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The activation of η^5-pyrrole complexes toward nucleophilic attack

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Contents

Abstract

Pyrrole is a five-membered aromatic heterocycle in which the nitrogen lone pair is delocalized over the π system of the ring. As a result of this π electron rich character, it reacts readily with electrophiles, but is not susceptible to nucleophilic attack. The η^5-coordination of pyrrole or of the pyrrolyl anion to certain transition metal fragments activates the heterocycle toward nucleophilic substitution or addition reactions. In the pyrrolyl complexes $(C_4H_4N)Re(PPh_3)_2(H)(I)$ and $(C_4H_4N)Ru(PEt_3)_2Cl$, nucleophilic substitution reactions at the 2-position of the ring follow a pathway that involves hydrogen transfer from the ring to

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the metal ion with displacement of a labile halide ligand from the metal center. Nucleophilic addition of hydride and methoxide anions to the neutral pentamethylpyrrole ligands in $[(MeNC_4Me_4)M(cymene)](OTf)_2$, M = Ru and Os, has been found to occur at the α carbon atom of the heterocycle. However, reactions of other pyrrole sandwich complexes with nucleophiles may display competing reaction sites. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Arene activation; Pyrrole; Nucleophilic substitution; Nucleophilic addition

1. Introduction

It has been well established that the η^6-coordination of an arene ring to an appropriate transition metal fragment activates the ring to nucleophilic attack. Both nucleophilic addition and substitution reactions have been characterized for η^6-arene ligands as well as for η^6-coordinated polycyclic ring systems [1]. The nucleophilic activation has also been extended to η^6-arene ligands containing fused heterocycles, such as indoles [2–12], indolines [2,13], benzothiophenes [14,15] and mono- and dibenzofuran [2,16]. The general topic of nucleophilic activation of arenes has been reviewed in detail [17–19].

The η^5-coordination of aromatic five-membered rings to a transition metal also has the potential to activate the ligand toward nucleophilic attack, and this has been amply demonstrated with metal complexes of neutral η^5 ligands such as thiophenes [20,21]. Several examples of nucleophilic addition to the anionic η^5-cyclopentadienyl ligand have also been reported [22–28]. However, even though many η^5-pyrrole or pyrrolyl complexes have been synthesized [29–33], relatively few examples of the activation of this coordinated heterocycle toward nucleophilic attack have been reported. Two major problems have been identified in the nucleophilic activation of pyrrole. The first is that pyrrole is the most electron-rich of the common five-membered aromatic heterocycles, and it is in general less susceptible to activation toward nucleophiles [34]. A second problem is that many η^5-complexes have been found to be less kinetically stable than their cyclopentadienyl analogs [29,30]. The tendency for pyrrolyl rearrangements from η^5 to η^1 bonding or for decomposition via pyrrole ligand dissociation has, in many cases, limited useful reactivity studies on these heterocycles. Nevertheless, it may be anticipated that the coordination of pyrrole by appropriate metal fragments will lead to useful synthetic manipulations of this ring system.

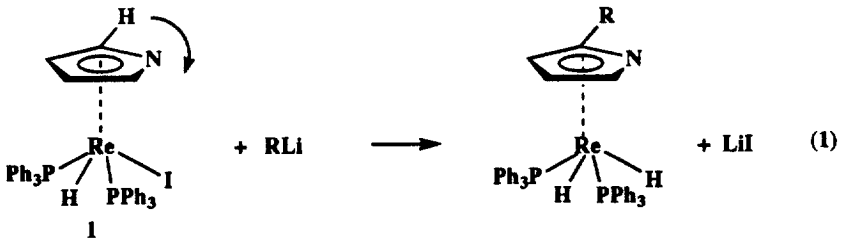
The activation of pyrrole toward nucleophilic attack by reversible metal ion coordination is of particular interest because this type of reaction would provide a basis for a more versatile and flexible approach to the synthesis of natural products and biologically active molecules that incorporate the pyrrole ring. In addition to the incorporation of pyrroles into large molecules such as porphyrins, chlorophylls and prodigiosins, certain substituted pyrroles have been found to show activity as analgesics and anti-inflammatory drugs [35,36]. Aminopyrroles are included in an important class of antibiotics with a wide range of biological activities. Derivatives of 1-vinyl pyrroles with substituents at α and/or β positions have also found applica-

tions as antibiotics. In addition, appropriately substituted pyrroles have been useful in the syntheses of substituted indoles, which are important in natural product syntheses [37,38]. New routes to regioselectively-substituted pyrroles through nucleophilic attack would expand the synthetic methods available for the syntheses of these derivatives. In this paper, we review the known reactions of η^5-pyrrole and pyrrolyl complexes with nucleophiles, and assess the factors which make these systems feasible for the nucleophilic activation of pyrrole.

