

SYNTHESIS AND REACTIVITY OF FORMAMIDINATO RHODIUM(I) COMPLEXES

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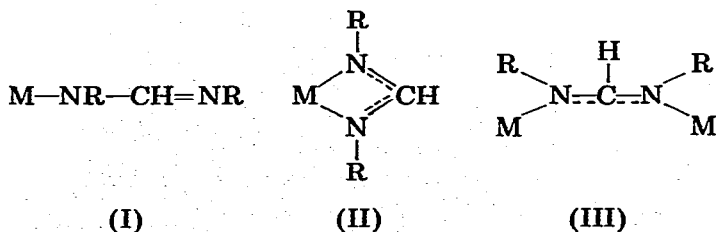
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Summary

The syntheses of $[\text{Rh}(\text{diol})(\text{formamidino})]_2$ complexes (diol = cycloocta-1,5-diene (**1**); diol = norbornadiene (**2**); formamidino = *N,N'*-di-*p*-tolylformamidino) are reported. These complexes are dimeric and contain the bridging formamidino ligand. They react with CO, dppe and PPh_3 with displacement of the diene ligand to yield the known $[\text{Rh}(\text{CO})_2(\text{formamidino})]_2$, $[\text{Rh}(\text{dppe})_2]^+$ and $[\text{Rh}(\text{PPh}_3)_2(\text{formamidino})]$, respectively; the last complex, in which the formamidino acts as a chelating ligand, was isolated only as the O_2 adduct. With HCl or HBF_4 aqueous **1** and **2** do not form hydrides but instead the formamidino cation $[p\text{-tolyl-NH=CHNH-tolyl-}p]^+$ and the complexes $[\text{Rh}(\text{diol})\text{X}]_2$ ($\text{X} = \text{Cl}, \text{F}$); a possible scheme for the reaction with HCl is proposed. The $[\text{Rh}(\text{C}_8\text{H}_{12})(\text{formamidino})]_2$ complex reacts with heterocumulenes as CS_2 , SO_2 , PhNCS and PhNCO with diene displacement; the only product isolated was $[\text{Rh}(\text{CS}_2)_2(\text{formamidino})]$, to which a polymeric structure is assigned.

Introduction

Formamidino ligands, R-N=CH-NHR , in their deprotonated form, lead to an interesting series of transition metal complexes which exhibit a variety of structural types. Thus, being potentially one- or three-electron donors towards low valent transition metals, they can bond in a monodentate (I), bidentate (II) or bridging (III) fashion:



Compounds of all three types have been isolated, but in most previous investigations spectroscopic and structural studies have indicated that the formamidinato anion prefers to act as a three-electron donor ligand, leading to chelate [1-3] or bridging [4,5] σ -bonded derivatives, II or III; compounds of type I appear limited to a few cases [6,7]. A remarkable feature of these ligands pointed out by Vrieze is their ability to stabilize metal-metal bonds to give five membered bimetallic rings [8,9], and Cotton showed that the amidinato anion is an useful ligand in the preparation of compounds with multiple metal-metal bonds [10].

In contrast to the extensive literature on the preparation and characterization of formamidinato-metal complexes there appear to be no reports on the chemical reactions of such compounds. Our work has involved investigation of a number of such reactions, and has led to the isolation of previously unreported diolefin and phosphine formamidinato complexes of rhodium(I) and provided some information on the factors which effect the formation of chelate or bridging structures. We performed also some reactions in order to compare the reactivity of the obtained compounds with the isostructural triazenido and carboxylato derivatives.

