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Preparation and reactions of rhodium complexes of some alkynylamines

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Abstract

Reactions of $[Rh(CO)_2Cl]_2$ with the alkynylamines Ph—≡—$(CH_2)_2NH_2$ **1** and *p*-MeC_6H_4—≡—$(CH_2)_3NH_2$ **2** give the corresponding alkynylamine dicarbonyl rhodium(I) chloride complexes **3** and **4** in which ligand bonding is monodentate through nitrogen. Solutions of these complexes in benzene or chloroform isomerise on standing to give complexes involving 2-substituted-pyrroline derivatives as ligands. Attempts to convert this reaction into a catalytic process were unsuccessful using rhodium catalysts at 80°C but catalysis was achieved using $Ni(CO)_2(PPh_3)_2$ at 125°C.

Keywords: Rhodium; Nickel; Alkynylamines; Rearrangement; Stoichiometric complexes; Catalysis

1. Introduction

One of our research goals is the use of metal-catalysed reactions in the preparation of heterocyclic compounds [1–6]. In an attempt to help understand the varying chemo- and regioselectivities exhibited in these reactions we have undertaken a study of stoichiometric reactions of the substrates with metal species. Of particular interest to us were the rhodium-catalysed reactions of the but-3-ynylamine **1**, and its homologue, the pent-4-ynylamine **2** with $CO–H_2$ which had been shown to give cyclic lactams [5]. Krafft and her co-workers [7] have described extensive work in this area in which mono- and bidentate complexes were formed from alkenylamines and rhodium species and their subsequent cyclisation has also been studied [8].

2. Results and discussion

Reaction of the alkynylamine **1** with $[Rh(CO)_2Cl]_2$ in hexane at ambient temperature gave the complex **3**, isolated after chromatography in high yield (95%) (Scheme 1). The infrared (IR) spectrum showed two carbonyl absorptions at 2091 and 2015 cm^{-1} which are consistent with a *cis*-carbonyl geometry [7].

The ^1H NMR spectrum of **3** showed a downfield shift of the aminomethylene protons relative to those in **1** but the ^{13}C NMR spectrum showed little change for the alkyne carbons on forming **3** from **1**. It was found that the complex **3** in benzene or chloroform solution rearranged with cyclisation to give the dihydropyrrole complex **4**. The IR spectrum still showed *cis*-carbonyl geometry and the NMR spectra (^1H and ^{13}C) were very similar to those recorded for an authentic sample of the free ligand **5**. It was not possible to obtain correct analytical data for **4** owing to the presence of a small amount of a rhodium-containing impurity. Good crystals could not be obtained, nor could a parent ion be measured using a range of mass spectral techniques. However, removal of the metal from **4** by reaction with diphenylphosphinoethane (dppe) gave the dihydropyrrole **5** (33% yield) whose spectra were identical with those of an authentic sample. Krafft and Wilson [7] reported that bidentate complexes which did not form at ambient temperature could be prepared by warming a solution of the monodentate complex in chloroform containing a small excess of the free ligand. This procedure was carried out on a small scale with complex **3** and a larger excess of the free ligand **1** but did not lead to the isolation of a bidentate complex. The only product isolated appeared to be the chlorobridged dimeric

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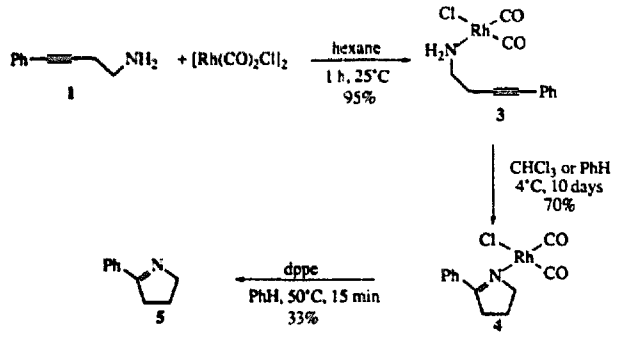
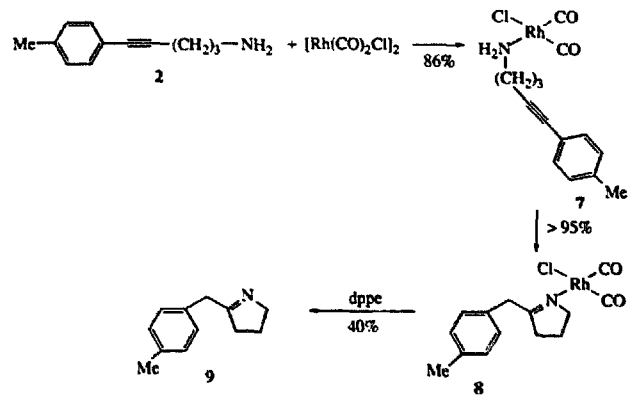