2. Nucleophilic substitution reactions of η^5-pyrrolyl ligands

2.1. Pyrrolyl complexes of rhenium

The first well defined transition metal system which promoted the nucleophilic substitution at an η^5-pyrrolyl ligand was reported by Felkin and Zakrzewski in 1989 [39,40] and further developed by Zakrzewski [41–43]. The complex (η^5-pyrrolyl)$Re(PPh_3)_2(H)(I)$, **1**, was prepared by the reaction of $ReH_7(PPh_3)_2$ with lithium pyrrole, followed by reaction with I_2/K_2CO_3 [39,40]. Complex **1** reacted with alkyl and aryl lithium reagents as shown in Eq. (1), and the products have been characterized spectroscopically. The reaction has been



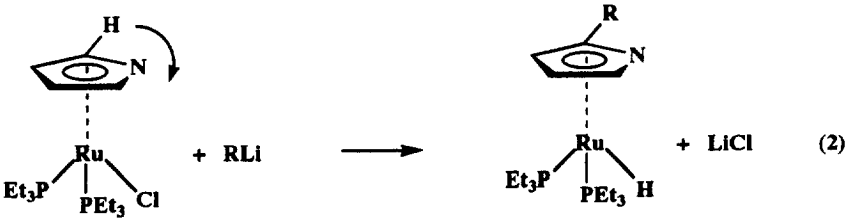
reported for the lithium reagents with R = Me, *n*-Bu, *t*-Bu, Ph and 5-methyl-2-furyl. The nucleophilic attack on the pyrrolyl ring is accompanied by hydrogen transfer from the ring to the metal ion and the loss of the iodide ligand. Similar nucleophilic substitutions of η^5-cyclopentadienyl ligands accompanied by hydrogen transfer to the metal ion have been proposed previously [25,44,45]. However, detailed mechanistic studies of this reaction type have not been carried out.

Although the resulting dihydride complex in Eq. (1) does not react with nucleophiles, this product can be converted back to an iodide complex by further reaction with I_2/K_2CO_3. Addition of a second equivalent of alkyl or aryl lithium leads to the formation of complexes with a disubstituted pyrrolyl ring. Spectroscopic data have been used to assign the regiochemistry of the 2,5-substituted derivatives.

Several approaches have been developed for removing the substituted pyrrole ring from the rhenium complex. These include reactions with electrophiles, such as methyl triflate or triflic acid in the presence of a donor solvent such as DMSO [42]. Acylation of the pyrrolyl nitrogen also results in facile dissociation of the heterocycle [43]. The fate of the rhenium-containing fragment in these reactions has not been discussed.

2.2. Pyrrolyl complexes of ruthenium

A second system that promotes the nucleophilic substitution of η^5-pyrrolyl ligands has been reported recently [46]. The complex $(\eta^5\text{-}NC_4H_4)Ru(PPh_3)_2Cl$, **2**, is prepared by the reaction of commercially available $Ru(PPh_3)_3Cl_2$ with pyrrolyl lithium. Several related derivatives have been prepared by phosphine substitution reactions in toluene and by halide substitution reactions carried out in ethanol. These synthetic conditions are very similar to those reported for the extensively studied cyclopentadienyl analogs $CpRu(PR_3)_2X$ [47]. The complex $(\eta^5\text{-}NC_4H_4)Ru(PEt_3)_2X$, **2**, where X=Cl or I, reacts with a range of alkyl or aryl lithium reagents. In a pathway similar to that of the rhenium system described above, the reaction involves a transfer of hydrogen from the pyrrolyl ring to the ruthenium ion to form the hydride ruthenium complex with a substituted η^5-pyrrolyl ligand, Eq. (2). The hydride products, which have been characterized spectroscopically, react in chloroform



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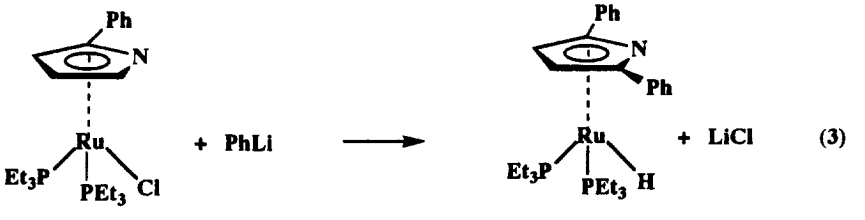
or dichloromethane solutions to form the corresponding chloride products. The chloride derivative with a phenyl-substituted pyrrolyl ligand has been characterized by an X-ray diffraction study [46], Fig. 1. The structure confirms that the substitution has occurred on an α position of the ring. The heterocycle is oriented so that the phenyl substituent is directed over the chloride ligand and away from the bulkier phosphine ligands. The plane of the phenyl ring is rotated relative to that of the pyrrole ring, and the angle between the normals to the two rings is 21°. The structural parameters of the planar heterocycle are similar to those identified for the unsubstituted parent compound, **2** [46].