Results and discussion

The formamidino diolefin complexes $[\text{Rh}(\text{diol})(\text{formamidine})]_2$ (diol = cycloocta-1,5-diene (1); diol = norbornadiene (2); formamidine = di-*p*-tolyl-formamidine) were prepared by treating $[\text{Rh}(\text{diol})\text{Cl}]_2$ at room temperature, with a toluene solution containing an equimolar amount of $[p\text{-tolyl-N}\equiv\text{CH}\equiv\text{NH-tolyl-p}]\text{K}$ generated in situ. After working up the resultant orange solution the complexes 1 and 2 were obtained in good yields, as air stable, yellow-orange or red crystals. Analytical data and molecular weight measurements in chloroform (Table 1) indicate that these compounds, like the analogous carboxylato, but different from the triazenido complexes, are dimeric, with the formamidino ligand bridging two rhodium atoms. The ^1H NMR spectra show, beside other signals arising from the olefinic and aromatic hydrogens, a single sharp band at 2.25 τ arising from the protons of the tolyl groups. This suggests, as found for related derivatives [5], that the formamidinato anion is bonded symmetrically. A notable feature of the IR spectra is a strong band at 1660 cm^{-1} which can be assigned to the stretching $\text{N}\equiv\text{C}\equiv\text{N}$. The value of 110 for $\Delta\nu$ with respect to the free ligand, may, as previously suggested [6], be taken as an approximate indicator of extensive electronic delocalization.

The chelate complex $[\text{Rh}(\text{PPh}_3)_2(\text{formamidine})\text{O}_2]$ (3) was obtained, as monomer, by refluxing a benzene solution of $[p\text{-tolyl-N}\equiv\text{CH}\equiv\text{N-tolyl-p}]\text{K}$ and $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$ in equimolar ratio. Recrystallization of the crude product from benzene/diethyl ether gave orange needles, with analytical data in agreement with the above formulation. The IR spectrum of complex 3 shows $\nu(\text{N}\equiv\text{C}\equiv\text{N})$ at 1635 cm^{-1} , and a medium band at 900 cm^{-1} which can be assigned to the stretching $\nu(\text{O}-\text{O})$. A high value for $\nu(\text{C}-\text{O})$ has been also reported for the isostructural complex $[\text{Rh}(\text{PPh}_3)_2(\text{ArNNNAr})\text{O}_2]$ [11], and these values can be explained in terms of the strong σ -donor powers of the formamidinato and the triazenido anions. The ^1H NMR spectrum of

TABLE 1
ANALYTICAL, IR AND NMR DATA

Complex	Analysis found (calcd.) (%)				M.w. (calcd.) (CHCl ₃)	IR (cm ⁻¹) (Nujol mull)		1H NMR (δ, ppm) (CDCl ₃)	
	C	H	N	S		ν(N—C—N)	Others	CH ₃	Diolefin
1	64.13 (63.59)	6.13 (6.26)	6.01 (6.44)		887 (868.7)	1565vs		2.25	4.32 (4 H, m, br, CH olefinic) 2.83 (4 H, m, br, CH ₂ saturated) 1.88 (4 H, m, br, CH ₂ saturated)
2	63.19 (63.16)	5.49 (5.54)	6.68 (6.69)		858 (836.6)	1555vs		2.28s	4.1 (4 H, m, br, CH olefinic) 3.75 (2 H, m, br, CH saturated) 1.35 (2 H, s, br, CH ₂ saturated)
3	69.39 (69.39)	5.68 (5.13)	2.99 (3.17)		908 (882.7)	1530 vs	ν(O—O) 890	2.18s	
4	65.98 (66.33)	4.5 (4.54)	5.71 (5.6)		975 (998.7)	1565vs	ν(CO) 1978s 1995vs 2060vs	2.1s 2.23s	
5	42.51 (42.67)	3.38 (3.16)	5.69 (5.85)	26.55 (26.8)		1640s(br) 1605(sh) 1635s(br)		2.35br s 2.3br s	
6	33.74 (33.86)	3.11 (2.84)	3.91 (4.38)	19.61 (20.08)					
7	69.09 (69.09)	6.49 (6.56)	10.61 (10.74)	13.75 ^a (13.59)		1695vs		2.32s	

^a Cl analysis.

