Nucleophilic Substitution of η^5-Pyrrolyl Ligands in Ruthenium(II) Complexes

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The reaction of $RuCl_2(PPh_3)_3$ with pyrrolyllithium results in the formation of the pyrrolyl complex $(NC_4H_4)RuCl(PPh_3)_2$, **1**, which has been characterized by an X-ray diffraction study. The structure confirms the η^5-bonding mode for the pyrrolyl ligand. Ligand substitution reactions with **1** have led to the facile synthesis of related η^5-pyrrolyl ruthenium complexes with other suppporting ligands. Reactions of the PEt_3 derivatives $(NC_4H_4)RuX(PEt_3)_2$, X = Cl and I, with aryl- and alkyllithium reagents resulted in nucleophilic substitution of the pyrrolyl ligand accompanied by hydrogen transfer to the metal ion, forming $(2\text{-}RNC_4H_3)RuH(PEt_3)_2$. The hydride products could be converted to the corresponding chloride derivatives in chlorinated solvents, and the complex $(2\text{-}PhNC_4H_3)RuCl(PEt_3)_2$ has been structurally characterized. A second nucleophilic substitution reaction on the coordinated pyrrolyl ligand has been characterized in some cases, and protonation of the substituted pyrrole complex led to isolation of the free substituted pyrrole with recycling of the ruthenium complex. The nucleophilic substitutions are sensitive to the electronic features of the supporting ligands in the complex and to the strength of the nucleophiles.

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Introduction

Synthetic routes for the derivatization of indole rings are of interest in the synthesis of natural products,[1,2] and several η^6-indole complexes, e.g., of Cr, Mn, and Ru, have been developed that facilitate regioselective nucleophilic addition or substitution reactions on the carbocyclic ring.[3−6] Substituted pyrrole heterocycles also show important biological activity. For example, various substituted pyrroles are known to act as analgesics, anti-inflammatory agents, or to have antibacterial properties.[7] However, relatively few transition-metal−pyrrole complexes have been found to be synthetically useful in the preparation of substituted pyrrole rings, and the syntheses of substituted pyrroles have been largely limited to electrophilic additions to the free ligand and to ring-closing reactions of appropriate precursors.[8] A notable exception is the η^2-pyrrole complex of osmium pentammine, which undergoes selective electrophilic attack at the C3 position. The metal-induced activation of the η^2-ligand has led to facile tautomerizations, Diels−Alder condensations, and further synthetic elaborations to form highly substituted indoles.[9] Selective electrophilic substitution reactions at the C3 position have also been observed for pyrrolylimido complexes of molybdenum and tungsten,[10] and electrophilic addition reactions to and rearrangements of η^1-N-bonded pyrrolyl complexes of $CpRe(NO)(PPh_3)$ have been characterized.[11]

Free pyrrole is generally not susceptible to nucleophilic attack, but η^5-coordination to a metal ion has the potential for activating the ring toward reaction with nucleophiles. In recent work, we have synthesized new sandwich complexes of Ru(II) and Os(II) which contain the tetramethylpyrrolyl and pentamethylpyrrole ligands, $[(cymene)M(\eta^5\text{-}NC_4Me_4)]OTf$ and $[(cymene)M(\eta^5\text{-}MeNC_4Me_4)](OTf)_2$.[12] Nucleophilic addition to the monocation occurred at the cymene ligand to give η^5-cyclohexadienyl derivatives, but reactions of the dication with nucleophiles (H^-, OR^-) resulted in nucleophilic addition to the α-carbon in the pentamethylpyrrole ligand, eq 1. The resulting product of hydride addition, $[(cymene)Ru(\eta^4\text{-}MeNC_4(H)Me_4)]OTf$, contained a cyclic η^4 ligand with the substituted carbon of the ring bent out of the plane

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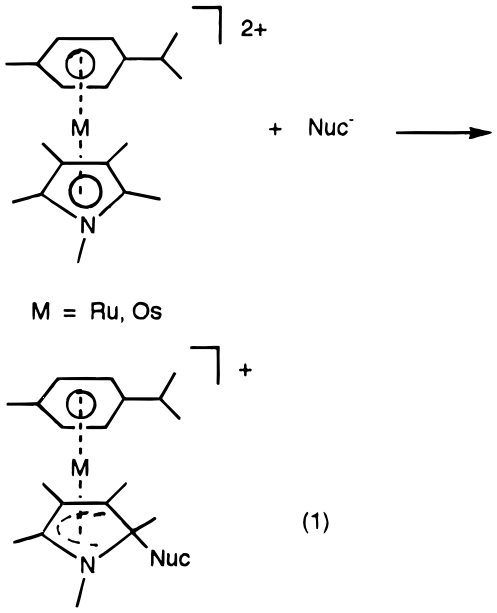
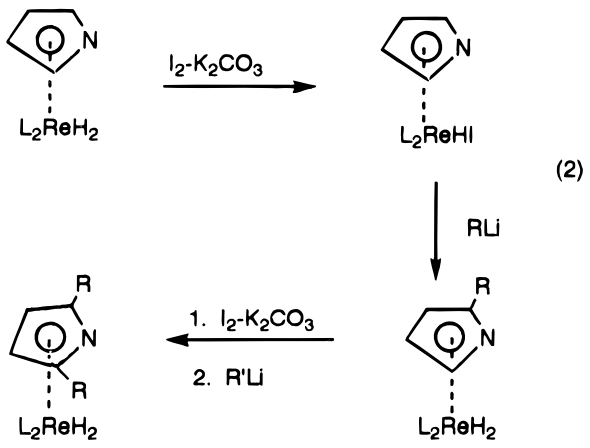


by a dihedral angle of 32°. Reaction with acid led to further ring reduction and elimination of a free cyclic iminium ion.

In earlier work, Zakrzewski developed the chemistry of pyrrolyl complexes of rhenium of the formula (η^5-NC_4H_4)$Re(PR_3)_2(H)I$.[13] These complexes were found to undergo nucleophilic substitution reactions at the α-carbon of the heterocycle, as shown in eq 2. The reactions



involve hydrogen transfer from the ring to the metal ion. Similar nucleophilic substitutions of η^5-cyclopentadienyl ligands with hydrogen transfer to the metal ion have been proposed.[14]

We report here new η^5-pyrrolyl complexes of ruthenium which promote nucleophilic substitutions at the heterocycle by a similar pathway of hydrogen transfer and metal hydride formation. The new pyrrole complexes are easily synthesized and modified by coligand substitution reactions, and the metal ion can be recycled upon removal of the substituted pyrrole. The complexes have the potential for synthetic utility in the synthesis of a variety of substituted pyrroles.

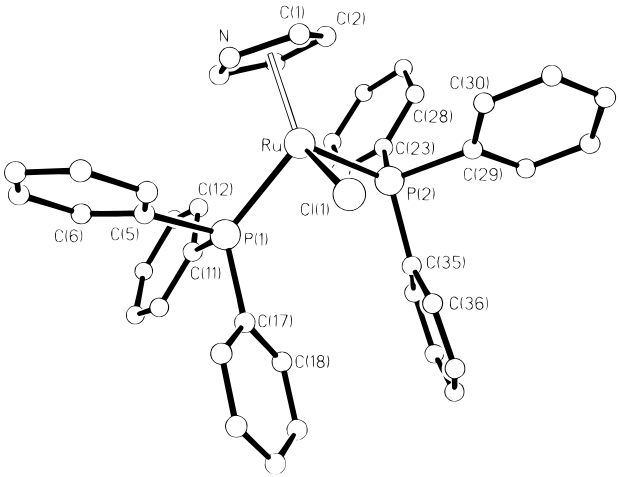
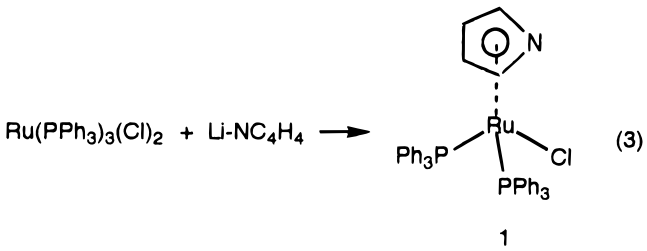


Figure 1. Perspective drawing and numbering scheme for (η^5-NC_4H_4)$Ru(PPh_3)_2Cl$, **1**.

Results and Discussion

Synthesis and Characterization of $(NC_4H_4)Ru(PR_3)_2X$ Derivatives. The reaction of $(PPh_3)_3RuCl_2$ with pyrrolyllithium in refluxing toluene led to the formation of a yellow crystalline product (NC_4H_4)-$Ru(PPh_3)_2Cl$, **1**, eq 3, which was isolated after chromatography in 60−70% yield. The procedure is similar to that reported for the synthesis of $CpRu(PPh_3)_2Cl$.[15] In



the ^1H NMR spectrum of **1**, the resonances for the pyrrolyl hydrogens are shifted upfield relative to the free ligand to 5.61 and 4.24 ppm. The ^{31}P NMR spectrum shows a singlet for the equivalent phosphine ligands at 41.4 ppm. The upfield shifts in the proton spectrum suggest an η^5-coordination of the ring to the ruthenium ion, and this bonding mode was confirmed by an X-ray diffraction study. The complex crystallized in space group $P\bar{1}$ with two molecules per unit cell. A perspective drawing of the molecule is shown in Figure 1, and selected bond distances and angles are given in Table 1. The structure consists of discrete molecules in which the ligands form a pseudotetrahedral coordination geometry about the ruthenium ion. The Ru−C distances for the pyrrole ring are similar to those reported for the η^5-ligand in the analogous Cp complex,[16] but the Ru−Cl and Ru−P bonds in **1** are 0.01−0.03 Å shorter than those for the Cp derivative. The P−Ru−P angle in **1**, 102.6(1)°, is also somewhat smaller than the same angle in the Cp complex (103.99(4)°).