Scheme 1.



Scheme 3.

compound **6** (Scheme 2). The material showed no carbonyl absorptions in its IR spectrum and its NMR spectra (^1H and ^{13}C) were very similar to those of the ligand **5**.

Similar behaviour was demonstrated by the homologous pentynylamine **2** (Scheme 3). The initial monodentate complex **7** was isolated in high yield (86%). This complex similarly isomerised on standing in chloroform solution with regiospecific cyclisation to the dihydropyrrole complex **8** from which the free dihydropyrrole **9** could be released by reaction with dppe.

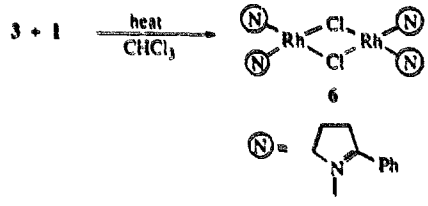
Aresta and De Fazio [9] have previously reported a related sequence of reactions starting with *N*-allylaniline and $[Rh(C_2H_4)_2Cl]_2$ which lead to an isomerised complex from which *N*-phenylazetidine could be released by reaction with dppe.

Attempts to prepare the dihydropyrrole **5** using catalytic amounts of the rhodium complex **3** in refluxing chloroform solution gave less than 5% conversion of the alkynylamine. Addition of triphenylphosphine (2 mol) did not lead to further reaction under these conditions.

The cyclisation of these alkynylamines was found to occur in low yields (ca. 30%) when they were heated for 20 h in ethanol under N_2 at 125°C. It was found that significantly higher yields (ca. 65%) were obtained when a small amount of $Ni(CO)_2(PPh_3)_2$ was added and the reaction carried out under CO. No carbonylation reactions occurred. Further investigation of this potential catalytic system was abandoned as a moderately efficient palladium-catalysed reaction of related alkynylamines had been reported [10]. In addition, efficient catalysis of these reactions under much milder conditions (25 or 60°C) had been reported using titanium [11,12] or samarium [13] compounds.

The failure to establish a catalytic system with rhodium could be due to the lack of lability of the Rh–N bonds in the complexes **4** or **8**. Hegedus reported overcoming a similar problem in palladium-catalysed cyclisations by the use of *N*-tosylamines as reactants [14]. However, attempted reaction of the *N*-tosyl derivative **10** of the amine **1** with a stoichiometric amount of $[Rh(CO)_2Cl]_2$ at ambient temperature gave no product, whilst a reaction in refluxing chloroform for 24 h gave only a small amount of the *N*-tosyldihydropyrrole derivative **11** (Scheme 4).

In conclusion, monodentate amino complexes of alkynylamines are readily formed by reaction with $[Rh(CO)_2Cl]_2$ but these complexes smoothly rearrange on standing in solution to give rhodium complexes of dihydropyrroles. The dihydropyrroles can be released by reaction with dppe. Catalytic reaction conditions were not established with rhodium but $Ni(CO)_2(PPh_3)_2$ was shown to promote cyclisation under more vigorous conditions.

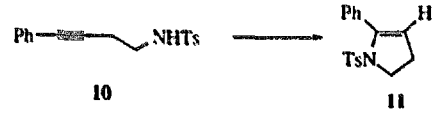


Scheme 2.

