

The regioselective elaboration of η -pyrrolyl ligands in (η -pyrrolyl)bis(triphenylphosphine)rhenium complexes: a way to 2,5-diphenylpyrrole and some of its *N*-derivatives

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Abstract

The η -pyrrolyl complex $(\eta\text{-C}_4\text{H}_4\text{N})(\text{Ph}_3\text{P})_2\text{ReH}_2$ (**1**) was prepared from $(\text{Ph}_3\text{P})_2\text{ReH}_7$, 3,3-dimethyl-1-butene and pyrrole, and treated with $\text{I}_2\text{-K}_2\text{CO}_3$ to give $(\eta\text{-C}_4\text{H}_4\text{N})(\text{Ph}_3\text{P})_2\text{ReHI}$ (**2**). This was treated with PhLi to give $(\eta\text{-2-PhC}_4\text{H}_3\text{N})(\text{Ph}_3\text{P})_2\text{ReH}_2$ (**3**) in high yield. Repeated treatment of **3** with $\text{I}_2\text{-K}_2\text{CO}_3$ and PhLi gave $(\eta\text{-2,5-Ph}_2\text{C}_4\text{H}_2\text{N})(\text{Ph}_3\text{P})_2\text{ReH}_2$ (**4**) which was converted into 2,5-diphenylpyrrole, 1-methyl-2,5-diphenylpyrrole and 1-benzoyl-2,5-diphenylpyrrole.

Introduction

Recently we began [1,2] systematic studies of the chemistry of the η -pyrrolyl ligand in $(\eta\text{-C}_4\text{H}_4\text{N})(\text{Ph}_3\text{P})_2\text{ReH}_2$ (**1**) and $(\eta\text{-C}_4\text{H}_4\text{N})(\text{Ph}_3\text{P})_2\text{ReHI}$ (**2**). The aim of this research has been to discover novel, highly regioselective methods for the introduction of substituents into this heterocyclic ligand, which after demetalation leads to substituted pyrroles.

We have recently reported that the pyrrolyl ligand in **2** undergoes nucleophilic attack to give regioselectively (η -2-substituted pyrrolyl)bis(triphenylphosphine)rhenium dihydrides. Electrophiles attack **1** selectively at nitrogen.

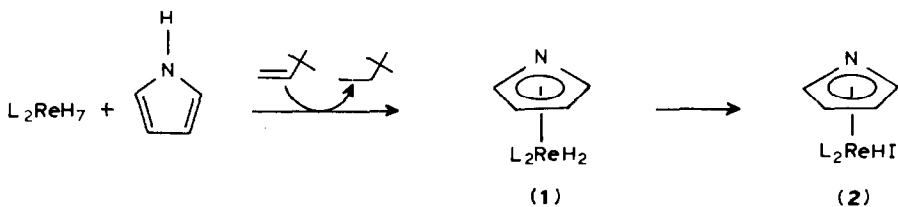
In this work I describe, in full experimental detail, the preparation of **1** and **2**, and the use of **2** in the regioselective synthesis of 2,5-diphenylpyrrole along with some of its *N*-derivatives. *C*-arylation of pyrrole is especially difficult to achieve and *C*-aryl pyrroles are usually prepared by ring-synthesis [3].

Shortly after our preliminary note [1] had appeared, an interesting example of bis-arylation of 1-benzoylpyrrole was published [4].

Results and discussion

*Preparation of $(\eta\text{-C}_4\text{H}_4\text{N})(\text{Ph}_3\text{P})_2\text{ReH}_2$ (**1**) and $(\eta\text{-C}_4\text{H}_4\text{N})(\text{Ph}_3\text{P})_2\text{ReHI}$ (**2**) (Scheme 1)*

The heptahydride $(\text{Ph}_3\text{P})_2\text{ReH}_7$ [5] in the presence of 3,3-dimethyl-1-butene

Scheme 1. L = PPh₃.

reacts with pyrrole in refluxing THF to give the yellow air-stable complex **1**, which was isolated in 70% yield.