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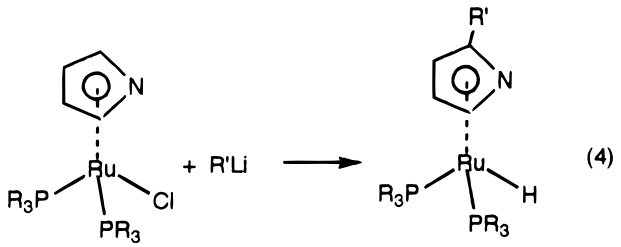
Table 1. Selected Bond Distances (Å) and Angles (deg) for (pyrr)RuCl(PPh_3)$_2$ (1)

		Distances	
Ru−N	2.239(3)	Ru−C(1)	2.208(4)
Ru−C(2)	2.222(3)	Ru−C(3)	2.187(3)
Ru−C(4)	2.161(3)	Ru−Cl(l)	2.427(1)
Ru−P(1)	2.327(1)	Ru−P(2)	2.304(1)
N−C(1)	1.393(6)	C(1)−C(2)	1.368(6)
C(2)−C(3)	1.419(6)	C(3)−C(4)	1.404(6)
N−C(4)	1.382(5)		
		Angles	
Cl(1)−Ru−P(1)	88.7(1)	Cl(1)−Ru−P(2)	90.7(1)
P(1)−Ru−P(2)	102.6(1)		

A similar reaction of RuH(Cl)(PPh_3)$_3$ with pyrrolyllithium resulted in the formation of the hydride analogue (η^5-NC_4H_4)RuH(PPh_3)$_2$, **2**, which has been isolated and characterized by spectroscopic data. In particular, the ^{1}H NMR spectrum for **2** showed a characteristic hydride resonance (triplet) in the NMR spectrum at −13.79 ppm. Complete spectroscopic data are provided in the Experimental Section. Despite the ease with which the syntheses of **1** and **2** proceed, the attempted reactions of the lithium salts of 2-acetylpyrrole, tetramethylpyrrole, and of 2,5-dimethylpyrrole with $RuCl_2$(PPh_3)$_3$ under similar reaction conditions did not proceed in the first two cases and in the latter system gave a mixture of products which were not readily separated.

Facile ligand substitution reactions have been characterized for **1**, which are similar to those reported for $CpRu(PPh_3)_2Cl$.[17] For example, reaction with KI in ethanol leads to the synthesis of the iodide complex (η^5-NC_4H_4)Ru(PPh_3)$_2$I, **3**, which has been isolated and characterized by elemental analyses and spectroscopic data. The chemical shifts for the ^{1}H NMR resonances for the pyrrolyl ligand in **3** at 5.64 and 4.46 ppm and for the single resonance in the ^{31}P NMR spectrum at 40.7 ppm are similar to those of the chloride derivative. The reaction of **1** with excess triethylphosphine in refluxing toluene led to the synthesis of the phosphine-substituted product (η^5-NC_4H_4)Ru(PEt_3)$_2$Cl, **4**, and further substitution with KI produced the iodide analogue, (η^5-NC_4H_4)Ru(PEt_3)$_2$I, **5**. The cationic η^5-pyrrolyl derivatives [(η^5-NC_4H_4)Ru(PEt_3)$_3$]PF_6, [(η^5-NC_4H_4)RuCO-(PEt_3)$_2$]PF_6, and (η^5-NC_4H_4)Ru(PEt_3)$_2$(CH_3CN)]BPh_4 have also been synthesized by procedures similar to those reported for related cyclopentadienyl derivatives.[16−18] Characterization data for all of the new complexes are presented in the Experimental Section.

Reactions with Nucleophiles. Although free pyrrole is quite electron rich and does not undergo nucleophilic attack, coordination of the pyrrolyl ligand to the ruthenium ion activates the ring toward nucleophilic substitution. For example, the triethylphosphine derivatives **4** and **5** react with strong nucleophiles, such as alkyl- and aryllithium reagents, to produce Ru(II)−hydride derivatives containing substituted pyrrolyl ligands, as shown in eq 4. During this reaction, the ring hydrogen was transferred to the metal ion displacing the labile halide ligand. The reaction with the more stabilized nucleophile $CH(Me)CN^-$ proceeded with the iodide as a leaving group, but not with the chloride



(4)

For **4**, R = Et, X = Cl,
R' = Me, Ph, Me_2N, BEt_3D

For **5**, R = Et, X = I, R' = CHMeCN

For **3**, R = Ph, X = I, R' = Me

For **1**, R = Ph, X = Cl, R' =n- Bu

derivative. The product containing the nonlabile hydride ligand did not undergo further nucleophilic substitution reactions.

The reactivity of the pyrrolyl ligand toward nucleophiles depends not only on the lability of the displaced ligand, but also on the properties of the phosphine ligand in the complex. For example, the triphenylphosphine derivative, (η^5-NC_4H_4)Ru(PPh_3)$_2$Cl, did not react with MeLi or PhLi under similar conditions, although the reaction of MeLi did proceed with the iodide analogue. Triethylphosphine has a somewhat smaller cone angle than PPh_3 (132° vs 145°, respectively) and is a significantly stronger σ-donor ligand (for the conjugate acid, pK_a = 8.69 vs 2.73 for PPh_3).[19] Electronic effects may account for the greater reactivity of the triethylphosphine derivatives since greater electron donation to the metal ion should enhance the lability of the halide ligand. A similar labilizing effect has been observed for the rate of Cl^- exchange in $CpRu(PR_3)_2Cl$ as the donor ability of the phosphine ligand was increased.[20] When the reactions of (η^5-NC_4H_4)Ru-(PEt_3)$_2$I and (η^5-NC_4H_4)Ru(PEt_3)$_2$Cl with an equivalent of PhLi were monitored by NMR spectroscopy in sealed tubes, both reactions were found to be complete within the time of mixing at room temperature and we were unable to compare relative rates as a function of the leaving ligand under these conditions.

The spectroscopic data for the substituted pyrrolyl complexes are distinctive. In the ^{1}H NMR spectrum, three new resonances are observed for the inequivalent ring hydrogens and a high-field pseudotriplet near −14 ppm confirms the formation of the hydride product. Spin−spin coupling between the pyrrole hydrogens is not resolved, and the pyrrole resonances are observed as singlets in the 400 MHz spectra. In the ^{31}P NMR spectrum, an AB pattern is observed, reflecting the loss of C_s symmetry in the molecule. Although the hydride products were identified spectroscopically, most of these were converted to the chloride derivatives prior to isolation. This was accomplished by quenching excess

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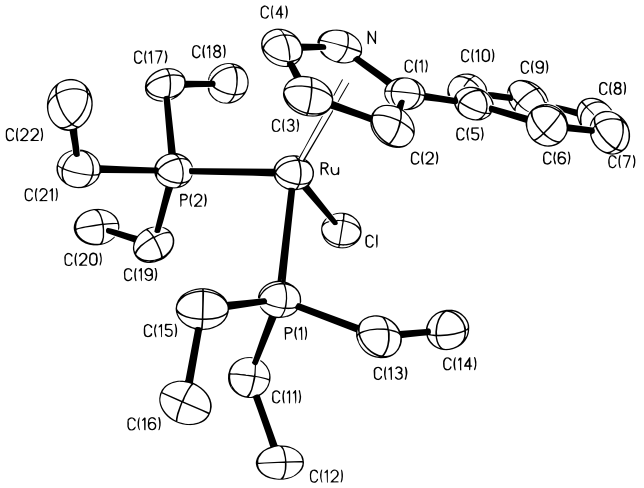

Figure 2. Thermal ellipsoid drawing and numbering scheme for (η^5-2-$PhNC_4H_3$)$Ru(PEt_3)_2Cl$, **6b**.

lithium reagent with *tert*-butyl chloride,[21] if necessary, and then placing the complex in a chloroform solution for a few minutes or in dichloromethane for 15−20 h.[22] Column chromatography was carried out to obtain the pure chloride derivatives with substituted pyrrolyl ligands. Isolated yields of the products at this stage were rather low, 25−35%, even though the NMR studies of the aryllithium substitutions indicated that those reactions proceeded quantitatively. Some decomposition was observed during the hydride to chloride conversion step in either solvent, even when the chlorinated solvents were carefully distilled and protected from air and light. A recent paper has reported that CH_3Cl in CH_2Cl_2 was a more effective reagent for the hydride/chloride conversion of rhenium hydrides than the more chlorinated solvents, and it was suggested that the reaction may proceed by a more selective mechanism.[23] However, in our systems, no hydride conversion was observed using CH_3Cl in THF and the yields of isolated ruthenium chlorides using CH_3Cl/CH_2Cl_2 were similar to those for the other chlorinated solvents.

