

REACTIONS OF ORGANIC AZIDES WITH NOBLE METAL CARBONYL HALIDES

I. THE REACTION OF BENZOYL AZIDE WITH DI- μ -CHLOROBIS(DICARBONYLRHODIUM)

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Summary

The preparation of some new organometallic derivatives of rhodium(III), obtained by the reaction of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ with benzoyl azide in C_6H_6 or THF, are described.

The chemical behaviour and IR and NMR data for the adducts with triphenylphosphine, *p*-toluidine, pyridine and 3,4-lutidine of formula $[\text{Rh}(\text{C}_6\text{H}_4\text{CONH})\text{L}(\text{CO})\text{Cl}]$ show that they can be considered as benzoylimido derivatives of rhodium(III).

Introduction

It is well known that transition metal complexes catalyze the decomposition of many azido compounds, and that nitrenes, which are assumed to be the immediate decomposition products of organic azides, may be trapped as ligands in metal complexes.

By treating azidobenzene [1] and aromatic diazides [2] with diiron enneacarbonyl, compounds containing the azobenzene skeleton have been obtained, as well as urea-based complexes and μ -phenylamido derivatives.

Fluoroalkylimido derivatives have been obtained by reaction between 2H-hexafluoropropyl azide and low valent metal complexes: the more significant appear to be those of iridium(I) and rhodium(I) of the type $(\text{PPh}_3)_2\text{MCl}(\text{NR}_F)$ [3], where $\text{M} = \text{Ir}, \text{Rh}$; $\text{R}_F = \text{CF}_3\text{CHF}_2$. Acyl azides react with *trans*-chlorocarbonylbis(triphenylphosphine)iridium(I) in alcohol-free solution to give acyl isocyanate complexes of the type $\text{IrCl}(\text{RCONCO})\text{L}_2$ ($\text{R} = \text{C}_4\text{H}_9\text{O}, \text{C}_6\text{H}_5, p$ -

$\text{NO}_2\text{C}_6\text{H}_4$, $p\text{-CH}_3\text{C}_6\text{H}_4$, $p\text{-CH}_3\text{OC}_6\text{H}_4$; $\text{L} = \text{PPh}_3$) [4], while in the presence of ethanol the stable molecular nitrogen complex $\text{IrL}_2(\text{N}_2)\text{Cl}$ and organic isocyanates are formed [5].

In order to investigate further the reaction of unsaturated organic systems with simple d^{10} halocarbonyls, such as $\text{Ir}(\text{CO})_3\text{X}$ and $\text{Pt}(\text{CO})_2\text{Cl}_2$ [6], we have now studied the reaction of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ with benzoyl azide, which allowed us to isolate some new benzoylimido complexes derived from the nitrene moiety.

Results and discussion

The reaction between benzoyl azide and di- μ -chlorobis(dicarbonylrhodium)

Di- μ -chlorobis(dicarbonylrhodium) reacts with benzoyl azide in benzene or tetrahydrofuran to give a red-violet insoluble compound. In both solvents the reaction needed an induction period: at room temperature the complete transformation of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ was observed only when four moles of benzoyl azide were treated with one mole of the chlorocarbonyl for at least 80 h.

The course of the reaction was followed by the IR spectra of the solution, and after 5 h a strong band at 2260 cm^{-1} (of intensity comparable to that at 2130 cm^{-1}), due to the asymmetric stretching of the benzoyl azide, became prominent while three other new bands appeared at 1725, 1645 and 1600 cm^{-1} . The intensities of these last bands increased slowly and then decreased while that of the peak at 2260 cm^{-1} reached a maximum. From this reddish solution, a red-violet solid separated. According to data reported by Collman [5], the 2260 cm^{-1} band can be assigned to free isocyanate; however, the simultaneous appearance of the three bands in the 1725-1600 cm^{-1} region suggests that most probably a benzoyl isocyanate rhodium complex was being formed, which was not isolated owing to its instability under the reaction conditions.