The spectroscopic properties as well as the elemental analyses (Table 1) are fully in accord with its formulation. The N–H stretching vibrations are absent in the IR spectrum of **1**. Pyrrolyl protons appear as singlets at δ 5.45 and δ 4.53 ppm (it is known that π -coordination reduces couplings in the pyrrole system [6]), and hydrides as a triplet at δ -10.07 ppm (J 41 Hz) in the ¹H NMR spectrum of **1**. Unequivocal confirmation of the presence of two hydrido ligands in **1** was provided by its ³¹P {Ar-H} spectrum, in which the triplet of ³¹P coupled with two hydrogens was observed at 33.61 ppm, downfield from external H₃PO₄.

Although $\pi(\eta)$ -coordination of pyrrolyl ligand has been known for many years, azaferrocene and $(\eta\text{-C}_4\text{H}_4\text{N})\text{Mn}(\text{CO})_3$ are still the only η -pyrrolyl transition metal complexes which have been studied up to now [7]. The preparation of **1** provides a route to such complexes. In this complex, not only can the hydrides be displaced by other ligands, but a C-2 substitution at the pyrrole ring is also readily feasible (vide infra). Accordingly, a variety of η -pyrrolyl half-sandwich rhenium complexes can be prepared starting from **1**.

Treatment of **1** with one equivalent of iodine and an excess of potassium carbonate at r.t. affords orange-red **2** in high yield. The iodo-hydrido structure of this complex is supported by the fact that a hydride signal is present in its ¹H NMR spectrum (Table 1), which corresponds to one proton.

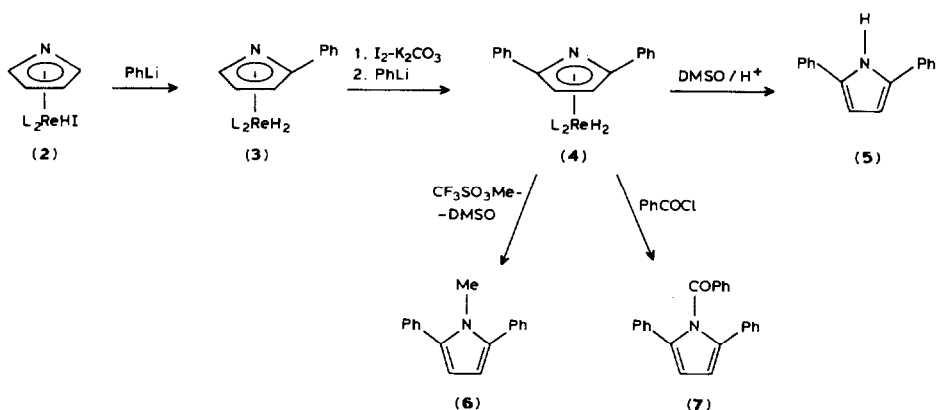
Table 1

¹H NMR spectral data ^a and elemental analyses for complexes 1–4

Complex	Pyrrolyl H's ^b	Hydrides ^b	Elemental analysis (Calcd. (Found). (%))			
			C	H	N	P
1	5.43,s,2H	-10.07,t(41),2H	61.68	4.66	1.80	7.95
	4.53,s,2H		(61.76)	(4.79)	(1.89)	(8.04)
2	5.64,s,2H	-10.23,t(48)1H	53.09	3.90	1.55	6.84
	4.49,s,2H		(53.37)	(4.11)	(1.67)	(6.62)
3	5.58,s,1H	-9.27,t(41),2H	64.62	4.71	1.64	7.25
	4.75,d(2.4), 1H		(64.83)	(4.75)	(1.84)	(7.27)
	4.60,d(2.4), 1H					
4	4.90,s,2H	-8.87,t(41),2H	67.08	4.76	1.50	6.65
			(67.00)	(4.78)	(1.69)	(6.58)

^a Recorded at 80 MHz in CD₂Cl₂ for complexes 1–2 and at 200 MHz in C₆D₆ for complexes 3–4.