X-ray Diffraction Study of ($2\text{-}PhNC_4H_3$)$Ru(PEt_3)_2Cl$. Single crystals of the phenyl-substituted product ($2\text{-}PhNC_4H_3$)$Ru(PEt_3)_2Cl$, **6b**, have been obtained. An X-ray diffraction study was carried out in order to verify the site of nucleophilic attack and to learn more about the potential steric interactions between the phosphine ligands and the ring substituent. A perspective drawing and numbering scheme of the structure are given in Figure 2, and selected bond distances and angles are presented in Table 2. The structure establishes that the η^5-pyrrolyl ring contains a phenyl substituent on an α carbon of the ring. The plane of the phenyl ring is rotated relative to that of the pyrrolyl ligand; the angle between the normals to the two rings is 20.9°. The orientation of the phenyl ring over the chloride ligand appears to minimize steric repulsions with the triethylphosphine ligands. The pyrrolyl ring also appears to have slipped slightly away from the phosphine ligands, as shown by the shorter distances from the metal to C(3) and C(4)compared to those between the metal and N, C(1), and C(2). The average Ru−P distance of 2.286 (2) Å is significantly shorter for this triethylphosphine derivative than that observed for the triphenylphosphine complex **1**.

Table 2. Selected Bond Distances (Å) and Angles (deg) for ($2\text{-}PhNC_4H_3$)$RuCl(PEt_3)_2$ (6b)

Distances			
Ru−N	2.276(5)	Ru−C(1)	2.279(6)
Ru−C(2)	2.296(5)	Ru−C(3)	2.238(6)
Ru−C(4)	2.172(6)	Ru−Cl	2.4246(14)
Ru−P(1)	2.288(2)	Ru−P(2)	2.284(2)
N−C(1)	1.418(9)	C(1)−C(2)	1.417(9)
C(2)−C(3)	1.462(10)	C(3)−C(4)	1.457(11)
N−C(4)	1.382(8)	C(1)−C(5)	1.462(8)

Angles			
P(1)−Ru−P(2)	95.56(6)	Cl−Ru−P(2)	89.22(5)
Cl−Ru−P(1)	89.44(6)		

Reactivity of Nucleophiles. The range of nucleophiles which can be used successfully in these substitution reactions has been studied with the derivatives (η^5-NC_4H_4)$Ru(PEt_3)_2X$, X = Cl, **4**, and I, **5**. Both alkyl- and aryllithium reagents reacted readily to give the substituted products, but the substitutions were not always successfully accomplished with Grignard reagents. For example, while the reaction of MeMgCl with **4** resulted in the formation of a product with a methylated pyrrole ligand, the reaction of MeMgBr (in diethyl ether) led to the formation of (η^5-NC_4H_4)$Ru(PEt_3)_2Br$, which was isolated by column chromatography in very low yield and identified by NMR and mass spectroscopy. Similar halogen-exchange products have been observed in the reactions of $CpRu(PPh_3)_2Cl$ with MeMgI and of Cp*Ru-$(PMe_3)_2Cl$ with RMgBr.[24] The NMR spectrum of the crude product from the MeMgBr reaction also showed evidence for the formation of free pyrrole, but other ruthenium containing products were not identified.

A series of other anionic nucleophiles have been reacted with (η^5-NC_4H_4)$Ru(PEt_3)_2Cl$, **4**. The amide derivative $LiNMe_2$ reacted to form two products in about equal amounts, which were tentatively identified as the ring-substituted derivative, (η^5-2-$(NMe_2)NC_4H_3$)Ru-$(PEt_3)_2H$, and the unsubstituted pyrrolyl product with a hydride ligand, (η^5-NC_4H_4)$Ru(PEt_3)_2H$, eq 5. These products could form by a pathway of intermolecular hydride transfer from the substituted pyrrole ligand, but it seemed more likely that the products resulted from competing reactions which involved nucleophilic attack on the ring and on the metal ion. The latter Ru−dimethylamide complex is proposed to undergo rapid β-hydrogen elimination to form the observed hydride product. The reaction of lithium dimethylamide with $RuCl_2(PR_3)_4$ has been reported to undergo a similar rapid β-hydrogen elimination,[25a] while the reaction of $Cp^*Ru(PMe_3)_2Cl$ with primary amides led to intractable products.[25b] The identities of the products formed from the reaction of **4** with $LiN(CD_3)_2$ were consistent with the proposed mechanism. In this case, we observed in

(21) Protic reagents were not used to quench Li alkyl reactants because protonation of the pyrrolyl ring led to complex decomposition. *t*-BuCl reacted with the carbanion to form the hydrocarbon and isobutene.

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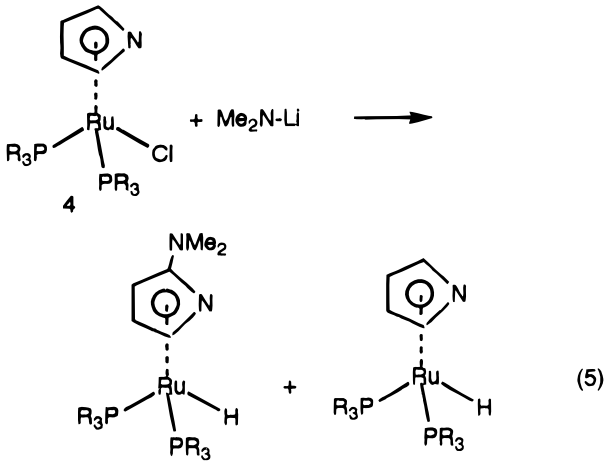
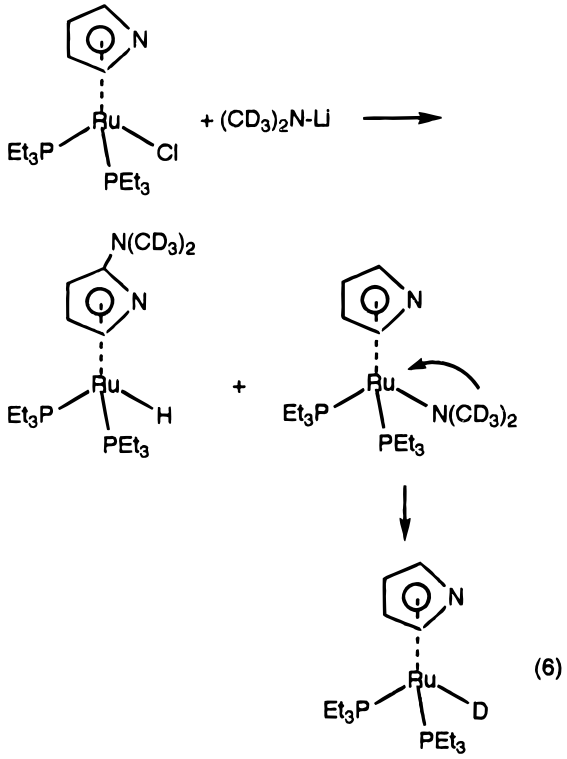


(5)

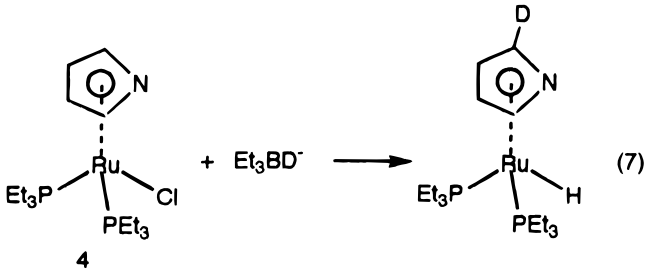
the ^{1}H and ^{2}D NMR spectra resonances for the substituted pyrrole complex (2-N(CD$_3$)$_2$NC$_4$H$_3$)Ru(PEt$_3$)$_2$H and a Ru−D complex with the unsubstituted heterocycle, eq 6. Both hydride products were converted to corresponding chlorides prior to isolation.



(6)

Other heteroatom-containing nucleophiles, such as SR$^-$ or OR$^-$, did not undergo nucleophilic attack on the pyrrolyl ligand in **4**. The reactions with NaSR (R = Me, *t*-Bu) appeared to form ruthenium−thiolate complexes (η^5-NC$_4$H$_4$)Ru(PEt$_3$)$_2$SR, which were tentatively identified by spectroscopic data. In contrast, no reaction at all was observed between **4** and NaOMe or NaO^{t}Bu.

