{-}NC_4H_2Me_2)$ (7). To a solution of **6** (0.041 g, 0.055 mmol) in 10 mL of dichloromethane was added methyl triflate (6 μL, 0.05 mmol). After 20 h, the solvent was removed in vacuo. The brown residue was redissolved in dichloromethane and the solution eluted on a neutral Al_2O_3 column with dichloromethane. The first yellow fraction contained $ReCl_3(PMe_2Ph)_3$, and the second yellow fraction contained a mixture of **1** and $ReCl_3(PMe_2Ph)_3$. The last fraction, which contained **7**, eluted as a red-brown band with a 10:1 mixture of dichloromethane and tetrahydrofuran. See Table 1 for NMR data. MS (ESI): *m*/*z* 766 (M); 671 (M − Me_2 − pyrr); 628 (M − PMe_2Ph). Anal. Calcd for $C_{30}H_{41}Cl_2NP_3Re$: C, 47.06; H, 5.40; N, 1.83. Found: C, 46.98, H, 5.28; N, 1.55.

Synthesis of $[(PMe_2Ph)_3ReCl_2(NC_4H_5)]OTf$ (8). Complex **1** (0.134 g, 0.182 mmol) was dissolved in 30 mL of Et_2O, and triflic acid (19 μL, 0.24 mmol) was added by syringe. A bright yellow precipitate formed immediately. The solution was stirred for 2 h at room temperature, and then the precipitate was allowed to settle, the solution was decanted, and the yellow solid was washed with diethyl ether. Yield: 0.155 g, 95%. The product was recrystallized by vapor diffusion of diethyl ether into a dichloromethane solution of the compound. See Table 1 for NMR data. Anal. Calcd for $C_{29}H_{38}Cl_2F_3NO_3P_3SRe$: C, 39.28; H, 4.28; N, 1.58. Found: C, 38.84; H, 4.02; N, 1.69.

X-ray Diffraction Study of 8. The crystal was mounted to a thin glass fiber on a tapered copper mounting pin. This assembly was aligned on a Siemens SMART CCD diffractometer equipped with an LT-2A low-temperature apparatus operating at 171 K. Data collection to 0.68 Å covered slightly more than a hemisphere of arbitrary orientation. Each 0.3° ω scan was exposed for 30 s. The initial orientation matrix was determined from 3 approximately orthogonal sets of 20 0.3° ω scans, each with a total exposure of 10 s. Standard uncertainties of the final cell parameters were refined from 8192 reflections of 49 568 with $I > 10\sigma(I)$ harvested from the data collection. Data collection was complete to 0.75 Å and 91.9% complete to 0.70 Å.

Structure solution via direct methods in the centrosymmetric space group *Pbca* revealed the non-hydrogen structure. No crystallographically imposed symmetry is present in either the cation or the anion. Disorder is manifest in two orientations of the SO_3 group of the triflate anion. Each group was successfully refined without restraints. A partial site occupancy factor was refined for each group such that the total would sum to full occupancy. The ratio of this occupancy is 0.6(2)/0.4(2). All non-hydrogen atoms were refined with anisotropic parameters for thermal motion. Hydrogens were intially placed at calculated positions and freely refined in subsequent cycles of least-squares refinement. Isotropic thermal parameters for hydrogen were also refined. The largest peak in the final difference map, 1.002 e/Å^3, is located near Re and is likely an artifact of absorption. Details of data collection and refinement are given in Table 5.

Attempted Reaction of 1 with HOAc. To a solution of **1** (0.0536 g, 0.0727 mmol) in dichloromethane was added acetic acid (8.0 μL, 0.14 mmol). The mixture was stirred at room temperature for approximately 4 days. The solvent was removed in vacuo, and the brown residue was characterized by ^{1}H NMR spectroscopy. Complex **1** and $(PMe_2Ph)_3ReCl_3$ were the major components of the mixture. No evidence for the complex containing a protonated pyrrolyl ligand was observed.

Protonation of $(PMe_2Ph)_3ReCl_2(3,4\text{-}NC_4H_2Me_2)$ (7). To a $CDCl_3$ solution of **7** (0.010 g, 0.013 mmol) and $AlCl_3$ (0.0013 g, 0.01 mmol) was added 1.8 μL of $CDCl_3$ saturated with gaseous HCl in an NMR tube. The tube was flame-sealed under vacuum and monitored by ^{1}H NMR spectroscopy. The solution immediately turned yellow, and the ^{1}H NMR spectrum indicated that the pyrrolyl ligand had been protonated at an α-carbon. After a period of 2−3 days, the spectrum indicated the quantitative formation of *mer*-$(PMe_2Ph)_3ReCl_3$. The free pyrrole was not isolated in this experiment. ^{1}H NMR of protonated complex ($CDCl_3$): δ −2.33, −1.86, −0.14 (s, 6 H each, PMe); 1.64 (s, 2H, NCH_2); 4.49, 5.95 (s, 3 H each, Me pyrr); 4.81 (s, 1 H, α-H, pyrr); 8.64 (t, 2 H J = 6.9 Hz, *m*-H, unique PPh); 8.91 (t, J = 6.9 Hz, 4 H, *m*-H, trans-PPh); 11.25 (t, J = 7.9 Hz, 2 H, *p*-H, trans-PPh); 11.45 (t, J = 7.9 Hz, 1 H, *p*-H, unique PPh); 12.29 (d, 2 H, J = 6.9 Hz, *o*-H, unique PPh); 13.29 (d, 4 H, J = 6.9 Hz, *o*-H, trans-PPh). ^{13}C NMR ($CDCl_3$): δ 122.39, 48.63, 154.39 (PMe); 27.93 (α-C, pyrr); 3.66 (α-CH_2, pyrr): 34.69, 13.80 (Me_2 pyrr); 122.45 (*p*-C, trans PPh); 122.47 (*p*-C, unique PPh); 134.95 (*o*-C, trans PPh); 138.41 (*m*-C, trans + unique PPh); 140.95 (*o*-C, unique PPh).