^b Reported as: δ in ppm relative to TMS, multiplicity (J in Hz), intensity.

Scheme 2. L = PPh₃.

Reaction of 2 with phenyllithium (Scheme 2)

It has been reported [1] that lithium alkyls react with 2 in THF to afford, surprisingly, η -2-alkylpyrrolyl dihydrido rhenium complexes. Phenyllithium behaves similarly to give the η -2-phenylpyrrolyl complex 3, isolated in 91% yield.

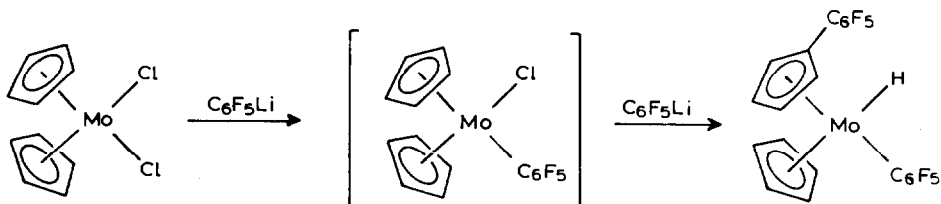
The structure of 3 is in accord with elemental analyses, ¹H NMR data (Table 1) and with its conversion into the η -2,5-diphenylpyrrolyl complexes 4, and finally into 2,5-diphenylpyrrole 5 (*vide infra*).

The 200 MHz ¹H NMR spectrum of the reaction mixture indicates that 3 is the sole regioisomer formed, provided that if other regioisomers were present in excess of 2% they would have been detected.

The remarkably facile arylation, 2 → 3, in which nucleophilic attack on η -pyrrolyl ligand is accompanied by migration of hydrogen from carbon to metal and simultaneous elimination of a good leaving group (halide) from the metal appears to have some precedent in cyclopentadienyl transition metal systems. For example, Green et al. [8] have reported that Cp₂MoCl₂ reacts with an excess of C₆F₅Li to give an unusual product (Scheme 3).

Preparation of (η -2,5-Ph₂C₄H₂N)(Ph₃P)₂ReH₂ (4) (Scheme 2)

The reaction of 2 with phenyllithium rebuilds the dihydrido structure at rhenium. This affords the possibility of introducing a second substituent into η -pyrrolyl ligand by repeating the treatment with I₂-K₂CO₃ and then with RLi. Indeed, 3 when treated successively with I₂-K₂CO₃ and PhLi, without isolating the inter-



Scheme 3

mediate iodo-hydrido complex, gives the η -2,5-diphenylpyrrolyl complex **4** (87% isolated yield), but no regioisomers were detected by ^1H NMR spectroscopy at 200 MHz.

Attempts to introduce into **4** the third phenyl substituent were unsuccessful. While **4** reacted with $\text{I}_2\text{-K}_2\text{CO}_3$, the product (uncharacterized), treated with phenyllithium was slowly converted, over 2–3 h at r.t., into a complex mixture of at least 6 products (TLC).

Decomplexation experiments with 4 (Scheme 2)

Complex **4** is thermally very stable. It decomposes only at 200–220 °C, losing triphenylphosphine rather than 2,5-diphenylpyrrole. However, protonation with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ converts it into a more labile, presumably *N*-protonated complex which in DMSO releases 2,5-diphenylpyrrole **5** on heating to 80 °C.

Similarly, treatment of **4** with methyl triflate (1.2 equiv.), and subsequent heating in DMSO to 80 °C for 1 h gave 1-methyl-2,5-diphenylpyrrole **6** in 88% yield. The reaction presumably proceeds via the *N*-methylated cationic complex (an analogous complex has been isolated and fully characterized from the reaction of **1** with methyl triflate [1]).