$[\text{Rh}(\text{PPh}_3)_2(\text{formamidine})\text{O}_2]$ shows no evidence for magnetic nonequivalence for the methyl groups, suggesting once again that the ligand is symmetrically bonded to the metal. Compound 3 was also obtained by treating $[\text{Rh}(\text{diol})\text{-(formamidine)}]_2$ with an excess of PPh_3 in refluxing toluene for several hours. Although PPh_3 is known to be able to bring about bridge splitting, we did not observe bond breaking of the bridged ligand with formation of a pendant structure, which emphasizes the stability and strength of the M—N bond in these complexes.

If the phosphine complex is rigorously prepared under N_2 , a compound without bands attributable to the stretching $\nu(\text{O—O})$ is obtained. We could not get a satisfactory analysis for this compound, which we formulate as $[\text{Rh}(\text{PPh}_3)_2\text{-(formamidine)}]$, because it probably contains small amounts of the dioxygen derivative. When the crude product is treated under nitrogen with iodine, a rapid reaction takes place with formation of a black neutral compound; the IR spectrum of the product shows the same pattern of the formamidino ligand stretching frequencies, as that exhibited by the starting complex, but does not show any bands assignable to the $\nu(\text{O—O})$, lending further support to the formulation of the starting phosphine complex as $[\text{Rh}(\text{PPh}_3)_2(\text{formamidine})]$. Unfortunately, in spite of performing several repeated elemental analyses, we could not reliably assign a formula to the iodine compound because of the variable iodine content, but, by analogy with the compound obtained by Connelly [12] from the reaction of $[\text{Rh}(\text{CO})_2\text{-}\mu\text{-(RN}\dots\text{X}\dots\text{NR)}]_2$ ($\text{X} = \text{N, CMe}$) with iodine, we tentatively formulate the product as $[\text{Rh}(\text{PPh}_3)_2\text{-}\mu\text{-(formamidine)I}]_2$, containing a rhodium metal—metal bond.

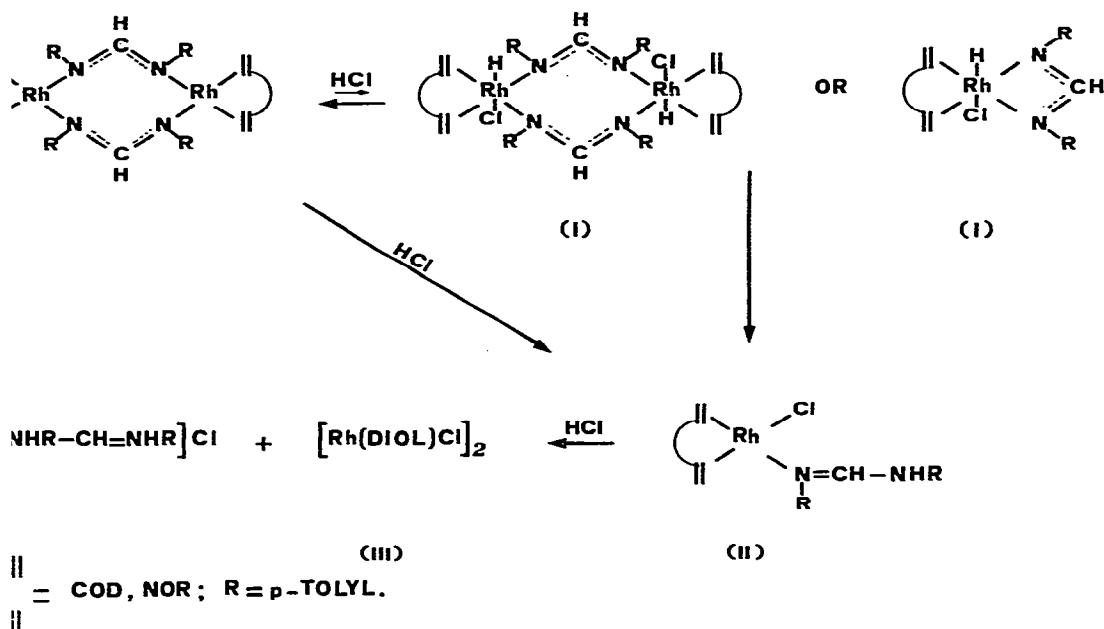
Reaction of $[\text{Rh}(\text{diol})(\text{formamidine})]_2$ with CO, dppe and dipyridyl