Isolation of 3-Methylpyrrole. Complex **1** (0.11 g, 0. 15 mmol) was dissolved in diethyl ether, and methyl triflate (0.70 μL, 0.62 mmol) was added by syringe. The solution was stirred overnight. The resulting yellow precipitate was filtered under nitrogen and washed with diethyl ether. A portion of this cationic product was redissolved in CD_3CN, and LiCl (4 equiv) and $AlCl_3$ (2 equiv) were added. The salts did not completely dissolve, but the solution was stirred at room temperature for 4 days. The acetonitrile was removed under vacuum at room temperature, the residue was dissolved in $CDCl_3$, and the volatiles were vacuum-transferred while the solution was heated at 45 °C. The resulting pyrrole products were identified by NMR and GC/mass spectroscopy as 3-methylpyrrole (ca. 65%), 2-methylpyrrole (ca. 15%), and pyrrole (20%). ^{1}H NMR ($CDCl_3$: 3-methylpyrrole, δ 2.09 (s, Me), multiplets at 6.80, 6.55, 6.04; 2-methylpyrrole, δ 2.26 (s, Me), multiplets at 6.63, 6.06, and 5.88; pyrrole, multiplets at δ 6.68 and 6.23. The NMR spectrum of the remaining residue confirmed that no Re−pyrrole complexes remained. Resonances were observed for $(PMe_2Ph)_3ReCl_3$ and a second unidentified pyrrole-free Re complex.

Synthesis of $(PMe_2Ph)_3Cl_2Re[3\text{-}NC_4H_3\text{-}C(CO_2Me)CH(CO_2Me)]$ (9). Complex **1** (0.105 g, 0.142 mmol) was dissolved in 40 mL of toluene. To the yellow-brown solution was added dimethyl acetylenedicarboxylate (DMAD) (0.0208 g, 18.0 μL, 0.146 mmol) and glacial acetic acid (8.0 μL). The solution was stirred for 3 days at room temperature; then the solvent was removed in vacuo to give a brown oil. The NMR spectrum of the crude product showed a mixture of 15% **1** and 85% **9**. The brown oil was redissolved in dichloromethane and loaded onto

a neutral alumina chromatography column. Complex **1** was eluted with dichloromethane in the first yellow band in approximately 51% yield. Complex **9** was eluted in the last yellow band. See Table 1 for NMR data. MS (ESI): *m*/*z* 880 (M). Anal. Calcd for $C_{34}H_{43}Cl_2NO_4P_3Re \cdot 2H_2O$: C, 44.59; H, 4.73; N, 1.53. Found: C, 44.61; H, 4.87; N, 1.55.

Attempted Reaction of 1 with Dimethyl Fumarate. Complex **1** (0.115 g, 0.156 mmol) and dimethyl fumarate (0.0224 g, 0.155 mmol) were dissolved in 20 mL of toluene. Glacial acetic acid (1.0 μL) was added and the reaction mixture stirred at room temperature for 5 days. No reaction was observed by ^{1}H NMR spectroscopy. Additional fumarate (0.0241 g, 0.167 mmol) and HOAc (5 mL) were added, and the reaction mixture was stirred at room temperature for another 7 days. No reaction was observed by NMR spectroscopy.

Attempted Reaction of $(PMe_2Ph)_3ReCl_2(3\text{-}NC_4H_3Me)$ (6) with Methyl Propiolate. To a solution of **6** (0.015 g, 0.020 mmol) in dichloromethane was added methyl propriolate (3.0 μL) and HOAc (3.5 μL). The solution was stirred at room temperature for 4 days, and solvent was then removed in vacuo to give a red oil. The ^{1}H NMR spectrum of the crude product showed a mixture of **6**, $(PMe_2Ph)_3ReCl_3$, and a new Re(III) product. Attempts were made to separate the mixture by elution with dichloromethane on a neutral alumina column, but a new product was not successfully isolated.

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Supporting Information Available: Tables giving crystal data, positional and thermal parameters, bond distances, and bond angles for **1**, **5**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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