3. Experimental section

3.1. General

IR spectra were recorded on a Perkin–Elmer 1600 FTIR spectrophotometer. Proton (^1H) and carbon (^{13}C) magnetic resonance spectra were recorded on a Bruker AC-200 or Bruker AM-300 spectrometer using Me_4Si as the internal standard in $CDCl_3$. Phosphorus (^{31}P) magnetic resonance spectra were recorded on a Bruker



Scheme 4.

AM-300 spectrometer using external 85% H_3PO_4 as reference. Mass spectra (EI) were obtained on a VG TRIO-1 mass spectrometer at 70 eV. High resolution mass spectra (HRMS) were recorded on a VG Micromass 7070F spectrometer by peak matching with an internal standard. FAB mass spectra were obtained on a Jeol JMS DX300 (samples in 3-nitrobenzyl alcohol) by Mr. S. Thompson at the Department of Medicinal Chemistry, Monash University. Elemental analyses were carried out by NAL Pty Ltd., Melbourne or CMAS, Melbourne.

All manipulations were carried out under a nitrogen atmosphere. All solvents were dried and distilled prior to use. $Ni(CO)_2(PPh_3)_2$ was obtained from the Pressure Chemical Company, PA. $[Rh(CO)_2Cl]_2$ was prepared from $RhCl_3 \cdot H_2O$ by a literature method [15] and the amines (**1**, **2**) were prepared as described previously [5]. *N*-Tosyl-4-phenylbut-3-ynylamine **10** was prepared from **1** by reaction with tosyl chloride–pyridine in dichloromethane (60%), m.p. 91–92°C. Anal. Found: C, 68.2; H, 5.8; N, 4.7. $C_{17}H_{17}NO_2S$. Calc.: C, 68.2; H, 5.7; N, 4.7%. IR (Nujol): 3286m, 1597m, 1490m, 1339s, 1314s, 1154s cm^{-1}. ^1H NMR (200 MHz): δ 2.43 (s, 3H, CH_3); 2.58 (t, 2H, $J = 6.5$ Hz, H2); 3.20 (q, 2H, $J = 6.5$ Hz, H1); 4.79 (bs, 1H, NH); 7.31 (m, 7H, ArH); 7.78 (d, 2H, $J = 8.3$ Hz, ArH). ^{13}C NMR (50 MHz): δ 20.67 (C2); 21.47 (CH_3); 41.87 (C1); 82.73, 85.52 (C3,4); 122.86 (ArC); 127.03, 128.08, 128.22, 129.73, 131.58 (ArCH); 136.90, 143.51 (ArC). MS(EI): *m/z* 299(M^+, 1%), 184(62), 155(100), 115(47), 91(92).

3.2. Reactions of the alkynylamines 1, 2, and 10 with $[Rh(CO)_2Cl]_2$

3.2.1. 4-Phenylbut-3-ynylamine 1

A solution of the alkynylamine **1** (30.5 mg, 0.21 mmol) in hexane (1 ml) was added under nitrogen to a solution of $[Rh(CO)_2Cl]_2$ (38.9 mg, 0.1 mmol) in hexane (5 ml). The mixture was stirred at 25°C for 1 h to give a purple-red suspension. The solvent was removed under reduced pressure and the residue was dissolved in ethyl acetate–hexane (1 : 1) and passed down a short silica column. Evaporation of the yellow solution gave a purple solid which was washed with hexane to remove any residual $[Rh(CO)_2Cl]_2$ to give blue-purple irridescent crystals of (4-phenylbut-3-ynylamine)dicarbonylrhodium(I) chloride **3** m.p. 66–68°C. Anal. Found: C, 42.0; H, 3.1. $C_{12}H_{11}ClNO_2Rh$. Calc.: C, 42.4; H, 3.3%. IR($CHCl_3$): (ν CO) 2091s, 2015s cm^{-1}. ^1H NMR (200 MHz): δ 2.81 (t, 2H, $J = 5.9$ Hz, H2); 3.14 (apparent pentet, 2H, $J \simeq 6$ Hz, H1); 3.31 (bs, 2H, NH_2); 7.3–7.5 (m, 5H, Ph). ^{13}C NMR (50 MHz): δ 2 9 (C2); 44.44 (C1); 84.17, 84.52 (C3,4); 122.42 (ArC); 128.36, 128.47, 131.73 (ArCH). MS(FAB): *m/z* 339(M^+, 19%), 311(15), 304(55), 283(12), 276(27), 248(23), 155(38), 146(45), 138(43), 137(85), 120(23), 115(22), 107(58).