The diene ligands are easily displaced in compounds 1 and 2 by reaction with carbon monoxide and bis(1,2-diphenylphosphino)ethane (dppe), while dipyridyl has no effect even at the reflux temperature. When a toluene solution of $[\text{Rh}(\text{diol})(\text{formamidine})]_2$ was refluxed for 4 h with dppe a yellow compound was obtained from which the known $[\text{Rh}(\text{dppe})_2]^+$ was isolated as the tetraphenylborate salt. By reaction with carbon monoxide, 1 and 2 gave the recently reported $[\text{Rh}(\text{CO})_2(\text{formamidine})]_2$ [4]. Attempts to cleave the formamidino bridges by treating $[\text{Rh}(\text{CO})_2(\text{formamidine})]_2$ with an excess of PPh_3 failed; after chromatography on alumina, a red product was isolated whose analytical data, molecular weight measurements and IR bands suggest that it is $[\text{Rh}_2(\text{PPh}_3)(\text{CO})_3(\text{formamidine})_2]$ (4). An analogous compound, in which the formamidine is $[\text{RNC}(\text{Me})\text{NR}]$ ($\text{R} = \text{Ph}$ or *p*-tolyl), has been reported [12].

Reactions with acids

When 1 or 2 were treated with HCl gas or aqueous HBF_4 no hydride compounds were isolated. Bubbling HCl gas through a benzene solution of $[\text{Rh}(\text{diol})(\text{formamidine})]_2$ gave a white microcrystalline precipitate, which was found to contain the cation $[\textit{p}\text{-tolyl—NH=CHNH—tolyl—}\textit{p}]^+$ (7). Work up of the benzene solution led to the isolation of the complex $[\text{Rh}(\text{diol})\text{Cl}]_2$. For this reaction the mechanisms shown in Scheme 1 can be considered. Species I result from an initial oxidative addition of HCl to the rhodium atoms; with these Rh^{III} species, transfer of hydrogen from the metallic atoms to the nitrogen

EME 1



leads to formation of the intermediate II. It is more likely, however, that species II is formed by simple protonation of the nitrogen atom of the coordinated formamidine of the starting substrate. Further attack of HCl on species II gives the formamidino cation and complex III. Since formation of rhodium(III) chloride compounds is generally unfavourable [13] and since we observed that diene complexes 1 and 2 do not react with H₂ or CH₃I, we think that formation of species (I) is unlikely or that at best it is formed only reversibly. In the case formation of the complex II is necessary to explain the final products; existence of the intermediate II is supported by a report [14] of the isolation of the cationic complex [Rh(PPh₃)₂(CO)(RN=CMe-NHR)]⁺, in which the formylacetamido ligand is monodentate.

The acetone solutions of 1 and 2 also react with an aqueous solution of F₄ to give [Rh(diol)F]₂ along with the formamidino cation as the tetrafluoroborate salt.

Reactions with etherocumulenes

The reagents CS₂, SO₂, PhNCO and PhNCS react with complex 1 to displace the diene ligand, as shown also by ¹H NMR spectroscopy. Only in the case of CS₂ could we isolate the product in a pure form. Thus refluxing a carbon disulfide solution of [Rh(C₈H₁₂)(formamidine)]₂ for 48 h gave a deep-red solution, from which was isolated a red-black compound whose elemental analysis is consistent with the formulation [Rh(CS₂)₂(formamidine)]_n (5). Molecular weight measurements show it to be a polymer, while the IR and ¹H NMR spectra display very broad bands which do not permit reasonable speculation about polymer structure.