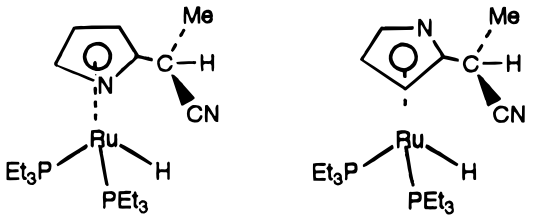
The reaction of Super-Hydride, LiEt$_3$BH, with **4** at room temperature proceeded to form the hydride complex (η^5-NC$_4$H$_4$)Ru(PEt$_3$)$_2$H, which was characterized by spectroscopic data. The product appears to form by hydride attack on the pyrrolyl ligand and hydrogen transfer from the ring to the metal ion. When the analogous reaction with Super-Deuteride was characterized by ^{2}H NMR spectroscopy, a resonance was observed only for the deuterated pyrrolyl ligand at 5.87 ppm while a resonance for a Ru−D ligand was not observed, eq 7. Although LiAlH$_4$ has been used to



(7)

displace the halide ligand in CpRu(PR$_3$)$_2$Cl,[24a,26] the same reagent appears to lead to decomposition of the (η^5-NC$_4$H$_4$)Ru derivatives. Resonances for a coordinated pyrrolyl ligand were not observed in the NMR spectrum of the products of the latter reaction.

The reaction of **5** (but not **4**) with the stabilized carbanion LiCH(Me)CN appeared to form the pyrrole-substituted product 2-(CN(Me)CH)NC$_4$H$_3$)Ru(PEt$_3$)$_2$H in low yield. In the ^{1}H NMR spectrum, resonances were observed for the two diastereomers, e.g., A and B, expected for the product. Unreacted starting material



was also present, but addition of excess lithium reagent to this reaction led to decomposition. Attempts to convert the hydride product to the chloride derivative with dichloromethane or chloroform were unsuccessful in this case, and the substituted product has not been successfully isolated. Nevertheless, this apparent reactivity toward stabilized carbanions is significant because it extends the range of nucleophilic pyrrole substitutions to less basic reagents than have been observed previously, and further work to optimize these types of reactions is in progress.

Syntheses of Complexes with Disubstituted Pyrrolyl Rings. The facile conversion of the nonlabile hydride ligand to a labile chloride in the substituted pyrrolyl products permits the repetition of the nucleophilic substitution reaction. For example, the reaction of (2-PhNC$_4$H$_3$)Ru(PEt$_3$)$_2$Cl with an equivalent of PhLi proceeded at room temperature to form the product with a disubstituted pyrrolyl ligand, (2,5-Ph$_2$NC$_4$H$_2$)Ru(PEt$_3$)$_2$H, which was identified by ^{1}H NMR data. The hydride product was converted to the chloride derivative (2,5-Ph$_2$NC$_4$H$_2$)Ru(PEt$_3$)$_2$Cl, **7**, which was further purified by chromatography and characterized spectroscopically. The ^{1}H NMR spectrum of **7** showed a single resonance for equivalent pyrrole hydrogens at 5.05 ppm, and the ^{31}P spectrum also showed a single resonance at 35.4 ppm. Similar disubstituted pyrrolyl ligands have been synthesized with the Re system described above.[13] In contrast, the reaction of (2-PhNC$_4$-

(26) Davies, S. G.; Moon, S. D.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1278.

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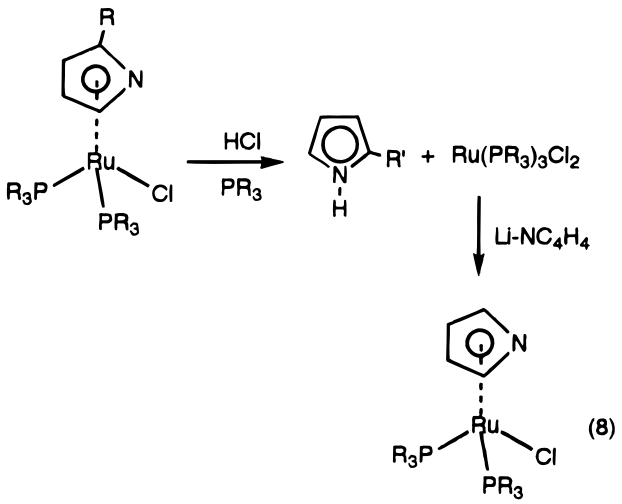
$H_3)Ru(PEt_3)_2Cl$ with an equivalent of MeLi did not proceed at room temperature to give a disubstituted ring. The ease of the second substitution on the ring may be dependent on the steric bulk of the substituent group.

Reactions of (η^5-NC_4H_3(R))$Ru(PR_3)_2X$ Derivatives with Electrophiles. (η^5-NC_4H_4)$Ru(PPh_3)_2Cl$ reacted with 1 equiv of triflic acid to form the product with a protonated pyrrole nitrogen, [(η^5-HNC_4H_4)-$Ru(PPh_3)_2Cl$]OTf, **9**. This complex was identified by ^{1}H NMR data, but it showed limited stability in solution and was not successfully isolated in pure form. The N−Me analogue, which was prepared by a reaction with MeOTf, could be isolated, but it also tended to decompose via loss of the neutral methylpyrrole ligand. Much weaker acids, such as pyridinium chloride (1 equiv) or excess ammonium chloride, also lead to the protonation and dissociation of the η^5-pyrrole ligand.

The lability of the neutral pyrrole ligands in these complexes can be used in the isolation of free substituted pyrrole heterocycles. For example, the reaction of (2-$PhNC_4H_3$)$Ru(PEt_3)_2Cl$ with gaseous HCl resulted in the displacement of 2-phenylpyrrole, which was separated from the ruthenium products by chromatography on an alumina column, isolated in near quantitative yield, and characterized by ^{1}H NMR and mass spectroscopy. The pyrrole could be further purified by sublimation, but this reduced the yield to 45%. Ruthenium phosphine products were not successfully isolated from the chromatography columns, but similar protonations of (R-pyrrolyl)-$Ru(PR_3)_2Cl$ derivatives coupled with further reactions with pyrrolyllithium did allow us to regenerate the starting reagent (η^5-NC_4H_4)$Ru(PR_3)_2Cl$, eq 8. For example, addition of HCl to (2-$BuNC_4H_3$)$Ru(PPh_3)_2Cl$ led to the formation of free 2-Bupyrrole, which was extracted with multiple aliquots of ether and isolated in 65% yield. Addition of triphenylphosphine to the remaining ruthenium-containing residue led to the formation of $Ru(PPh_3)_3Cl_2$, and this complex was converted to the η^5-pyrrolyl derivative in an overall yield of 33% based on the initial substituted pyrrolyl complex. It may be possible to improve these yields. However, effective separation of the neutral substituted pyrrole from the phosphine ruthenium products can be difficult, and addition of pyrrolyllithium to the latter reaction residue often leads to the formation of a mixture of products. This was a particular problem for the highly soluble complexes with triethylphosphine ligands; (η^5-NC_4H_4)$Ru(PEt_3)_2Cl$ has been successfully isolated by chromatography from the recycling reaction, but the yields were very low.



(8)

The cationic derivatives of the formulas [(NC_4H_4)Ru-$(PR_3)_2L]^+$ and [(RNC_4H_4)$Ru(PR_3)_2X]^+$ also have the potential for promoting nucleophilic attack on the η^5-heterocyclic ligand, although mechanistic features and competing reactions may vary. The characterizations of the reactivities of these derivatives will be the subject of future studies.

Conclusions. The new (η^5-NC_4H_4)$Ru(PR_3)_2X$ derivatives reported here are synthesized in high yield from readily available starting materials, and their electronic properties can be modified and tuned by ligand substitution reactions. The new complexes facilitate the nucleophilic substitution of the η^5-pyrrolyl ligand with a range of nucleophiles, and both 2- and 2,5-substituted pyrrolyl products have been isolated and characterized. Protonation or alkylation of the substituted ligand produces the free substituted pyrrole heterocycles. The systems have potential for applications in the syntheses of a wide range of substituted pyrrole molecules.

Experimental Section

$RuCl_2(PPh_3)_3$,[27] $RuHCl(PPh_3)_3$,[28] and tetramethylpyrrole[29] were synthesized according to literature procedures. Pyrrole was distilled from CaH_2 and stored over Linde 4 Å molecular sieves. Pyrrolyllithium salts were synthesized by combining the appropriate reagent with 1 equiv of *n*-butyllithium in hexane at room temperature. The insoluble product was filtered and used immediately or stored at low temperature. Diethyl ether, toluene, and benzene-d_6 were distilled from sodium benzophenone ketyl and stored over 4 Å molecular sieves before use. Hexane, pentane, and deuterated chloroform were distilled from CaH_2 and stored over 4 Å molecular sieves before use. All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques.

^{1}H NMR spectra were recorded at 400.13 MHz, ^{13}C NMR spectra were recorded at 100.62 MHz, and ^{31}P NMR were recorded at 161.98 MHz on a Bruker AM-400 NMR spectrometer. Chemical shifts were referenced to tetramethylsilane by using the deuterated solvent signal as a secondary reference. Mass spectra were obtained on a VG Analytical 7070 EQ-HF mass spectrometer.