The complex $(2\text{-}Ph\text{-}C_4H_3N)Ru(PEt_3)_2Cl$, **3**, reacted with a second equivalent of phenyl lithium to produce the ruthenium hydride complex with the 2,5-disubstituted ligand, Eq. (3) [46]. Reaction with chloroform led to the formation of the chloride



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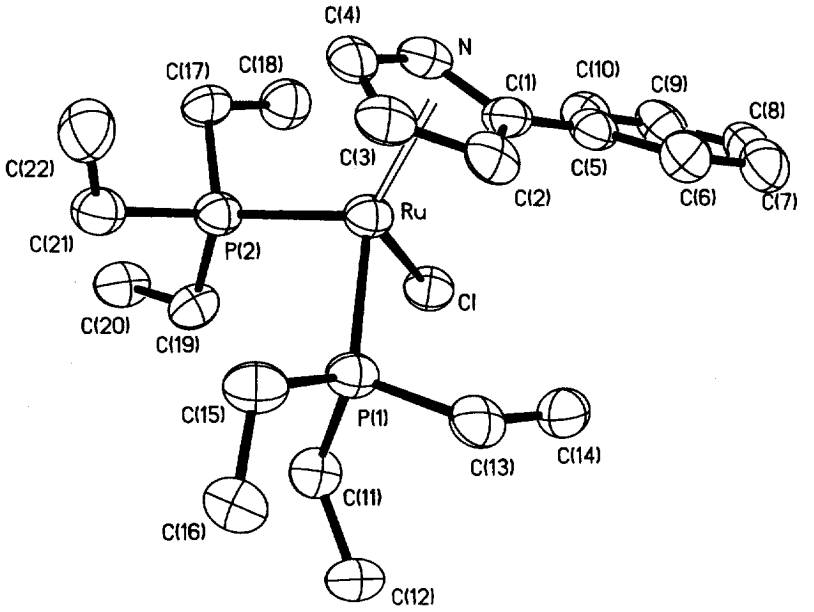


Fig. 1. Perspective drawing of the nucleophilic substitution product (η^5-2-Ph–NC_4H_3)Ru(PEt_3)$_2$Cl. Taken from Ref. [46], reprinted with permission from the American Chemical Society.

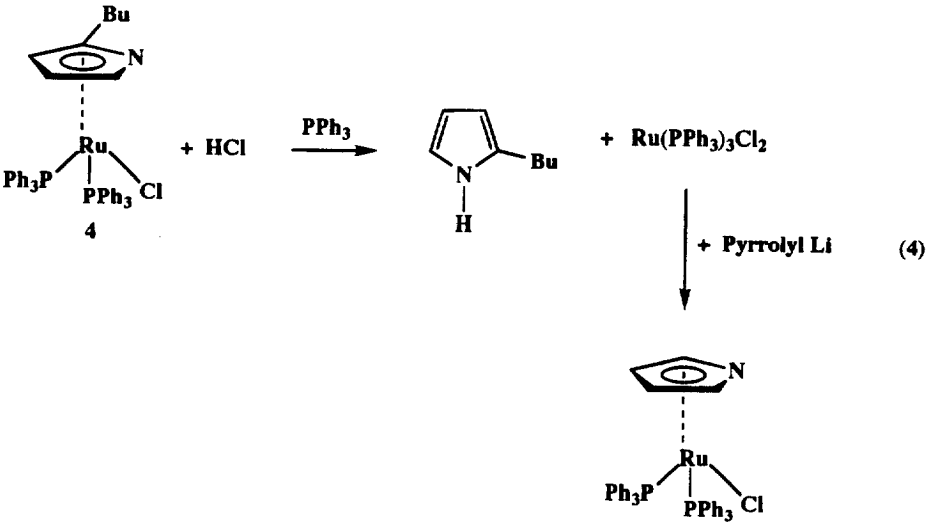
analog (2,5-Ph_2–C_4H_2N)Ru(PEt_3)$_2$Cl, which was isolated and characterized by spectroscopic methods. Conversion of the hydride ligand to the more substitutionally labile chloride is necessary before a second nucleophilic substitution on the pyrrolyl ligand can be effected.