3.2.2. 5-p-Tolylpent-4-ynylamine 2

A solution of the alkynylamine **2** (36.4 mg, 0.21 mmol) in hexane (1 ml) was added under nitrogen to a solution of $[Rh(CO)_2Cl]_2$ (38.9 mg, 0.1 mmol) in hexane (5 ml) and stirred at 25°C for 1 h. Workup as described above gave a yellow solution which gave (5-*p*-tolylpent-4-ynylamine)dicarbonylrhodium(I) chloride **7** as a purple solid (86%); m.p. 115–118°C. Anal. Found: C, 45.7; H, 3.8; N, 4.2. $C_{14}H_{15}ClNO_2Rh$. Calc.: C, 45.7; H, 4.1; N, 3.8%. IR($CHCl_3$): (ν CO) 2089s, 2013s cm^{-1}. ^1H NMR (200 MHz): δ 1.96 (apparent pentet, 2H, $J = 6.6$ Hz, H2); 2.36 (s, 3H, CH_3); 2.58 (t, 2H, $J = 6.6$ Hz, H3); 3.2 (m, 4H, H1 and NH_2); 7.12 (d, 2H, $J = 8.0$ Hz, ArH); 7.32 (d, 2H, $J = 8.1$ Hz, ArH). ^{13}C NMR (50 MHz): δ 16.85 (C2); 21.41 (CH_3); 30.51 (C3); 46.28 (C1); 82.50, 86.76 (C4,5); 119.91 (ArC); 129.05, 131.43 (ArCH); 138.12 (ArC). MS (FAB): *m/z* no M^+, 339(13%), 332(59), 311(29), 304(59), 276(43), 174(85), 146(38), 137(48), 131(36), 129(37), 128(37), 115(40), 107(38).

3.2.3. N-Tosyl-4-phenylbut-3-ynylamine 10

A solution of the *N*-tosylamine **10** (63 mg, 0.21 mmol) in hexane and dichloromethane (1 : 2, 5 ml) was added to a solution of $[Rh(CO)_2Cl]_2$ (38.9 mg, 0.1 mmol) in hexane (5 ml). The pale yellow solution was stirred at 25°C for 1 h under nitrogen and the solvent removed under reduced pressure to give an orange solid. The ^1H NMR spectrum of a sample in $CDCl_3$ was identical to that of the starting *N*-tosylamine **10**. The solid was dissolved in dry chloroform (10 ml) and stirred at 70°C for 24 h under nitrogen. The solvent was removed under reduced pressure to give a red-brown solid. The crude ^1H NMR spectrum showed no starting *N*-tosylamine **10** was present. The solid was purified on a short column (silica, ethyl acetate) to give *N*-tosyl-2-phenyl-4,5-dihydropyrrole **11** (10 mg, 16%) as the only identified product. EI-HRMS: Found *m/z* (M^+) 299.098 ± 0.003. $C_{17}H_{17}NO_2S$. Calc.: 299.098. IR: 1352s, 1166s cm^{-1}. ^1H NMR (200 MHz): δ 1.99 (td, 2H, $J = 8.1$, $J = 2.9$ Hz, H4); 2.43 (s, 3H, CH_3); 4.03 (t, 2H, $J = 8.1$ Hz, H5); 5.49 (t, 1H, $J = 2.9$ Hz, H3); 7.27 (m), 7.35 (m) and 7.55 (m) (9H, ArH). ^{13}C NMR (50 MHz): δ 21.58 (CH_3); 28.26 (C4); 51.96 (C5); 117.90 (C3); 127.59, 127.85, 127.92, 128.62, 129.34 (Ar and Tosyl CH); 133.07, 133.96, 143.72, 145.17 (C2, Ar and Tosyl C). MS(EI): *m/z* 299(M^+, 32%), 144(73), 143(39), 115(38), 91(100).