Synthesis of (NC_4H_4)$Ru(PPh_3)_2Cl$, 1. $RuCl_2(PPh_3)_3$ (1.0 g, 1.0 mmol) and pyrrolyllithium (0.090 g,1.2 mmol) were combined in 100 mL of toluene, and the solution was stirred at 40 °C under nitrogen for 3 h. The previously brown solution changed to orange, and a white precipitate formed. The solution was filtered through a bed of Celite, and the filtrate was concentrated *in vacuo*. This solution was loaded onto an alumina/toluene chromatography column, and 150 mL of toluene were passed through to remove any triphenylphosphine. **1** was eluted as a yellow band with a 15:1 mixture of toluene:acetonitrile and isolated by removal of solvent. Yield: 0.50 g, 69%. Crystals suitable for X-ray diffraction were grown by vapor diffusion of pentane into a concentrated dichloromethane solution. ^{1}H NMR ($CDCl_3$): δ 7.36, 7.29, 7.20, 7.10 (m, PPh_3), 5.61, 4.24 (2s, each 2H, pyrr). ^{31}P NMR ($CDCl_3$): δ 41.4 (s, PPh_3). ^{13}C NMR ($CDCl_3$): δ 137.2, 134.0, 127.6 (m, PPh_3), 129.1 (s, PPh_3), 108.4, 82.7 (2 s, pyrr). FAB^+ MS (3-NOBA matrix): *m/z* 727 (M), 692 (M − Cl), 661 (M −

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(28) Schunn, R. A.; Wonchoba, E. R. *Inorg. Synth.* **1971**, *13*, 131.
(29) Johnson, A. W.; Markham, E.; Price, R.; Shaw, K. B. *J. Chem. Soc.* **1958**, 4254.

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Table 3. Crystal Data for Compounds 1 and 6b

	1	6b
formula	$C_{41}H_{36}NP_2Cl_3Ru$	$C_{22}H_{38}ClNP_2Ru$
fw	812.1	514.99
cryst syst	triclinic	orthorhombic
unit cell dimensions		
a (Å)	9.924(2)	22.1440(10)
b (Å)	13.951(3)	39.726(3)
c (Å)	14.370(3)	10.8680(7)
α (deg)	100.950(10)	90
β (deg)	105.370(10)	90
γ (deg)	99.240(10)	90
volume, Å^3	1836.1(7)	9560.5(10)
space group	$P\bar{1}$	*Fdd*2
Z	2	16
density, calcd, g/cm^3	1.274	1.431
λ(Mo Kα) (Å)	0.710 73	0.710 73
temp (K)	298(1)	123(2)
scan type	$\theta-2\theta$	oscillation, 3.0°
2θ range (deg)	3.0−50.0	2.05−25.18
no. of independent reflns	7061	3760
no. of reflns obsd	5306	3439
abs coeff (mm^{-1})	0.754	0.909
R^a	0.0327	0.0536
R_w	0.0430[b]	0.1342[c]
GOF	1.00	1.063
largest peak in final diff map e$^-$/Å^3	0.63 and −0.41	1.821 and −1.165

[a] $R = R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$. [c] $R_w = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

pyrr). Anal. Calcd for $C_{40}H_{34}ClNP_2Ru$: C, 66.07; H, 4.68. Found: C, 66.46; H, 4.49.

X-ray Diffraction Study of 1. The crystal was mounted with epoxy cement on a glass fiber and placed into the four-circle goniometer of a Nicolet P3/f automated diffractometer. Cell dimensions were determined upon centering reflections chosen from a 10 min ϕ rotation photograph and were refined after centering 25 strong reflections chosen between 22° and 34° 2θ. Data collection through the range 3.0−50.0° 2θ employed a variable speeed $2\theta-\theta$ scan. A hemisphere plus one redundant layer was collected. Data were corrected for Lorentz and polarization effects. All equivalent reflections were merged, $R_{int} = 0.0193$. Crystal data are given in Table 3.

The structure was solved by Patterson function, and additional non-hydrogen atoms were located during subsequent cycles of least-squares refinement followed by difference Fourier synthesis. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed at calculated geometries and allowed to ride on the position of the parent atom. Hydrogen thermal parameters were fixed at 0.08 Å^2. The asymmetric unit contains one molecule of dichloromethane in addition to the ruthenium complex.

Synthesis of $(NC_4H_4)RuH(PPh_3)_2$, 2. $RuHCl(PPh_3)_3$ (0.28 g, 0.30 mmol) and pyrrolyllithium (0.022 g, 0.30 mmol) were combined in 25 mL of toluene. The solution was stirred and refluxed under nitrogen for 14 h. The resulting orange solution was filtered and concentrated *in vacuo*. This solution was chromatographed on an alumina/toluene column, and **2** was eluted as a yellow band with a 15:1 mixture of toluene:acetonitrile. Yield: 0.107 g, 52%. ^{1}H NMR (C_6D_6): δ 7.56, 6.92 (2m, PPh_3), 5.33, 5.03 (2s, each 2H, pyrr), −13.79 (t, J = 33 Hz, 1H, Ru−H). ^{13}C NMR (C_6D_6): δ 140.3 (m, PPh_3), 134.3, 127.5 (2m, PPh_3), 129.3 (s, PPh_3), 110.0, 82.0 (2s, pyrr). ^{31}P NMR ($CDCl_3$): δ 66.1 (d, PPh_3). CI$^+$ MS: *m*/*z* 692 (M), 626 (M − pyrr). Anal. Calcd for $C_{40}H_{35}NP_2Ru$: C, 69.38; H, 5.05. Found: C, 69.17; H, 5.19.

Synthesis of $(NC_4H_4)Ru(PPh_3)_2I$, 3. Complex **1** (0.17 g, 0.24 mmol) and potassium iodide (0.81 g, 4.9 mmol) were combined in 75 mL of degassed 95% ethanol. The solution was refluxed with stirring for 20 h, and the solvent was removed from the resulting orange solution on a rotary evaporator. The orange residue was extracted with 2 × 25 mL of toluene, and the combined extracts were concentrated *in vacuo* and chromatographed on an alumina/toluene column. Complex **3** was eluted as an orange-red fraction with toluene. An orange, air-stable, crystalline solid was obtained after solvent removal. Yield: 0.18 g, 94%. ^{1}H NMR ($CDCl_3$): δ 7.34, 7.25, 7.14 (3m, PPh_3), 5.64, 4.46 (2s, each 2H, pyrr). ^{13}C NMR ($CDCl_3$): δ 137.7 (m, PPh_3), 134.3, 127.5 (2m, PPh_3), 129.2 (s, PPh_3), 107.4, 84.3 (2s, pyrr). ^{31}P NMR ($CDCl_3$): δ 40.7 (s, PPh_3). FAB$^+$ MS (NOBA): *m*/*z* 819 (M), 753 (M − pyrr), 692 (M − I). Anal. Calcd for $RuC_{16}H_{34}ClNP_2$: C, 43.78; H, 7.82; N, 3.19. Found: C, 43.60; H, 7.68; N, 3.16.

Synthesis of $(NC_4H_4)Ru(PEt_3)_2Cl$, 4. Triethylphosphine (1.4 mL, 7.7 mmol) was added to a solution of **1** (0.70 g, 0.96 mmol) in 150 mL of toluene. This solution was refluxed with stirring for 6 h. The solvent was removed from the resulting yellow-green solution *in vacuo*. The green residue was dissolved in toluene and chromatographed on a neutral alumina/toluene column. The major yellow fraction was eluted with a 10:1 mixture of toluene:acetone. Yield: 0.24 g, 57%. ^{1}H NMR ($CDCl_3$): δ 5.85, 4.85 (2s, each 2H, pyrr), 2.06, 1.58 (2m, each 6H, PEt_3), 1.09 (m, 18H, PEt_3). ^{31}P NMR ($CDCl_3$): δ 37.8 (s, PEt_3). ^{13}C NMR ($CDCl_3$): δ 105.7, 75.4 (2s, pyrr), 20.7 (m, PEt_3), 8.2 (s, PEt_3). EI$^+$ MS: *m*/*z* 439 (M), 321 (M − PEt_3). Anal. Calcd for $C_{16}H_{34}ClNP_2Ru$: C, 43.78; H, 7.81; N, 3.19. Found: C, 43.43; H, 7.72; N, 2.87.

Synthesis of $(NC_4H_4)Ru(PEt_3)_2I$, 5. Complex **4** (0.210 g, 0.478 mmol) and potassium iodide (0.159 g, 0.960 mmol) were combined in 25 mL of degassed 95% ethanol. The mixture was refluxed with stirring for 4 h, and the solvent was removed from the resulting red solution on a rotary evaporator. The red residue was extracted with 2 × 10 mL of toluene, and the combined extracts were concentrated *in vacuo* and chromatographed on a toluene/alumina column. Complex **5** was eluted as a red fraction with a 20:1 mixture of toluene:acetone. A red crystalline solid was obtained after solvent removal. Yield: 0.198 g, 78%. ^{1}H NMR ($CDCl_3$): δ 5.96, 4.55 (2s, each 2H, pyrr), 1.95, 1.31 (2 m, each 6H, PEt_3), 0.88 (m, 18 H, PEt_3). ^{31}P NMR ($CDCl_3$): δ 34.70 (s, PEt_3). FAB$^+$ MS (NOBA): *m*/*z* 530 (M), 412 (M − PEt_3).