The activation of the pyrrolyl ligand in the ruthenium systems depends on the nature of the phosphine and halide ligands in the complex. For example, (η^5-NC_4H_4)Ru(PPh_3)$_2$Cl did not react with PhLi or MeLi, but a substitution reaction was observed for BuLi [46]. The iodide derivative was found to be somewhat more reactive and a substitution reaction with MeLi was observed. The triethylphosphine derivatives were more effective at activating the pyrrolyl ligand toward nucleophilic attack, and a broader range of reagents, RLi, were successfully used in reactions with (η^5-NC_4H_4)Ru(PEt_3)$_2$X, X=Cl, I. Reactants included RLi where R=Bu, Me, Ph, CHMe(CN), NMe_2, as well as $NaBEt_3H$ and RMgCl reagents. In contrast, the reaction with thiolate anions resulted in halide substitution and thiolate coordination to the metal ion, while no reaction was observed with MeO^- or t-BuO^- salts [46].

The greater range of reactivity observed for the triethylphosphine derivatives, compared to the triphenylphosphine complexes, is somewhat surprising since the more basic trialkylphosphine might be expected to reduce the nucleophilic activation of the pyrrolyl ring. The enhanced reactivity is attributed to the ability of the more basic ligand to promote the loss of the halide ligand, and thereby facilitate hydrogen transfer from the pyrrolyl ring. In previous studies of related cyclopentadienyl

derivatives, the rate of halide substitution was found to increase as a function of the basicity of the phosphine ligand [48]. Further studies of the ruthenium pyrrolyl derivatives are warranted in order to determine the phosphine characteristics which maximize the reactivity of the pyrrolyl ring.

The substituted pyrrolyl ligands have been removed from the ruthenium chloride complexes by protonation with HCl [46]. For example, when gaseous HCl was bubbled through a THF solution of (2-*n*-Bu–C_4H_3N)Ru(PPh_3)$_2$Cl, **4**, for 15 s, the free substituted heterocycle was formed. This product was extracted from the reaction solution with ether and isolated in 65% yield. Addition of triphenylphosphine to the ruthenium-containing residue led to the formation of Ru(PPh_3)$_3$Cl$_2$ and this product was converted to the η^5-pyrrolyl derivative by further reaction with pyrrolyl lithium, Eq. (4).



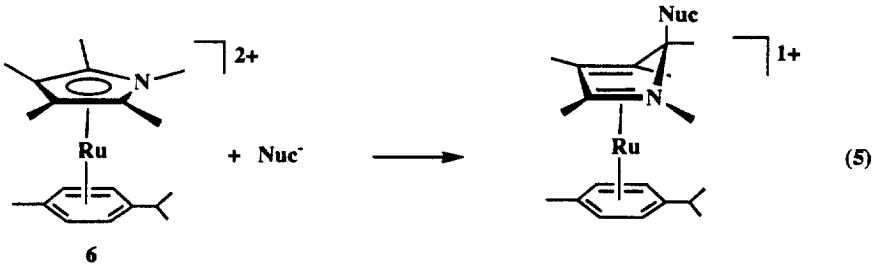
3. Nucleophilic additions to η^5-pyrrole ligands

3.1. Pyrrole complexes of ruthenium and osmium

The pyrrolyl substitution reactions described above proceeded rapidly, and the initial nucleophilic addition product has not been detected in these systems. However, nucleophilic addition to a neutral η^5-pyrrole ligand has been characterized in related ruthenium, osmium and rhenium complexes. Sandwich complexes of ruthenium- and osmium-containing tetramethylpyrrole and pentamethylpyrrole have been prepared with the formulas [(cymene)M(NC_4Me_4)]OTf, **5**, and [(cymene)M($MeNC_4Me_4$)](OTf)$_2$, **6**, (M=Ru, Os) [49]. Attempts to prepare the analogous complexes with unsubstituted pyrrole ligands were unsuccessful because the electrophilic (cymene)M^{+2} fragments appeared to promote polymerization of the unsubstituted pyrrole ring. The use of the alkylated pyrrole ligands has been

observed previously to stabilize η^5-pyrrole and pyrrolyl complexes because of their greater steric bulk and greater electron donation to the metal ion [30].

The pentamethylpyrrole ligand in the dicationic complexes **6** was found to react with nucleophiles, such as MeO^-, OH^- and H^- to give nucleophilic addition products, as shown in Eq. (5) for the ruthenium derivative. These products were



(5)

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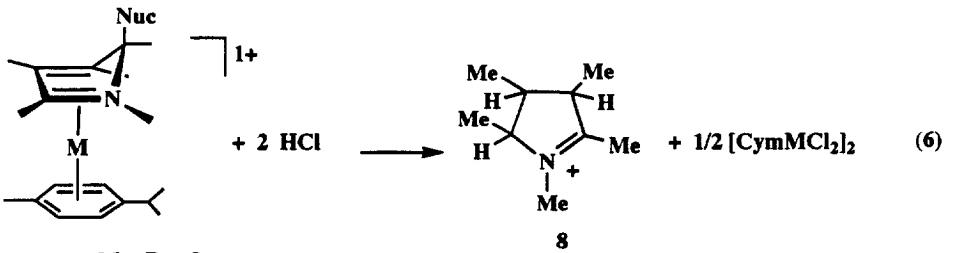
isolated and purified by column chromatography, and their structures were assigned on the basis of one- and two-dimensional NMR spectroscopy. For example, for the product of hydride addition to the ruthenium complex, five inequivalent pyrrole methyl resonances were observed, and one of these (at 1.4 ppm) was split into a doublet; the resonance for the added hydride was observed as a quartet at 4.18 ppm [49].