The main reaction product was the red-violet solid, which was insoluble in all the common organic solvents, and was characterized by its elemental analysis (reported in Table 1), IR spectrum and chemical behaviour, as a rhodium complex derived from the nitrene radical formed via azide coordination, to which can be assigned the formula $[\text{Rh}(\text{CO})(\text{C}_6\text{H}_4\text{CONH})\text{Cl}]_n$ (I).

It is worth noting that I was formed only after the isocyanate species had appeared in the solution, indicating that the first step of the reaction could be the extraction of a carbon monoxide molecule bonded to the rhodium through the initial coordination of the azide to the metal. The formation of the isocyanate makes the metal centre available to attack by the nitrene moiety which, being formed through the subsequent coordination of the azide to the unsaturated rhodium species, competes in complex formation.

The formation of benzoyl isocyanate, by extraction of the CO bonded to the rhodium atom, appeared to be an important step in the reaction, as has been proved by experiments carried out in the presence of ethanol which led to the quantitative isolation of ethyl *N*-benzoyl carbamate, derived by nucleophilic attack of ethanol to the benzoyl isocyanate.

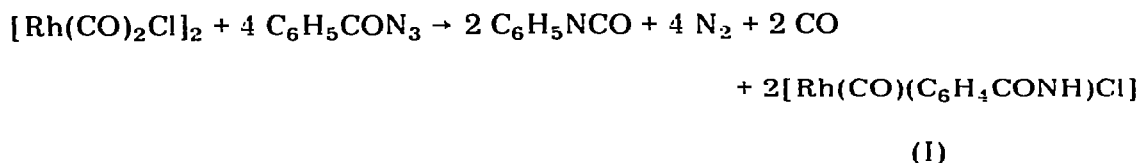
Conversely, the isocyanate species, whose formation is always evident during the reaction, has been shown to be phenyl isocyanate. In fact, when a small amount of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ is treated in benzene with an excess of benzoyl azide under carbon monoxide, the benzoyl azide is entirely transformed to phenyl isocyanate, as

TABLE 1
ANALYTICAL AND PHYSICAL DATA

Compd.	Colour	Melting point	Analysis found (calcd.) (%)			Molecular weight found (calcd.)
			C	H	N	
I ^a	Red-violet	216-280(dec.)	35.00	2.30	4.40	
			32.25	2.08	4.11	
			35.50	2.36	4.16	
			34.75	2.05	4.11	
			(33.62)	(1.75)	(4.90)	
II	Deep-orange	180-182	56.19	3.48	2.05	1090
			(56.98)	(3.65)	(2.25)	(1095)
III	Red	150-152	47.91	2.80	3.10	
			(48.98)	(3.00)	(3.36)	
IV	Dark-yellow	210-215(dec.)	45.31	3.96	6.87	
			(45.85)	(3.56)	(7.13)	
V	Yellow	203-208(dec.)	43.52	3.08	7.72	
			(42.79)	(2.74)	(7.68)	
VI	Orange-yellow	195-200(dec.)	44.48	3.72	6.71	770
			(45.85)	(3.56)	(7.13)	(785)

^a The elemental analyses reported for compound I refer to samples obtained in different preparations.

shown by the strong absorption band at 2260 cm^{-1} and the absence of any band in the 1700 cm^{-1} region. Further definite evidence of phenyl isocyanate formation comes from reaction with aniline which gives *N,N'*-diphenylurea. This is not surprising, since it is known that aroyl derivatives can be decarbonylated in the presence of rhodium complexes [7,8], and that organic isocyanates are catalytically formed when organic azides are treated with CO in the presence of Rh and Ir carbonyl complexes [9]. The fact that $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ is quantitatively transformed when benzoyl azide was added in the ratio 1/4 seems to suggest the following stoichiometry:



Compound I, which is sparingly soluble in all the common organic solvents, can be considered as a benzoylimido derivative of rhodium(III) on the basis of the IR spectrum, reported in Table 2, as well as by its reactivity with donor ligands, such as triphenylphosphine, pyridine, *p*-toluidine, 3,4-lutidine and carbon monoxide.