Nucleophilic Substitution Reactions. Synthesis of $(2\text{-}PhNC_4H_3)Ru(PEt_3)_2H$, 6a. Complex **4** (0.25 g, 0.57 mmol) was dissolved in 20 mL of tetrahydrofuran, and 1.6 M phenyllithium (0.36 mL, 0.57 mmol) was added dropwise. The yellow-green solution turned orange within 5 min, and the mixture was stirred for 16 h at room temperature. The solvent was removed from the resultant orange solution, and the oily residue was eluted on a toluene/alumina column. Complex **6a** was eluted with toluene as an orange band and after solvent removal was converted to the chloride (*vide infra*). ^{1}H NMR for **6a** (C_6D_6): δ 8.04 (d, 2H, Ph), 7.17 (t, 2H, Ph), 7.03 (t, 1H, Ph), 6.24, 5.46, 5.02 (3s, each 1H, pyrr), 1.30 (m, 12H, PEt_3), 0.92 (m, 18H, PEt_3), −14.22 (t, J = 37 Hz, 1H, RuH). ^{31}P NMR (C_6D_6): δ 55.0 (m, PEt_3). FAB$^+$ MS (glycerol): *m*/*z* 480 (M − H).

Synthesis of $(2\text{-}PhNC_4H_3)Ru(PEt_3)_2Cl$, 6b. The oily, orange residue of **6a** was dissolved in dichloromethane. Pentane was layered on top of the resultant green solution, and the mixture was allowed to stand at room temperature for 1 week. Orange crystals of **6b**, suitable for X-ray diffraction, had formed at this point, and the nearly colorless mother liquor was decanted from the crystals. Yield: 0.075 g, 27%. ^{1}H NMR ($CDCl_3$): δ 7.70 (d, 2H, Ph), 7.33 (t, 2H, Ph), 7.31 (t, 1H, Ph), 5.64, 5.36, 4.71 (3s, each 1H, pyrr), 2.10 1.58 (2m, each 6H, PEt_3), 1.10 (m, 18H, PEt_3). ^{31}P NMR ($CDCl_3$): δ 42.1, 36.5 (AB, J = 47 Hz, PEt_3). ^{13}C NMR (C_6D_6): δ 128.7, 128.4, 128.1 (3s, Ph), 94.5, 75.3, 74.4 (3s, pyrr), 21.1 (m, PEt_3), 9.1 (m, PEt_3). FAB$^+$ MS (NOBA): *m*/*z* 515 (M), 480 (M − Cl). Anal. Calcd for $C_{22}H_{38}ClNP_2Ru$: C, 51.31; H, 7.41. Found: C, 51.69; H, 7.42.

X-ray Diffraction Study of $(2\text{-}PhNC_4H_3)Ru(PEt_3)_2Cl$, 6b. The crystal used was selected from a sample under Paratone oil and mounted on the drawn tip of a glass capillary

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with a small quantity of silicone sealer. This assembly was then placed in the 123 K nitrogen stream of a Rigaku R-Axis II image plate diffractometer at Molecular Structure Corp. Examination of the data frames from the image plate showed the presence of satellite peaks neighboring each indexed reflection. These satellites undoubtedly lead to the large disagreement observed for refinement against all data as collected on a Nicolet P3 instrument.

Data reduction was performed on a Silicon Graphics Indy workstation, and a solution obtained from a preliminary dataset was applied to these structure factors. Final refinement was performed on a Silicon Graphics Indigo2 workstation using a β-release of SHELXTL version 5. The largest peaks in the final difference map were located near the heavy atoms and are likely to be absorption artifacts. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed at calculated distances and allowed to ride on the position of the parent atom. Values for hydrogen thermal parameters were set to be 1.2 times the U_{eq} of the corresponding carbon atom.

Synthesis of (2,5-$Ph_2NC_4H_2$)RuCl(PEt_3)$_2$, 7. Phenyllithium (1.6 M, 0.37 mL, 0.59 mmol) was added to a solution of **6b** (0.305 g, 0.592 mmol) in 25 mL of tetrahydrofuran. The reaction mixture was stirred for 2 h, and the solvent was removed from the orange solution *in vacuo*. The Ru−H product was dissolved in $CHCl_3$ to form the chloride derivative. After 5 min, the solvent was removed and the resulting product was purified by chromatography on a toluene/alumina column. Complex **7** was eluted as an orange band with a 10:1 mixture of toluene:acetone. Yield: 0.085 g, 24%. ^{1}H NMR (C_6D_6): δ 7.98 (d, 4H, Ph), 7.23 (t, 4H, Ph), 7.11 (t, 2H, Ph), 5.05 (s, 2H, pyrr), 1.79 (m, 6H, PEt_3), 1.31 (m, 6 H, PEt_3), 0.90 (m, 18H, PEt_3). ^{31}P NMR (C_6D_6): δ 35.4 (s, PEt_3). FAB$^+$ MS: *m/e* 591 (P), 556 (P − Cl), 473 (P − PEt_3), 436 (P − PEt_3, Cl). Anal. Calcd for $C_{28}H_{42}ClNP_2Ru$: C, 56.90; H, 7.11. Found: C, 56.97; H, 7.10.

Syntheses of (2-$MeNC_4H_3$)Ru(PEt_3)$_2$H and (2-$MeNC_4H_3$)Ru(PEt_3)$_2$Cl. Complex **4** (0.12 g, 0.27 mmol) was dissolved in 15 mL of tetrahydrofuran, and the solution was cooled to 0 °C. MeLi (1.2 M, 0.22 mL, 0.27 mmol) was added dropwise with stirring. The reaction mixture was stirred at room temperature for 16 h, and the solvent was removed *in vacuo* providing a brown residue. A concentrated toluene solution of the residue was chromatographed on an alumina column. A yellow fraction was eluted with 10:1 toluene:acetone and was found to be (2-Mepyrr)RuH(PEt_3)$_2$, which was isolated as an oily, yellow solid. Approximate yield: 0.035 g, 31%. ^{1}H NMR (C_6D_6): δ 5.92, 4.90, 4.59 (3s, each 1H, pyrr), 2.53 (s, 3H, pyrrMe), 1.98, 1.39 (2m, each 6H, PEt_3), 1.02 (m, 18H, PEt_3), −13.45 (t, J = 35 Hz, 1H, RuH). ^{31}P NMR (C_6D_6): δ 59.5, 55.0 (2m, PEt_3). FAB$^+$ MS (NOBA): *m/z* 419 (M).

(2-$MeNC_4H_3$)RuH(PEt_3)$_2$ (0.035 g, 0.16 mmol) was dissolved in 10 mL of chloroform. The brown solution was stirred for 5 min, and the solvent was removed *in vacuo*. A concentrated toluene solution of the residue was chromatographed on a toluene/alumina column, and a yellow band was eluted with a 10:1 mixture of toluene:acetone. The product (2-$MeNC_4H_3$)RuCl(PEt_3)$_2$ was isolated as a yellow residue. Yield: 0.009 g, 24%. ^{1}H NMR ($CDCl_3$): δ 5.37, 4.74, 4.51 (3s, each 1H, pyrr), 2.12, 2.01, 1.61, 1.50 (4m, each 3H, PEt_3), 1.98 (s, 3H, pyrrMe), 1.08 (m, 18H, PEt_3). ^{31}P NMR ($CDCl_3$): δ 42.5, 35.0 (AB, J = 44 Hz, PEt_3). ^{13}C NMR ($CDCl_3$): δ 90.9, 79.8, 76.9, 73.1 (4s, pyrr), 20.8 (m, PEt_3), 14.7 (s, pyrrMe), 8.3 (m, PEt_3). EI$^+$ MS: *m/z* 453 (M), 335 (M − PEt_3). Anal. Calcd for $C_{17}H_{36}ClNP_2Ru$: C, 45.08; H, 7.45. Found: C, 45.14; H, 7.87.

Synthesis of [2-(NMe_2)NC_4H_3]RuH(PEt_3)$_2$ and [2-(NMe_2)-NC_4H_3]RuCl(PEt_3)$_2$. Complex **4** (0.102 g, 0.23 mmol) and lithium dimethylamide (0.012 g, 0.24 mmol) were combined in 10 mL of tetrahydrofuran. The yellow solution was stirred for 16 h, and the solvent was removed from the resultant orange solution *in vacuo*. The resulting hydride product was identified by NMR spectroscopy. ^{1}H NMR (C_6D_6): δ 5.91, 5.14, 3.93 (3s, each 1H, pyrr), 2.53 (s, 6H, NMe_2), 1.40 (m, 12H, PEt_3), 0.92 (m, 18H, PEt_3), −12.61 (m, 1H, RuH). ^{31}P NMR (C_6D_6): δ 61.3, 53.9 (m, PEt_3). EI$^+$ MS: *m/z* 448 (M). Some starting material and another compound, tentatively formulated as (pyrr)RuH(PEt_3)$_2$, were also present in the crude reaction mixture. However, NMR resonances were shifted compared to those of the isolated hydride (see below). ^{1}H NMR (C_6D_6): δ 6.03, 5.02 (2s, each 2H, pyrr), 1.25 (m, 12H, PEt_3), 0.98 (m, 18H, PEt_3), −14.86 (t, J = 35 Hz, 1H, RuH). ^{31}P NMR (C_6D_6): δ 55.82 (d, PEt_3).