Reaction of the complex 5 with the methylating agent [(CH₃)₃O]⁺PF₆⁻

recovered the cation $[\text{Rh}(\text{CS}_2)(\text{CSMe})(\text{formamidine})]^+$ which was isolated analytically pure as the PF_6 and BPh_4 salts. Since the ^1H NMR spectrum of the polymeric material does not show any bands attributable to a methyl group bonded to the metal we suggest that the reaction involves alkylation of sulphur, but in the absence of suitable spectroscopic data or an X-ray analysis we cannot with any confidence suggest formula for the polymer.

These reactions can be understood by taking into account the high *trans* effect of the formamidino ligand. Probably the reactions occur with initial formation of an adduct between the complex 1 and the heterocumulene, and labilization of the diene in this intermediate leads to the formation of polymers, or inseparable product mixtures.

Experimental

N,N'-Di-*p*-tolylformamidine [15], $[\text{Rh}(\text{diol})\text{Cl}]_2$ (diol = cycloocta-1,5-diene [16]; diol = norbornadiene [17]) and $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$ [18] were prepared by published procedures. Elemental analyses were by the Laboratory of Organic Chemistry, Institute of Milan, Italy, and by Bernhardt Mikroanalytisches Laboratorium, Elbach, Germany. Infrared spectra were recorded on a Perkin-Elmer 457 spectrometer calibrated with polystyrene. The ^1H NMR spectra were recorded on a 60 MHz Perkin-Elmer R 24B. Molecular weights measurements were determined with a Knauer vapour-pressure osmometer. All reactions were carried out under dry nitrogen.

Preparation of $[\text{Rh}(\text{C}_8\text{H}_{12})(\text{CH}\{\text{NC}_6\text{H}_4\text{-}p\text{-CH}_3\}_2)]_2$. $\text{K}[\text{CH}(\text{NC}_6\text{H}_4\text{-}p\text{-CH}_3)_2]$ was prepared by stirring for ca. 2 h a toluene solution of *N,N'*-di-*p*-tolylformamidine with an equimolar ratio of freshly prepared KOBu^t . To this solution which contained 0.53 g (2.02 mmol) of potassium formamidinate, was added 0.5 g (1.01 mmol) of $[\text{Rh}(\text{C}_8\text{H}_{12})\text{Cl}]_2$, and the mixture was stirred for 6 h at room temperature. The resultant yellow-orange solution was filtered and reduced in volume to ca. 20 ml. Hexane was added until a yellow-range compound began to precipitate. Cooling gave 0.45 g of complex, which was filtered off and recrystallized from benzene-diethyl ether.

Preparation of $[\text{Rh}(\text{C}_7\text{H}_8)(\text{CH}\{\text{NC}_6\text{H}_4\text{-}p\text{-CH}_3\}_2)]_2$. To a benzene solution of $\text{K}[\text{CH}(\text{NC}_6\text{H}_4\text{-}p\text{-CH}_3)_2]$ (0.39 g, 1.3 mmol), prepared as before, was added 0.56 mmol of $[\text{Rh}(\text{C}_7\text{H}_8)\text{Cl}]_2$. The resulting deep-red solution was stirred at room temperature for 5 h and then all the solvent was removed in vacuo. The red solid residue was washed with pentane and dissolved in benzene, and the solution was chromatographed on a neutral alumina column (activity 3) saturated with benzene. Pentane was used as eluant to give the desired compound in 40% yield.

Preparation of $[\text{Rh}(\text{PPh}_3)_2(\text{CH}\{\text{NC}_6\text{H}_4\text{-}p\text{-CH}_3\}_2)(\text{O}_2)]$. A solution of potassium formamidinate (0.12 g, 0.48 mmol) in benzene, prepared in the usual way, was refluxed for 3 h with 0.45 g (0.48 mmol) of $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$. After filtration the red solution was evaporated to dryness, and the red-brown solid residue was washed with diethyl ether and recrystallized twice from benzene/diethyl ether, to give orange crystals.