The most significant bands observed in the IR spectrum registered in nujol mull appear to be those at 2085 and 2070 cm^{-1} , which can be assigned to non-equivalent terminal CO groups, and the two bands at 1595 and 1550 cm^{-1} which are related to the organic part of the ligand coordinated to the metal.

The presence of a single band at 3390 cm^{-1} in the stretching region of the N-H bond, which remained practically unchanged in the donor ligand adducts, seems to exclude the formation of an amido complex, and suggests that a further

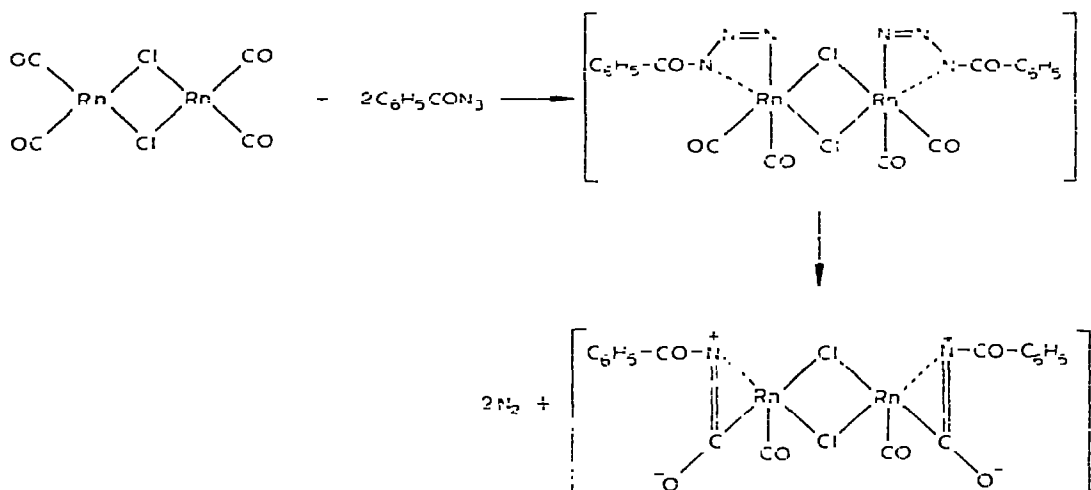
TABLE 2
INFRARED SPECTRA

Compound	IR data (cm ⁻¹) ^a		
	$\nu(\text{NH})$	$\nu(\text{CO})$	Other bands
I	3390	2070, 2085	1595, 1550, 1230
II	3370	2045, 2065	1598, 1565, 1250
III	3380	2050, 2075	1595, 1555, 1245
IV	3330	2048, 2063	1595, 1565, 1245
V	3320	2045, 2060	1595, 1555, 1240
VI	3385	2040, 2060	1595, 1560, 1235

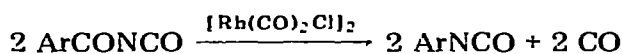
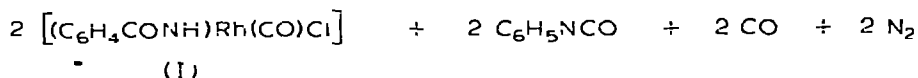
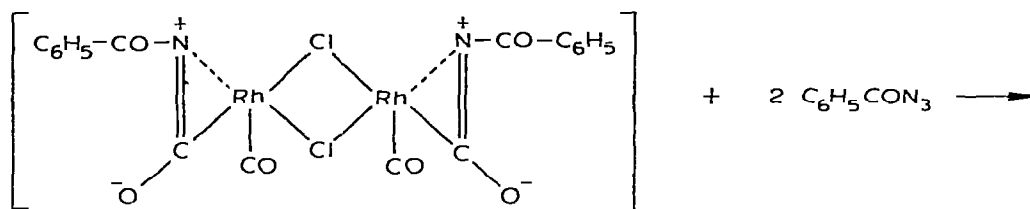
^a In Nujol mulls. ^b Assigned to NH stretching of the *p*-toluidine.

bond may involve the rhodium atom so stabilizing the N—Rh bond, by ortho-metallation of the phenyl ring.