The crude mixture of hydride products was dissolved in 15 mL of chloroform and stirred for 5 min at room temperature. The solvent was removed from the brown solution, and the residue was chromatographed on an alumina/toluene column. The first yellow fraction contained the desired product and was eluted with a 20:1 mixture of toluene:acetone. Yield: 0.024 g, 22%. ^{1}H NMR (C_6D_6): δ 5.22, 4.39, 4.09 (3s, each 1H, pyrr), 2.10 (s, 6H, NMe_2), 2.00, 1.86, 1.46, 1.17 (4m, each 3H, PEt_3), 1.05, 0.89 (2m, each 9H, PEt_3). ^{31}P NMR (C_6D_6): δ 45.7, 35.4 (AB pattern, J = 45 Hz, PEt_3). Anal. Calcd for $C_{18}H_{39}ClN_2P_2Ru$: C, 44.85; H, 8.09. Found: C, 44.48; H, 7.87.

A second yellow fraction was eluted with a 10:1 mixture of toluene:acetone and was identified as the starting reagent **4**. Yield: 29%.

Reaction of 4 with $LiBEt_3H$ and $LiBEt_3D$. Complex **4** (0.118 g, 0.269 mmol) was dissolved in 20 mL of tetrahydrofuran. The hydride reagent (1 M in THF) (0.27 mL, 0.269 mmol) was added dropwise, and the solution was stirred at room temperature under nitrogen for 8 h. The solvent was removed from the resultant yellow solution *in vacuo*, yielding a yellow oil, which was formulated as (η^5-NC_4H_4)Ru(PEt_3)$_2$H. ^{1}H NMR (C_6D_6): δ 5.84, 4.85 (2 s, each 2 H, pyrr), 1.34, 1.19 (2 m, each 6 H, PEt_3), 0.81 (m, 18 H, PEt_3), −16.58 (t, 1 H, Ru−H). ^{31}P NMR (C_6D_6): δ 48.93 (m, PEt_3). FAB MS: *m/e* 404 (m). The same procedure was followed for the reaction of **4** with $LiBEt_3D$ to form (η^5-NC_4H_3D)Ru(PEt_3)$_2$H. ^{1}H NMR (C_6D_6): same as above, but the resonance at δ 5.84 is reduced in intensity. ^{2}H NMR ($CDCl_3$): δ 5.87 (s, pyrr). No resonance observed in hydride region.

Synthesis of (η^5-2-CN(Me)CH)NC_4H_3)Ru(PEt_3)$_2$H. (η^5-NC_4H_4)Ru(PEt_3)$_2$I, **5**, (0.342 g, 0.645 mmol) was dissolved in 25 mL of THF and cooled to −78 °C. A solution of LiCH(Me)-CN in 10 mL of THF, prepared *in situ* at −78 °C (0.139 g, 2.26 mmol), was added dropwise. The mixture was allowed to warm to room temperature and stirred for 14 h. The solvent was removed from the resultant orange solution, and the ^{1}H NMR spectrum of the residue was recorded. The spectrum showed resonances for unreacted **5** (60%) and for two new products, which were tentatively identified as diasteromers of 2-((CH(Me)CN)C_4H_3N)RuH(PEt_3)$_2$. Attempts to isolate these products by chromatography on an alumina column led to decomposition of the hydride derivatives. ^{1}H NMR (both isomers, C_6D_6): δ 6.00, 5.96, 5.18, 5.13, 4.73, 4.69 (6 s, each 1 H, pyrr), 3.84 (q, CHMeCN) (second quartet may be obscured by THF (solvent) resonance), 1.66 (d, 6 H, Me), 1.41, 1.15 (2m, each 18 H, PEt_3), 0.92 (m, 36 H, PEt_3), −12.94, −13.01 (2 t, each 1 H, RuH). ^{31}P NMR (C_6D_6): δ 54.32, 59.64 (2 m, PEt_3). Attempts to convert the hydride product to the chloride derivative with chloroform or CH_2Cl_2 over a period of 1 day were not successful.

Reaction of (η^5-C_4H_4N)RuCl(PEt_3)$_2$ with NaSMe. Complex **4** (0.055 g, 0.125 mmol) and sodium methylthiolate (0.018 g, 0.257 mmol) were combined in 5 mL of tetrahydrofuran. The mixture was stirred at 45 °C for 2 days, and the solvent was removed from the resultant brown solution *in vacuo*. The NMR spectrum showed the presence of starting material and a small amount (ca. 20%) of a new product, which was tentatively identified as (η^5-C_4H_4N)Ru(SMe)(PEt_3)$_2$. There was no evidence for nucleophilic attack at the pyrrolyl ring. ^{1}H NMR (C_6D_6): δ 5.95, 4.75 (2s, each 2H, pyrr), 2.65 (s, 3H, SMe),

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2.10, 1.82 (2m, each 6H, PEt_3), 0.91 (m, 18H, PEt_3). ^{31}P NMR (C_6D_6): δ 39.1 (s, PEt_3). FAB^+ MS (glycerol): *m/z* 451 (M).

Reaction of (η^5-C_4H_4N)RuCl(PEt_3)$_2$ with LiS-*t*-Bu. Complex **6** (0.039 g, 0.089 mmol) and lithium *tert*-butylthiolate (0.009 g, 0.09 mmol) were combined in 5 mL of tetrahydrofuran and stirred at 45 °C for 2 days. The solvent was removed from the resultant brown solution, and the residue was examined via NMR spectroscopy. The major portion was unreacted **6** (ca. 50%), but a new product (ca. 30%) was present along with unidentified impurities. ^1H NMR for (η^5-C_4H_4N)RuS^{t}Bu(PEt_3)$_2$ (C_6D_6): δ 6.15, 4.79 (2s, each 2H, pyrr), 1.69 (s, 9H, S^{t}Bu), 1.88, 1.28 (2m, each 6H, PEt_3), 0.92 (m, 18H, PEt_3). ^{31}P NMR (C_6D_6): δ 37.1 (s, PEt_3). FAB^+ MS (glycerol): *m/z* 493 (M).

Attempted Reaction of 4 with Alkoxides. Complex **4** (0.019 g, 0.043 mmol) and a molar excess of NaOR (R = Me, 1.2 equiv, or R = *t*-Bu, ca. 5 equiv) were combined in 5 mL of tetrahydrofuran. The solution was heated at 45 °C in an oil bath for 2 days. No evidence for a reaction was seen by NMR.

Nucleophilic Substitutions of Triphenylphosphine Derivatives. Synthesis of (2-MeNC$_4$H$_3$)RuH(PPh_3)$_2$ and (2-MeNC$_4$H$_3$)RuI(PPh_3)$_2$. (η^5-NC_4H_4)Ru(PPh_3)$_2$I, **3** (0.027 g, 0.033 mmol), was dissolved in 10 mL of tetrahydrofuran. Methyllithium (1.2 M, 0.035 mL, 0.029 mmol) was added to the orange solution. The reaction mixture slowly (ca. 30 min) became yellow, and the reaction mixture continued to stir for 16 h. The solvent was removed *in vacuo*, providing a orange-yellow, oily residue. ^1H NMR (C_6D_6): δ 7.65, 7.53 (2m, each 6H, PPh_3), 6.95 (m, 18H, PPh_3), 5.19, 4.90, 4.87 (3s, each 1H, pyrr), 2.10 (s, 3H, pyrrMe), −14.12 (t, J = 34 Hz, 1H, RuH). ^{31}P NMR (C_6D_6): δ 68.5, 66.7 (2m, PEt_3). FAB^+ MS (NOBA): *m/z* 706 (M − H), 626 (M − H − Mepyrr), 444 (M − H − PPh_3).

This product was converted to the iodide complex by the following procedure. Iodine (0.036 g, 0.14 mmol) was added to a slurry of the crude hydride product and potassium carbonate (0.5 g) in dichloromethane. The solution immediately became dark orange as the iodine dissolved and was stirred for an hour. The solvent was removed *in vacuo*, yielding a dark brown residue. ^1H NMR ($CDCl_3$): δ 7.40, 7.33, 7.21, 7.12 (4m, PPh_3), 4.90, 4.54, 3.18 (3s, each 1H, pyrr), 2.25 (s, 3H, Me). ^{13}C NMR ($CDCl_3$): δ 137.6 (m, PPh_3), 134.0 (m, PPh_3), 128.8 (m, PPh_3), 126.9 (m, PPh_3), 102.3, 76.8 (2s, pyrr), 84.7 (s, pyrr), 14.0 (s, Me). ^{31}P NMR (C_6D_6): δ 45.2, 41.7 (2d, J = 44 Hz, PEt_3). FAB^+ MS (NOBA): *m/z* 834 (M + H), 754 (M − Mepyrr), 707 (M − I).

Synthesis of (2-BuNC$_4$H$_3$)RuCl(PPh_3)$_2$. Complex **1** (2.00 g, 2.75 mmol) was dissolved in 25 mL of tetrahydrofuran. *n*-Butyllithium (1.2 M, 2.29 mL, 2.75 mmol) was added dropwise, and the solution was stirred at room temperature for 4 h. The solvent was removed *in vacuo*, and the red oil was dissolved in $CHCl_3$ and stirred for 5 min to convert the hydride product to the chloride. The solvent was removed, and the oil was eluted as a red band on a toluene/alumina column with a 10:1 mixture of toluene:acetone. Yield: 0.75 g, 35%. ^1H NMR ($CDCl_3$): δ 7.73, 7.64 (2m, each 6H, PPh_3), 5.13, 4.59, 3.24 (3s, each 1H, pyrr), 2.92, 1.81, 1.41 (3m, 2H each, Bu), 0.90 (t, 3H, Bu). ^{31}P NMR ($CDCl_3$): δ 45.2, 43.2 (AB, PPh_3).