3.3. Isomerisation reactions and isolation of dihydropyrroles 5, 9

3.3.1. 5-Phenyl-3,4-dihydro-2H-pyrrole 5

A solution of the complex **3** (31.3 mg, 0.09 mmol) in base-washed deuterochloroform (1.5 ml) was allowed to stand at 4°C for 10 days. A small amount of precipitate

was removed and a ^{1}H NMR spectrum of the remaining solution showed complete conversion to the rhodium complex **4**. The solvent was removed to give **4** as an orange-brown solid (22 mg, 70%). IR ($CHCl_3$):(ν CO) 2088s, 2015s cm^{-1}. ^{1}H NMR (200 MHz): δ 2.24 (apparent pentet, 2H, $J \simeq 8$ Hz, H3); 3.20 (tt, 2H, $J = 8.2$, $J = 1.9$ Hz, H4); 4.32 (tt, 2H, $J = 7.7$, $J = 1.9$ Hz, H2); 7.56 (m, 3H); 8.28 (m, 2H). ^{13}C NMR (50 MHz): δ 21.92 (C3); 37.71 (C4); 63.13 (C2); 128.59, 129.18, 136.66 (ArCH).

A similar rearrangement occurred when a solution of complex **3** (8 mg) was allowed to stand in base-washed deuterochloroform at 16°C for 5 days.

A solution of the complex **4** (0.02 g, 0.06 mmol) and 1,2-bisdiphenylphosphinoethane (dppe) (0.10 g, 0.24 mmol) in benzene (5 ml) was stirred at 50°C for 15 min. The solution was concentrated and hexane added to give a pale yellow precipitate which was washed with hexane and dried and identified as $Rh(dppe)_2Cl$ by ^{31}P NMR spectroscopy (δ 58.04, d, $J = 132.8$ Hz). The filtrate was evaporated to give an off-white solid (10 mg) which was shown by ^{1}H and ^{13}C NMR spectroscopy to be a mixture of 5-phenyl-3,4-dihydro-2*H*-pyrrole **5** (ca. 33% yield) and the phosphine. The spectral data from **5** was identical to literature data [16] and to that obtained from a sample of **5** prepared by a nickel-catalysed reaction (see below).

3.3.2. Attempted preparation of a bidentate complex

A solution of the complex **3** (80 mg, 0.24 mmol) and the alkynylamine **1** (1 drop) in base-washed chloroform (10 ml) was refluxed under nitrogen for 6 h. The solvent was removed under reduced pressure to give an orange-brown oily solid (76 mg). The ^{1}H and ^{13}C NMR spectra suggested the complex **6**, IR ($CHCl_3$): no ν CO. ^{1}H NMR (200 MHZ): δ 2.02 (apparent pentet, 2H, $J \simeq 7.8$ Hz); 2.94 (m, 2H); 4.06 (m, 2H); 7.24 (m), 7.45 (m) and 7.84 (m) (ArH). ^{13}C NMR (50 MHz): δ 22.53; 34.84; 61.35; 127.51; 128.33; 130.26. MS(EI): *m/z* no M^+; 145(32%), 117(100).

3.3.3. Attempted catalytic isomerisation of the alkynylamine 1

A solution of the alkynylamine **1** (0.26 g, 1.79 mmol) and the complex **3** (6 mg, 0.0177 mmol) (ratio ca. 100:1) in base-washed chloroform (10 ml) was heated under reflux for 24 h. The solvent was removed in vacuo and the ^{1}H NMR spectrum of the residue showed mainly starting alkynylamine with small peaks consistent with the dihydropyrrole **9** (ca. 5% conversion). The IR spectrum showed no ν CO in the 2000–2100 cm^{-1} region.

3.3.4. 5-(4-Tolylmethyl)-3,4-dihydropyrrole 9

A solution of the complex **7** (20 mg, 0.05 mmol) in deuterochloroform (1.5 ml) was allowed to stand at 4°C for 10 days. The ^{1}H NMR spectrum showed complete conversion to the rhodium complex **8** IR($CDCl_3$): (ν CO) 2088s, 2013s cm^{-1}. ^{1}H NMR (200 MHz): δ 2.02 (m, 2H, H3); 2.34 (s, 3H, CH_3); 2.59 (m, 2H, H4); 4.01 (m, 2H, H2); 4.11 (s, 2H, ArCH_2); 7.18 (m, 4H, ArH). ^{13}C NMR (50 MHz): δ 21.05 (CH_3); 21.75 (C3); 37.02, 41.89 (C4, ArCH_2); 62.32 (C2); 129.05, 129.73 (ArCH); 131.02, 137.32 (ArC); 186.83 (C5).