When the reaction was carried out under a CO atmosphere in either benzene or tetrahydrofuran, the benzoylimido derivative was not formed, as expected, confirming that its formation was strongly dependent on both the extraction of a carbon monoxide molecule from the coordination sphere of the metal and of the further bonding of the benzoyl azide to the rhodium. On the basis of the data reported above it seems that the reaction proceeds from the initial formation of an unstable intermediate azide adduct, similar to that proposed by Collman [10]. This intermediate was not experimentally detected owing to its transformation into an isocyanate complex [5], whose existence is suggested by the IR bands at 1725, 1645 and 1600 cm⁻¹ in the solution.



The removal of benzoyl isocyanate allows further coordination of benzoyl azide, which leads to the benzoylimido derivative I, while benzoyl isocyanate undergoes a decarbonylation process, being transformed into phenyl isocyanate:



This last reaction is strongly favoured by the presence of an excess of carbon monoxide which probably prevents benzoyl azide from further bonding to rhodium, di- μ -chlorobis(dicarbonylrhodium) being formed.

Reactivity of benzoylimidocarbonylchlororhodium(III)

Characterization of the organic ligand coordinated to the rhodium in compound I could be achieved only with derivatives; in fact, the insolubility of I precluded other physical data, such as NMR spectra and molecular weight measurements, from being obtained.

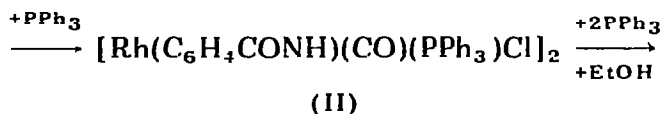
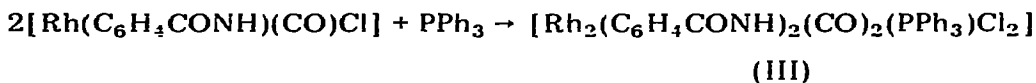
Compound I readily reacted in ethanol with one mole of triphenylphosphine to give a deep-orange insoluble species which has been identified as $[\text{Rh}(\text{C}_6\text{H}_4\text{CONH})(\text{CO})(\text{PPh}_3)\text{Cl}]_2$ (II) by its elemental analysis, IR spectrum, and molecular weight measurement in CHCl_3 . It should be noted that the IR spectrum (see Table 2) does not greatly differ from that of compound I in the region $1700\text{-}1500 \text{ cm}^{-1}$, suggesting that the organic part of the ligand derived from the nitrene moiety is basically unchanged.

When the reaction with triphenylphosphine was carried out in benzene, the product formed was strongly dependent on the amount of triphenylphosphine used. In fact, by adding to the red-violet compound I in benzene half a mole of triphenylphosphine per Rh atom, a dark-red species quite soluble in benzene was formed, whose elemental analysis was in agreement with the formula $[\text{Rh}_2(\text{C}_6\text{H}_4\text{CONH})_2(\text{CO})_2(\text{PPh}_3)\text{Cl}_2]_n$ (III), which can be considered as an adduct of the compound I with phosphine.

When compound III was treated in benzene with another half mole of triphenylphosphine, it was transformed into II, while with an excess of phosphine a yellow crystalline solid was formed which corresponded to the known $\text{Rh}(\text{PPh}_3)_2(\text{CO})\text{Cl}$ [11], showing that the benzoylimino ligand on the metal had been replaced by the phosphine. Moreover, in the presence of ethanol, the organic ligand can be recovered as benzamide.