No reaction of **1** was observed with PhLi or $LiEt_3BH$ at room temperature or with MeLi at 60 °C.

Reaction of (2-PhNC$_4$H$_3$)RuH(PEt_3)$_2$, 6a, with HCl and Isolation of 2-Phenylpyrrole. Complex **6a** (0.079 g, 0.15 mmol) was dissolved in 10 mL of tetrahydrofuran. Hydrogen chloride gas was then passed through the solution for 1 min. The orange solution immediately became red-brown, and the solvent was removed after 5 min. The residue was redissolved in toluene and loaded onto an alumina column. Toluene, 150 mL, followed by 150 mL of diethyl ether was passed through the column to elute crude 2-phenylpyrrole as a tan solid in near quantitative yield. The product was identified by ^1H NMR spectroscopy (see below). A yellow band, presumably containing the ruthenium residue, remained behind on the column. The 2-phenylpyrrole could be further purified by sublimation; however, this reduced the yield to ca. 0.10 g, 45%. ^1H NMR ($CDCl_3$): δ 8.50 (br s, 1H, NH), 7.47 (d, 2H, Ph), 7.35 (t, 2H, Ph), 7.18 (t, 1H, Ph), 6.86, 6.51, 6.28 (3s, each 1H, pyrr). EI^+ MS: *m/z* 143 (M).

Reaction of (2-BuNC$_4$H$_3$)Ru(PPh_3)$_2$Cl with HCl and Regeneration of 1. (2-BuNC$_4$H$_3$)RuCl(PPh_3)$_2$Cl (0.242 g, 0.309 mmol) was dissolved in 20 mL of THF. Hydrogen chloride was bubbled through the solution for 15 s, resulting in a deep red solution. The solvent was evaporated *in vacuo*, and the neutral pyrrole, 2-BuHNC$_4$H$_3$, was extracted from the red residue with 5 × 5 mL of diethyl ether and identified by NMR spectroscopy. Yield: 65%. ^1H NMR (C_6D_6): δ 7.65 (br, 1 H, NH), 6.37, 6.29, 6.08 (br, 1 H each, pyrr), 2.3, 1.63, 0.72 (m, Bu).

PPh_3 (0.154 g, 0.587 mmol) was added to the remaining yellow residue, and the mixture was refluxed in methanol for 18 h. A red-brown precipitate formed, which was identified by NMR spectroscopy as $RuCl_2(PPh_3)_3$. Yield: 0.110 g, 37%. After the product was washed with 2 × 5 mL of hexane, pyrrolyllithium was added (0.018 g, 0.246 mmol) and the mixture was dissolved in toluene. The solution was refluxed for 3 h, then the solvent was removed and the product, **1**, was purified by chromatography as described above. Yield: 0.075 g, 33%.

Synthesis of [(NC_4H_4)Ru(PEt_3)$_3$]PF_6. Complex **4** (0.497 g, 0.683 mmol) and $LiPF_6$ (0.10 g, 0.69 mmol) were dissolved in 125 mL of degassed 95% ethanol. Triethylphosphine (0.80 mL, 5.5 mmol) was added, and the solution refluxed while stirring under nitrogen for 2 h. The initial orange solution had become pale yellow. The solvent was removed *in vacuo*, and a concentrated dichloromethane solution of the residue was layered with pentane to precipitate the product as a light gray solid. Yield: 0.565 g, 75%. ^1H NMR ($CDCl_3$): δ 6.15, 5.62 (2s, each 2H, pyrr), 1.82 (m, 18H, PEt_3), 1.16 (m, 27H, PEt_3). ^{31}P NMR ($CDCl_3$): δ 30.0 (s, PEt_3), −64.39 (PF_6^-). FAB^+ MS (NOBA): *m/z* 521 (M^+), 404 (M^+ − PEt_3). Anal. Calcd for $C_{22}H_{49}NP_2F_6Ru$: C, 39.66; H, 7.36. Found: C, 39.40; H, 7.32.

Synthesis of [(NC_4H_4)Ru(PEt_3)$_2$(CO)]PF_6. Complex **4** (0.125 g, 0.285 mmol) and $LiPF_6$ (0.045 g, 0.296 mmol) were dissolved in 15 mL of tetrahydrofuran, and the mixture was warmed to 65 °C. Carbon monoxide gas was then bubbled through the solution for 5 h in a fume hood. The initial orange solution changed to pale yellow. The solvent was removed *in vacuo*, and the residue was purified via recrystallization with dichloromethane/diethyl ether to yield a white powder. Yield: 0.103 g, 63%. ^1H NMR (DMSO): δ 6.90, 6.26 (2 s, each 2 H, pyrr), 1.98, 1.88 (2 m, each 6 H, PEt_3), 1.05 (m, 18 H PEt_3). ^{31}P NMR (DMSO): 41.5 (br, PEt_3). FAB^+ MS (NOBA): *m/e* 421 (M^+), 303 (M^+ − CO). IR (KBr): 1968 cm^{-1} (ν_{CO}). Anal. Calcd for $C_{17}H_{34}NOPF_6Ru$: C, 35.42; H, 5.89. Found: C, 35.22; H, 5.66.

Synthesis of [(η^5-NC_4H_4)Ru($NCCH_3$)(PEt_3)$_2$]BPh_4. Complex **4** (0.242 g, 0.551 mmol) and sodium tetraphenylborate (0.375 g, 1.10 mmol) were dissolved in 15 mL of EtOH. Acetonitrile (0.057 mL, 1.10 mmol) was syringed into the solution, which was stirred for 14 h. The orange color changed to green, and an off-white precipitate formed. The solid was filtered and washed with 3 × 10 mL of EtOH. Yield: 0.247 g, 58%. ^1H NMR ($CDCl_3$): δ 7.33 (m, 8H, BPh_4), 6.91 (t, 8 H, BPh_4), 6.76 (t, 4 H, BPh_4), 6.24, 5.36 (2s, each 2 H, pyrr), 2.57 (s, 3 H, CH_3CN), 2.03, 1.82 (2 m, each 6 H, PEt_3), 1.13 (m, 18 H, PEt_3). ^{31}P NMR ($CDCl_3$): δ 37.8 (PEt_3). FAB^+ MS (NOBA): *m/z* 443 (M), 404 (M − CH_3CN). Anal. Calcd for $C_{42}H_{57}N_2PBRu$: C, 66.10; H, 7.47. Found: C, 65.85; H, 7.68.

Synthesis of [(HNC_4H_4)RuCl(PPh_3)$_2$]OTf. Complex **1** (0.100 g, 0.138 mmol) was dissolved in 10 mL of toluene. Trifluoromethanesulfonic acid (0.012 mL, 0.14 mmol) was added, and the solution stirred for 14 h. The solvent was removed *in vacuo*. Yield: 0.102 g, 84%. Attempts at purification via recrystallization with dichloromethane/pentane and chromatography with a toluene/alumina column both led to decomposition of the product via loss of pyrrole. ^1H NMR

($CDCl_3$): δ 7.36−7.00 (br m, 30H, PPh_3), 6.32, 4.62 (2s, each 2H, pyrr). ^{31}P NMR ($CDCl_3$): δ 37.9 (s, PPh_3). FAB^+ MS (NOBA): *m/z* 728 (M − OTf), 727 (M − HOTf).

Synthesis of [(1-Me-NC_4H_4)$RuCl(PPh_3)_2$]OTf. Complex **1** (0.16 g, 0.22 mmol) was dissolved in 13 mL of toluene. Methyl trifluoromethanesulfonate (0.026 mL, 0.22 mmol) was added dropwise, and the solution stirred for 1 h. A pale orange, crystalline precipitate formed, and the colorless solvent was removed by cannula. Yield: 0.050 g, 26%. ^1H NMR ($CDCl_3$): δ 7.33−7.20 (m, 30H, PPh_3), 6.30, 4.75 (2s, each 2H, pyrr), 2.21 (s, 3H, NMe). ^{31}P NMR ($CDCl_3$): δ 37.3 (s, PPh_3).

Attempted Reactions of $RuCl_2(PPh_3)_3$ with (Tetramethylpyrrolyl)lithium and (2-Acetylpyrrolyl)lithium. $RuCl_2(PPh_3)_3$ (0.017 g, 0.018 mmol) and (tetramethylpyrrolyl)lithium (0.003 g, 0.023 mmol) were combined in 0.6 mL of C_6D_6 in an NMR tube. The tube was flame-sealed under vacuum and placed in a 45 °C oil bath. NMR spectroscopy showed no evidence of tetramethylpyrrole coordination after 3 days. In a similar procedure, no reaction was observed with (2-acetylpyrrolyl)lithium.

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Supporting Information Available: Tables of data collection and refinement details, atomic coordinates, bond distances and angles, hydrogen atom coordinates, and thermal parameters for **1** and **6b** (23 pages). Ordering information is given on any current masthead page.

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