The same compound was obtained by refluxing 0.49 g (0.46 mmol) of $[\text{Rh}(\text{C}_8\text{H}_{12})(\text{CH}\{\text{NC}_6\text{H}_4\text{-}p\text{-CH}_3\}_2)]_2$ for 5 h with 0.72 g (2.7 mmol) of PPh_3

n toluene. Work up as before gave 0.17 g of the dioxygen adduct.

Preparation of $[Rh(CO)_2(CH\{NC_6H_4-p-CH_3\}_2)]_2$. Carbon monoxide was bubbled for 2 h through a dichloromethane solution of $[Rh(C_8H_{12})-CH\{NC_6H_4-p-CH_3\}_2]_2$. Removal of the solvent left a red solid, from which the dicarbonyl compound was isolated by chromatography on Al_2O_3 saturated with benzene.

Preparation of $[Rh_2(CO)_3(PPh_3)(CH\{NC_6H_4-p-CH_3\}_2)]$. To a solution of $Rh(CO)_2(CH\{NC_6H_4-p-CH_3\}_2)_2$ (0.2 g, 0.26 mmol) in diethyl ether was added 0.41 g (1.5 mmol) of PPh_3 , and the mixture was stirred for 24 h at room temperature. After removal of the solvent the red solid obtained was chromatographed on a neutral Al_2O_3 column saturated with CH_2Cl_2 . Eluting with pentane gave the pure dimer.

Reactions with HCl. HCl gas was bubbled into a benzene solution of $Rh(C_8H_{12})(CH\{NC_6H_4-p-CH_3\}_2)_2$ (0.25 g, 0.28 mmol) for 3 h during which the solution turned yellow and a white microcrystalline solid separated. The solid was filtered off, washed with benzene, and crystallized from CH_3OH /diethyl ether to give $[p\text{-tolyl-NH=CH-NH-tolyl-}p]Cl$. The complex $Rh(C_8H_{12})Cl_2$ was obtained from the supernatant liquor.

Similarly, the reaction of $[Rh(C_7H_8)(CH\{NC_6H_4-p-CH_3\}_2)]_2$ with HCl gave the chloride of formamidino cation and the complex $[Rh(C_7H_8)Cl]_2$.

Reactions with HBf_4 . To a suspension of $[Rh(\text{diol})(CH\{NC_6H_4-p-CH_3\}_2)]_2$ in acetone were added a few drops of aqueous HBf_4 48%. After stirring for 5 h the resultant pale-yellow solution was filtered and evaporated to dryness. The solid residue was extracted with benzene to leave a white solid, which was recrystallized from CH_3OH /diethyl ether to give $[p\text{-tolyl-NH-CH=NH-tolyl-}p]BF_4$. The benzene solution was found to contain $[Rh(\text{diol})F]_2$.

Preparation of $[Rh(CS_2)_2(CH\{NC_6H_4-p-CH_3\}_2)]_n$. A solution of 0.3 g (0.34 mmol) of $[Rh(C_8H_{12})(CH\{NC_6H_4-p-CH_3\}_2)]_2$ in carbon disulphide was refluxed for 35 h. The deep-red solution was filtered and the filtrate to leave a black residue, which was washed several times with benzene, then recrystallized twice from CH_2Cl_2 /hexane to give an almost black product.

Preparation of $[Rh(CS_2)(CSMe)(CH\{NC_6H_4-p-CH_3\}_2)]PF_6$. To a stirred solution of $[Rh(CS_2)_2(CH\{NC_6H_4-p-CH_3\}_2)]_n$ (0.2 g, 0.4 mmol) in CH_2Cl_2 was added a suspension of $[(CH_3)_3O]PF_6$ in the same solvent, and the mixture was stirred for 6 h at room temperature. The red solution was then filtered, and the filtrate was reduced in volume to ca. 10 ml. Addition of diethyl ether and cooling gave 0.05 g of the red desired complex.

Acknowledgement

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