A similar rearrangement occurred when a solution of the complex **7** (6 mg) was allowed to stand in base-washed deuterochloroform at 16°C for 7 days.

A solution of the complex **8** (0.02 g, 0.05 mmol) and dppe (0.09 g, 0.22 mmol) in benzene (5 ml) was stirred at 50°C for 30 min as described above to give $Rh(dppe)_2Cl$ and an off-white solid (0.06 g) which was shown by ^{1}H and ^{13}C NMR spectroscopy to be a mixture of 5-[(4-tolyl)methyl]-3,4-dihydro-2*H*-pyrrole **9** (ca. 40% yield) and dppe. The spectral data for **9** was identical to that obtained from a sample of **9** prepared by nickel catalysis (see below).

3.4. Nickel-catalysed reactions

3.4.1. 5-Phenyl-3,4-dihydro-2H-pyrrole 5

A mixture of the alkynylamine **1** (0.61 g, 4.19 mmol) and $Ni(CO)_2(PPh_3)_2$ (85 mg, 0.13 mmol) in dry ethanol (8.8 ml) and water (0.44 ml) was reacted under carbon monoxide (200 psi) at 125°C for 20 h in a 100 ml Parr autoclave. Evaporation of the solvent gave a yellow oil (0.82 g) which was distilled under reduced pressure to give a clear oil (0.60 g, 100%). ^{1}H NMR spectroscopy indicated a mixture of recovered alkynylamine **1** and the dihydropyrrole **5** in a 1:2 ratio (67% yield for **5**). The dihydropyrrole **5** was purified by chromatography on silica (ether–light petroleum 50%) b.p. (oven) 120°C/0.5 mm (Ref. [16] 102–104°C/5 mm). ^{13}C NMR (50 MHz): δ 22.66 (C3); 34.91 (C4); 61.51 (C2); 127.58, 128.40, 130.28 (ArCH); 134.58 (ArC); 173.29 (C5). The IR, ^{1}H NMR and MS data were identical with literature values [16].

3.4.2. 5-(4-Tolylmethyl)-3,4-dihydro-2H-pyrrole 9

In a similar manner, the alkynylamine **2** (0.35 g, 2.0 mmol) and $Ni(CO)_2(PPh_3)_2$ (45 mg, 0.07 mmol) were reacted at 125°C for 20 h. Workup gave a slightly green oil (0.38 g) which was shown (^{1}H NMR) to be a 10:1 mixture of the dihydropyrrole **9** and the isomeric 6-tolyl-2,3,4,5-tetrahydropyridine. Purification by chromatography on silica (ethyl acetate–light petroleum 50%) gave the dihydropyrrole **9** as a yellow oil (0.14 g, 40%) b.p. (oven) 125°C/0.1 mm (Ref. [17] 117°C/0.1 mm). IR (neat): 1642s, 1606 cm^{-1}. ^{1}H NMR (300 MHz): δ 1.82 (apparent pentet, 2H, $J \simeq 8$ Hz, H3); 2.32 (s, 3H, CH_3); 2.41 (m, 2H, H4); 3.64 (s, 2H, ArCH_2); 3.82 (tt, 2H, $J = 7.3$, $J = 1.6$ Hz, H2); 7.11 (bs, 4H, ArH). ^{13}C NMR (75 MHz): δ 22.55 (C4); 36.42 (C3);

40.16 ($ArCH_2$); 60.79 (C5); 128.79, 129.17 (ArCH); 133.79, 136.03 (ArC); 177.00 (C2). MS (EI): *m/z* 173(M^+, 2%), 172(6), 159(18), 131(41), 119(100), 91(55), 65(20). The ^1H and ^{13}C NMR data were comparable with data for the corresponding 5-benzyl homologue [11,18].

Acknowledgements

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