Treatment of **4** with 1.2 equiv. of benzoyl chloride in CH_2Cl_2 at r.t. gives 1-benzoyl-1,5-diphenylpyrrole **7** in 91% yield. In this case decomplexation was spontaneous.

The pyrroles **5–7** were identified by comparing their m.p.s, IR and ^1H NMR spectra with those of authentic samples prepared by published procedures [4,9,10].

The nucleophilic properties of nitrogen in the η -pyrrolyl ligand have already been established for azaferrocene and $(\eta\text{-C}_4\text{H}_4\text{N})\text{Mn}(\text{CO})_3$. The former is known to behave as a base ($\text{p}K_a = 4.5$) and to form an unstable salt with methyl iodide [10]. The latter, upon reaction with electrophiles gives mainly complex bi- and polynuclear products [7]. In one case, namely in the reaction of $(\eta\text{-C}_4\text{H}_4\text{N})\text{Mn}(\text{CO})_3$ with diphenylketene partial formation of free *N*-acylpyrrole occurred [12].

The reactions described here thus constitute the first clean and efficient route to the formation of *N*-H as well as *N*-substituted pyrroles from the corresponding η -pyrrolyl transition metal complexes.

Conclusion

The reaction of $(\text{Ph}_3\text{P})_2\text{ReH}_7$ with pyrrole and 3,3-dimethyl-1-butene, giving $(\eta\text{-C}_4\text{H}_4\text{N})(\text{Ph}_3\text{P})_2\text{ReH}_2$ (**1**) provides a new route to (η -pyrrolyl) half-sandwich rhenium complexes. The highly regioselective substitution at C-2 of the pyrrolyl ligand with subsequent decomplexation allowed the preparation of a number of 2,5-diphenylpyrroles which up to now were accessible only by ring-synthesis.

Experimental

All the reactions described were carried out under nitrogen. All the solvents were distilled and dried thoroughly before use. $(\text{Ph}_3\text{P})_2\text{ReH}_7$ was prepared by a published procedure [5]. The ^1H NMR spectra were recorded with Tesla BS 487 (60 MHz), Bruker WP 80 (80 MHz) and Bruker WM 200 (200 MHz) spectrometers. The ^{31}P {Ar-H} spectrum was recorded on a Bruker WM 200 apparatus at 162 MHz.

The IR spectra (KBr pellets) were recorded on a Specord 71 IR spectrometer. Melting points were determined in a Boetius apparatus and are uncorrected.

Preparation of $(\eta\text{-C}_4\text{H}_4\text{N})(\text{Ph}_3\text{P})_2\text{ReH}_2$ (1)

A solution of $(\text{Ph}_3\text{P})_2\text{ReH}_7$ (2.0 g, 2.8 mmol), pyrrole (2.0 ml, 29 mmol) and 3,3-dimethyl-1-butene (5.0 ml, 39 mmol) in THF (150 ml) was refluxed for 5 min. The solvent was removed under vacuum and the residue was flash-chromatographed on alumina with CH_2Cl_2 to give a yellow foam which crystallized after addition of acetone. Yield: 1.55 g (70%). An analytical sample was recrystallized from dichloromethane-acetone. M.p. 177–179 °C (dec.). IR: no absorption at 3100–3600 cm^{-1} ^{31}P {Ar-H}: 33.61 ppm (downfield to external H_3PO_4), $t(J$ 41 Hz).

Preparation of $(\eta\text{-C}_4\text{H}_4\text{N})(\text{Ph}_3\text{P})_2\text{ReHI}$ (2)

A solution of **1** (0.50 g, 0.64 mmol) in CH_2Cl_2 (20 ml), containing anhydrous K_2CO_3 (2 g) was treated with iodine (0.165 g, 0.65 mmol) and stirred vigorously. The mixture was stirred for a further 30 min at r.t., and filtered on alumina. The solvent was removed under vacuum to give an orange-red foam which crystallized after addition of acetone. Yield: 0.470 g (80%). M.p. 191–193 °C (dec.).