An X-ray diffraction study of the hydride addition product, $[(cymene)Ru(MeNC_4Me_4–H)]^+$, **7**, was carried out, and a perspective drawing of the cation is shown in Fig. 2 [49]. Although the hydride nucleophile was not located directly, it is clear from the distortion of the heterocycle that the hydride addition occurred at an α carbon of the pyrrole ring in the *exo* position. The tetrahedral carbon, C(1), is displaced from the plane of the ring, and the plane of N–C(1)–C(2) intersects that of the remaining four atoms of the ring with a dihedral angle of 37.8°. The modified anionic pentamethylpyrrole–H ligand serves as an η^4-six-electron donor and maintains the 18 electron count for the ruthenium complex. Spectroscopic data for the products of nucleophilic addition to the osmium derivatives were similar to those of the ruthenium complexes, and analogous structures were assigned to the osmium products.

The reaction of the hydride addition products of both ruthenium and osmium with HCl led to further reduction of the pyrrole ligand and its displacement from the metal center, Eq. (6) [49]. The resulting cyclic iminium ion, **8**, was isolated after



(6)

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M = Ru, Os

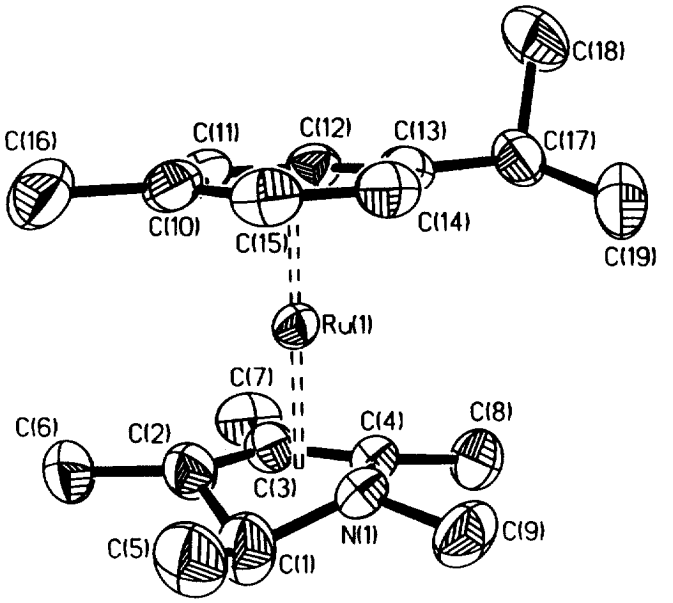
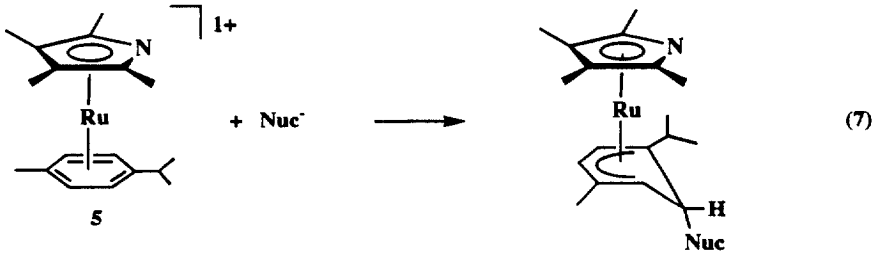


Fig. 2. Perspective drawing of the nucleophilic addition product [(η^6-cymene) Ru(η^4-MeNC$_4$Me$_4$–H)]OTf. Taken from Ref. [49], reprinted with permission from the American Chemical Society.

column chromatography and identified by ^{1}H and ^{13}C NMR data. The ruthenium and osmium species were isolated as the [(*p*-cymene)MCl_2]$_2$ derivatives.