The reaction with triphenylphosphine in benzene can be summarized as

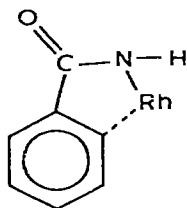
follows:



Such reactions indicate that the phosphine ligand reacts smoothly with the rhodium centre, formally rhodium(III), occupying the sixth coordination site which is vacant in compound I. Similar behaviour has been observed with other ligands, such as *p*-toluidine, pyridine, 3,4-lutidine: these nitrogen donor ligands allowed the isolation of a series of compounds, whose analytical data and spectra are reported in Tables 1 and 2, which are structurally similar to II and have been formulated as: $[\text{Rh}(\text{C}_6\text{H}_4\text{CONH})(\text{CO})\text{ClL}]_n$, where L = *p*- $\text{CH}_3\text{C}_6\text{H}_4\text{NH}_2$ (IV); $\text{C}_5\text{H}_5\text{N}$ (V); 3,4-(CH_3) $_2\text{C}_5\text{H}_3\text{N}$ (VI). The values of the molecular weights measured in CHCl_3 for compounds II and VI are in agreement with dimeric species and suggest the same molecular complexity also for the insoluble compounds IV and V. Particularly interesting is compound VI, whose solubility in chloroform and acetone enabled its NMR spectrum to be recorded; it shows a poorly resolved doublet at τ 7.66 assignable to the CH_3 groups of the coordinated 3,4-lutidine, a broad singlet at 4.75 due to the N-H proton, a multiplet centered at 2.75-2.95 assignable to the protons of the *ortho*-disubstituted phenyl ring, and a multiplet at 2.4-2.6 arising from the protons of the disubstituted pyridine ring. The intensity ratio of the signals 6/1/4/3 and the ABCD pattern of the phenyl resonances support the orthometallation of the phenyl ring which led to the formation of a stable five-membered rhodium heterocycle.

Compound I reacts slowly with carbon monoxide in THF: the red-violet solid dissolves to give a pale yellow solution. The IR spectrum of the solution shows that $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ was formed while the benzoylimido ring was transformed into an unknown organic substance.

The presence of the benzoylimido moiety chelated to the metal by N-Rh and C-Rh bonds to form a rhodiacycle system such as (A) has been confirmed



(A)

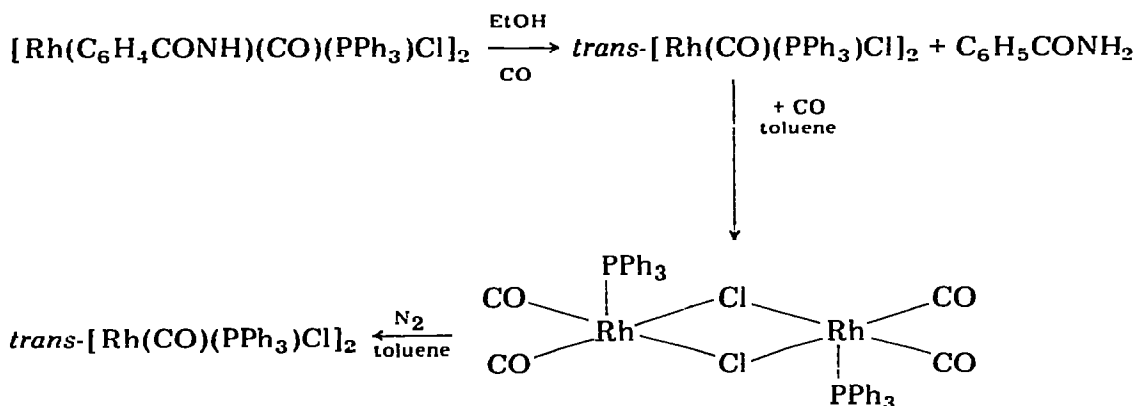
by the reaction of compound I both with hydrogen in ethanol and with NaAlH_4 in tetrahydrofuran. In both cases the formation of rhodium metal was observed while a white organic substance, identified as benzamide, was recovered from the

solution. However, compound I can not be an amido derivative because no reaction was observed when $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ and benzamide were allowed to react in benzene or in THF for several hours under nitrogen.