Reaction of 2 with phenyllithium

A solution of **2** (0.270 g, 0.30 mmol) in THF (10 ml) was cooled to 0 °C and treated with one equivalent of phenyllithium (1.0 M solution in Et_2O). The colour immediately turned yellow. The solvent was removed under vacuum and the residue was flash-chromatographed on alumina using CH_2Cl_2 as eluent to give a yellow foam which crystallized after addition of acetone to give **3** as yellow crystals. Yield: 0.233 g (91%).

Preparation of $(\eta\text{-2,5-Ph}_2\text{C}_4\text{H}_2\text{N})(\text{Ph}_3\text{P})_2\text{ReH}_2$ (4)

Complex **3** (0.200 g, 0.23 mmol) was dissolved in CH_2Cl_2 (5 ml) containing anhydrous K_2CO_3 (0.5 g), then iodine (0.060 g, 0.23 mmol) was added with vigorous stirring. The mixture was stirred for 10 min and filtered on alumina. The solvent was removed under vacuum, a 5 ml aliquot of THF was added and the resulting solution was evaporated to dryness. Then a second 5 ml aliquot of THF was added, and after cooling to 0 °C, one equivalent of PhLi (1.0 M solution in Et_2O) was added. The solvent was removed under vacuum and the residue was flash-chromatographed on alumina using CH_2Cl_2 as eluent to afford **4** as yellow crystals. Yield: 0.185 g (87%).

Conversion of 4 into 2,5-diphenylpyrrole (5)

A suspension of **4** (0.100 g, 0.1 mmol) in DMSO (1 ml) and toluene (0.5 ml) containing $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (0.01 ml) was heated to 80 °C for 1 h. The volatiles were removed at this temperature under vacuum (0.4 mmHg). The residue was dissolved in Et_2O and chromatographed on silica gel using Et_2O as eluent to give **5** as colourless crystals. M.p. 141–142.5 °C /lit. [8] 143.5 °C/. ^1H NMR (200 MHz, CDCl_3) 8.67 (b, 1H, NH) 7.7–7.3 (m, 10H, C_6H_5), 6.65 (d, J 3 Hz, 2H, H-3,4).

Conversion of 4 into 1-methyl-2,5-diphenylpyrrole (6)

Complex **4** (0.100 g, 0.1 mmol) dissolved in 2.5 ml of CH_2Cl_2 was treated at r.t.

with 0.12 mmol of $\text{CF}_3\text{SO}_3\text{Me}$ dissolved in CH_2Cl_2 (1 ml). After 5 min the solvent was removed under vacuum and then DMSO (2 ml) was added. The resulting solution was heated to 80°C for 1 h. After cooling, the reaction mixture was poured onto water (20 ml) and extracted 3 times with benzene. Separation by chromatography (silica gel/benzene eluent) gave **6** as colourless crystals in 86% yield. M.p. $200\text{--}202^\circ\text{C}$ /Lit. [10] $200\text{--}202^\circ\text{C}$ /. ^1H NMR (60 MHz, CDCl_3) 7.6–7.3 (m, 10H, C_6H_5), 6.52 (s, 2H, H-3,4), 3.48 (s, 3H, Me).

Conversion of 4 into 1-benzoyl-2,5-diphenylpyrrole 7

A solution of **4** (0.100 g, 0.1 mmol) in CH_2Cl_2 (5 ml) was treated at r.t. with benzoyl chloride (0.11 mmol). The colour turned rapidly green and a green solid precipitated. The solvent was removed under vacuum and the residue was triturated with benzene. Separation by chromatography on silica gel and benzene as a eluent gave **5** in 91% yield. M.p. $150\text{--}152^\circ\text{C}$ /Lit. [4] $153\text{--}154^\circ\text{C}$ / IR: 1710 cm^{-1} . ^1H NMR (60 MHz, CDCl_3) 7.6–7.1 (m, 15H, C_6H_5), 6.45 (s, 2H, H-3,4).

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