No evidence was observed for the competing nucleophilic addition to the cymene ligand in the reactions of the dicationic pentamethylpyrrole complexes. However, the cymene ligand was the preferred site of nucleophilic addition in the cationic tetramethylpyrrolyl complex, [(cymene)Ru(NC$_4$Me$_4$)]OTf, **5**, Eq. (7) [49]. The

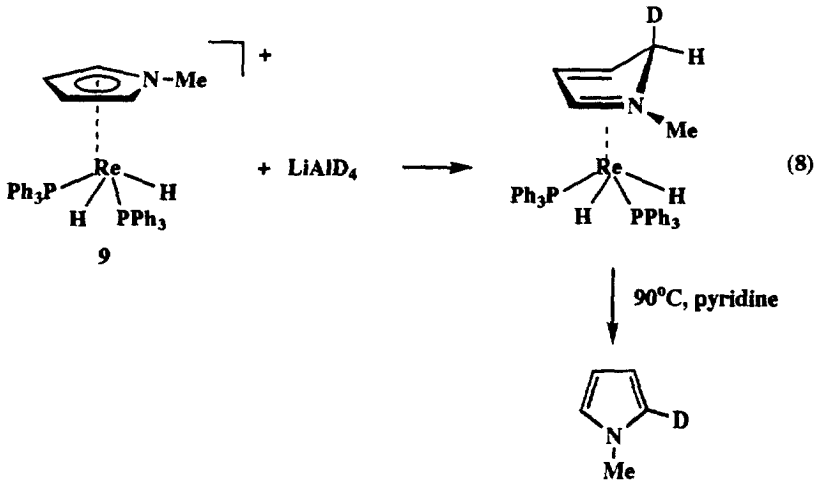


(7)

resulting cyclohexadienyl products were characterized by one- and two-dimensional NMR data. The regioselectivity of this nucleophilic addition is as expected in a competition between a neutral cyclic ligand (cymene) and an anionic heterocycle (Me$_4$-pyrrolyl).

3.2. Pyrrole complexes of rhenium

An example of a nucleophilic addition to an η^5-1-methyl-pyrrole ligand has been reported for the cationic rhenium system, $[(MeNC_4H_4)Re(PPh_3)_2H_2]^+$, **9**, [39,40]. Reaction of this complex with $LiAlH_4$ or $LiAlD_4$ gave the 2-pyrroleaddition product in 93% yield, Eq. (8), but tractable products were not observed with other

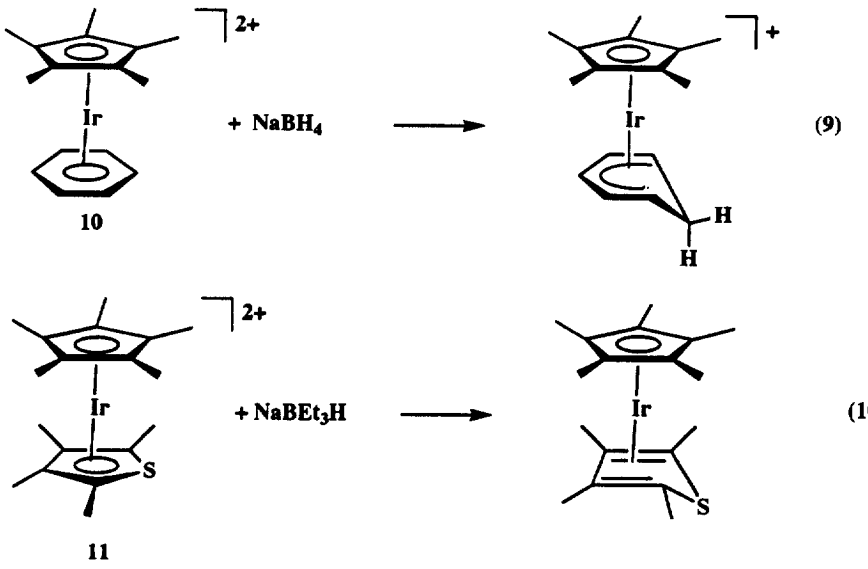


(8)

nucleophiles such as alkyl lithium reagents. The presence of the non-labile hydride ligands prevents the ring-to-metal hydrogen transfer step observed in the ring substitution reactions in related Re–iodo complexes. When the rhenium complex with the modified pyrrole ligand was heated in pyridine (10 min, 90 °C), free 1-Me pyrrole or its 2-D analog was recovered.

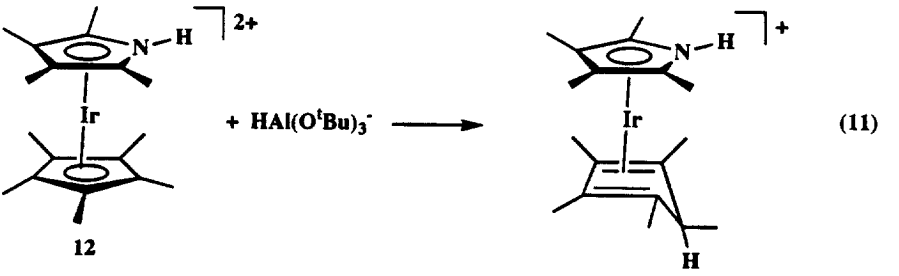
3.3. Other sandwich complexes with η^5-pyrrole ligands