All these experimental data seem to confirm that compound I is a chelated benzoylimido derivative of rhodium(III), stabilized by orthometallation which leads to the formation of a Rh—C bond.

Reactivity of di(benzoylimidocarbonyltriphenylphosphinechlororhodium) (II)

Compound II reacts slowly with carbon monoxide in ethanol at 50°C giving an orange-yellow solid which has been identified as $[\text{Rh}(\text{CO})(\text{PPh}_3)\text{Cl}]_2$ [12] by the band at 1965 cm^{-1} (nujol). When carbon monoxide was bubbled through a toluene solution of compound II, the colour of the latter turned to lemon yellow and the IR spectrum developed two bands at $2010\text{--}2090\text{ cm}^{-1}$ which can be assigned to $[\text{Rh}(\text{CO})_2(\text{PPh}_3)\text{Cl}]_2$ [12]. This complex could be transformed back into the initial compound $[\text{Rh}(\text{CO})(\text{PPh}_3)\text{Cl}]_2$ by bubbling nitrogen through the carbonylated solution. It seems clear that carbon monoxide was able to replace the benzoylimido moiety. On the other hand, when the reaction was run in ethanol, the benzoylimido moiety was transformed into benzamide, which can be thought as derived from the protonation of the unstable radical formed by replacement by carbon monoxide. The carbonylation of compound II can be summarized in the following scheme:



Conclusions

The reaction between di- μ -chlorobis(dicarbonylrhodium) and benzoyl azide may be compared with that of the rhodium(I) phosphino complexes and aroyl azides. The reaction course does not differ greatly from that already described [5], but significant changes occur as regards the final products. As far as the intermediates are concerned, no isocyanate compound was isolated at the end of the reaction: this is consistent with the instability of the carbonyl isocyanate complexes which can be ascribed to the electron density on the metal. The lability of the isocyanate species may explain the formation of the benzoylimido derivative: when the carbonyl group is extracted from the rhodium through isocyanate formation, the rhodium centre becomes available for further azide coordination.

dination. The azide adduct being labile, the formation of nitrene radicals is favoured by nitrogen elimination. It is possible that a nitrogen-bearing species is formed at this stage, as has been suggested by other authors [5] from IR evidence, but we have not found definite evidence for this reaction. Conversely, the active nitrene moiety interacts with the metal forming an unusual rhodium—nitrogen bond. The final stabilization of the metalimido species is probably due to the extraction of a proton from the phenyl ring to deactivate the remaining unpaired electron on the nitrogen atom. It is impossible at present to discern whether the proton extraction is promoted by the forthcoming formation of the metal—carbon bond or metallation is responsible for generating the nitrogen—rhodium bond. It is known that transition metals favour the formation of metal—carbon bonds when chelation takes place: in our case both the change of the oxidation state of the rhodium from I to III and the energy gain in formation of a five membered ring should play an important role in stabilizing the benzoylimido complex.

Such reactions are being extended to other metal halocarbonyls and to other azides in order to define the role of both the metal and the organic part of the ligand in the formation of these compounds.

Experimental

Starting materials were prepared as described in the literature [13,14]. The IR and ^1H NMR spectra were recorded on a Perkin—Elmer Model 457 and a Varian 60 MHz NV-14, respectively. The molecular weights were obtained using a Mechrolab Osmometer model 301.