A series of $[Cp^*Ir(arene)]^{n+}$ sandwich complexes has been prepared, where the arene ligand included benzenes, pyrrolyl, indole, thiophenes and benzothiophenes [14,15,50–52]. The reaction of $[Cp^*Ir(\eta^6\text{-benzene})]^{2+}$, **10**, and $[Cp^*Ir(\eta^6\text{-benzothiophene})]^{2+}$ with sodium borohydride proceeded readily via nucleophilic addition to the benzene and benzothiophene ligands, respectively, e.g. Eq. (9). The η^5-cyclohexadienyl products were isolated and characterized spectroscopically. The reaction of $[Cp^*Ir(thiophene)]^{2+}$, **11**, with $NaBEt_3H$ led to the formation of a $2e^-$ reduction product $Cp^*Ir(\eta^4\text{-thiophene})$, Eq. (10)



[14,15,53]. In contrast, no reaction with sodium borohydride was observed for the less electrophilic pyrrolyl complex $[Cp^*Ir(\eta^5\text{-}NC_4H_4)]^+$. Attempted reactions of the latter complex with other nucleophiles were not reported. More recently a related sandwich complex with the tetramethylpyrrole ligand, $[Cp^*Ir(HNC_4Me_4)](OTf)_2$, **12**, has been synthesized and characterized [54]. Although the pyrrole ligand in the Cp*Ir complex discussed above underwent spontaneous deprotonation upon coordination, for the tetramethylpyrrole analog **12** the elemental analyses, solution conductivity and IR data confirm that the complex is a dication with a neutral tetramethylpyrrole ligand. A related rhodium derivative, $[Cp^*Rh(\eta^5\text{-}MeNC_4H_4)]^{+2}$ has been reported previously [55].

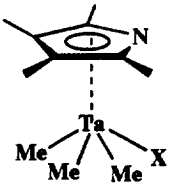
The reaction of the hydride reagent $LiAl(O^tBu)_3H$ with **12** proceeds to form a hydride addition product [54]. Rather unexpectedly, spectroscopic data for the product are consistent with the addition of the nucleophile to the anionic pentamethylcyclopentadienyl ligand rather than to the tetramethylpyrrole ring, Eq. (11).



In the ^1H NMR spectrum, which does not show evidence for fluxionality, one methyl resonance is split into a doublet and a new quartet for the added hydride is observed at 4.13 ppm. The fact that the product maintains a plane of symmetry in which two methyl singlets (each six H) are observed for the remaining methyl groups in each of the cyclic ligands indicates that the attack has occurred on the Cp* ring. Hydride addition to the tetramethylpyrrole ligand would lead to a product of lower symmetry. In contrast, the reaction of **12** with other hydride reagents such as $LiEt_3BH$ did not form any characterizable hydride addition products. The factors which dictate the efficiency and the site of nucleophilic attack in these mixed carbocycle/heterocycle dications are not well understood.

4. η^5-Pyrrolyl complexes with early, high valent transition metals

The examples of activation of pyrrole discussed above have involved coordination to d^4 and d^6 metal ions, which display good kinetic stability with respect to pyrrolyl dissociation. η^5-Coordination of the pyrrolyl ligand to early transition metals might be expected to more effectively promote nucleophilic attack on the heterocycle because of the Lewis acid character of the electron-deficient metal centers. An early example of a pyrrolyl complex in this class is $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}NC_4H_4)TiCl_2$, but reactivity studies of the coordinated pyrrolyl ligand were not reported for this derivative [56]. η^5-Tetramethyl-pyrrolyl complexes involving a d^0 metal ion have been synthesized and characterized recently with the complexes $(Me_4C_4N)Ta(Me)_3X$, **13**, where X = Cl, Me, σ-pyrrolyl and σ-indolyl [57]. These complexes were found to be very sensitive to moisture and other proton sources, and protonation of the tetramethylpyrrolyl ligand led to its rapid dissociation and to the decomposition of the tantalum complexes. Similar decompositions were observed in reactions with nucleophilic hydride sources, Eq. (12). In the latter cases



13

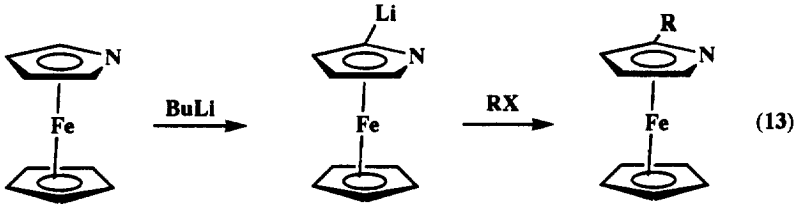
+ Proton or Hydride Source → Decomposition (12)

the dissociation of free tetramethylpyrrole may proceed through the initial formation of a tantalum hydride derivative, but intermediates in the decomposition process were not observed. Attempted reactions of the η^5-tetramethylpyrrolyl complexes with other nucleophiles such as alkyl lithium reagents also failed to yield characterizable products. In general the kinetic lability of the Ta(V) systems hampered attempts to characterize the nucleophilic activation of the η^5 heterocycle.

5. Other competing reactions with nucleophiles

5.1. Metallation reactions

Although the main focus of this review has been the nucleophilic addition to or substitution of pyrrole, the deprotonation of the pyrrolyl ligand is a competing reaction with certain basic nucleophiles. The reaction of the azametallocene complex (η^5-C_4H_4N)Fe(η^5-C_5H_5), **14**, with butyl lithium has been reported [58,59]. The reaction proceeds to form a 2-lithiopyrrolyl derivative, which undergoes further reactions with alkyl halides and with benzophenone to form the 2-alkylated pyrrolyl derivatives, Eq. (13).



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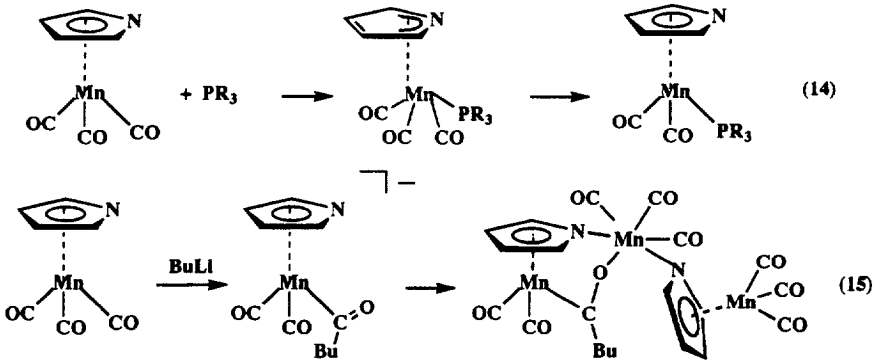
A competing reaction in the system with alkyl halides involves lithiation and alkylation of the cyclopentadienyl ligand. The rhenium complex $(C_4H_4N)Re(PPh_3)_2H_2$ reacted with butyl lithium to form the 2-lithiopyrrolyl ligand which could be further alkylated in high yield [60]. A similar pattern of metallation and alkylation at the 2-position is observed for free *N*-alkylpyrrole molecules [61].

5.2. Nucleophilic substitution of other ligands

The reaction of a series of η^5-pyrrolyl complexes of $Mn(CO)_3$ with phosphine nucleophiles has been studied [62–64]. Nucleophilic substitution of the carbonyl ligand was observed in these systems. The reactions proceeded at significantly faster rates than those of the analogous cyclopentadienyl derivatives. The rate enhancement was attributed to the ability of the pyrrolyl ligand to distort to an η^3-azaallyl bonding mode, which provided a vacant coordination site for the associative ligand substitution reaction, Eq. (14). The reaction of (η^5-NC_4H_4)$Mn(CO)_3$ with BuLi resulted in nucleophilic attack on a carbonyl ligand, and a product that incorporated a butylacyl ligand was characterized, Eq. (15) [65].



6. Conclusions

Although pyrrole is an electron-rich heterocycle which does not react with nucleophiles, several examples have been reported recently of the activation of pyrrole and pyrrolyl rings toward nucleophilic attack by its η^5-coordination to appropriate transition metal complexes. The most successful systems have included kinetically inert metal ions with electron counts of d^4 and d^6. Transition metal complexes containing the unsubstituted η^5-pyrrolyl ligand have been synthesized in several cases. However, when the reactant metal reagent is highly electrophilic in character, the polymerization of pyrrole or its σ-*N* coordination to the metal ion can be competing reactions. In these cases, alkylated pyrrole ligands, such as tetramethylpyrrole and pentamethylpyrrole, have been employed. In addition to the useful steric properties of the latter rings, their electron donating character has also proven useful in stabilizing the metal complexes.

The nature of the other ligands in the η^5-pyrrole complexes has been found to be important in influencing the reactivity of the complexes. For example, two systems have been identified in which nucleophilic substitution of the pyrrolyl ligand involves hydrogen transfer from the ring to the metal ion with displacement of a labile halide ligand. Phosphine co-ligands in these systems have been found to provide an efficient way of altering electron density at the metal ion and influencing reactivity of the pyrrolyl ligand. η^5-Pyrrole and -pyrrolyl complexes that contain other π-coordinated ligands often provide competing sites for nucleophilic attack.

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