Preparation of $[\text{Rh}(\text{C}_6\text{H}_4\text{CONH})(\text{CO})\text{Cl}]_n$ (I)

$[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (390 mg, 1 mmol) and $\text{C}_6\text{H}_5\text{CON}_3$ (600 mg, 4 mmol) were dissolved in THF (30 ml) and kept under nitrogen at 25–30°C for 4 days: a red-violet solid separated from the solution and was filtered off, washed with THF (20 ml) and benzene (10 ml) and dried in vacuo.

Preparation of $[\text{Rh}(\text{C}_6\text{H}_4\text{CONH})(\text{CO})(\text{PPh}_3)\text{Cl}]_2$ (II)

I (290 mg) was stirred in EtOH (10 ml) with PPh_3 (262 mg) at room temperature. After 15 minutes the colour of the solid turned to deep-orange. The new precipitate was filtered off, washed with warm ethanol (10 ml) and with diethyl ether (10 ml) and then recrystallized from acetone.

Preparation of $[\text{Rh}_2(\text{C}_6\text{H}_4\text{CONH})_2(\text{CO})_2(\text{PPh}_3)\text{Cl}_2]$ (III)

PPh_3 (131 mg) dissolved in benzene (10 ml) was added slowly to I (290 mg) suspended in benzene (20 ml). A red solution was obtained, which was reduced to 10 ml by evaporation in vacuo, whereupon a red precipitate separated which was filtered off, washed with diethyl ether (10 ml) and dried in vacuo.

Preparation of $[\text{Rh}(\text{C}_6\text{H}_4\text{CONH})(p\text{-toluidine})(\text{CO})\text{Cl}]_n$ (IV)

To the stirred solution of I (290 mg) in ethanol (10 ml) was added the nitrogen donor ligand (110 mg). After 15 minutes the dark yellow solid was filtered off, washed with ethanol (10 ml) and dried in vacuo.

Preparation of $[Rh(C_6H_4CONH)(pyridine)(CO)Cl]_n$ (V)

To I (290 mg) in ethanol was added pyridine (100 mg) dissolved in ethanol (50 ml). The yellow precipitate was filtered off, washed with ethanol (10 ml), and dried in vacuo.

Preparation of $[Rh(C_6H_4CONH)(3,4\text{-lutidine})(CO)Cl]_2$ (VI)

This complex was prepared by the same procedure described for IV and V. The orange-yellow solid was recrystallized from acetone.

Preparation of N,N' -diphenylurea

$[Rh(CO)_2Cl]_2$ (20 mg) was added to benzoyl azide (150 mg) in benzene (50 ml) under CO: the solution was kept at room temperature for 5 days without any apparent transformation of the rhodium carbonyl chloride. However, the IR spectrum showed that all the benzoyl azide was transformed into isocyanate [$\nu(NCO)$ 2260 cm^{-1}]. On adding aniline (200 mg) to the solution a white solid separated which, when recrystallized from diethyl ether, was found to be N,N' -diphenylurea, indicating that the benzoyl azide had previously been transformed catalytically into phenyl isocyanate. (Found: C, 72.32; H, 5.39; N, 12.85. $C_6H_5NHCONHC_6H_5$ calcd.: C, 73.58; H, 5.66; N, 13.2%. IR (cm^{-1}): $\nu(NH)$ 3280-3320, $\nu(CO)$ 1645, $\nu(CNH)$ 1560. M.p. 241°C, b.p. 263°C (dec.).)

Reaction of $[Rh(CO)_2Cl]_2$ with benzoyl azide in the presence of ethanol

Dichlorodicarbonylrhodium dimer (300 mg) and benzoyl azide (450 mg), were dissolved in tetrahydrofuran (25 ml) containing ethanol (7%) and kept under nitrogen at 25-30°C for 24 h. A red-violet solid separated from the solution, and was identified as I; the orange-brown solution was evaporated to dryness and the residue extracted with chloroform (5 ml). The chloroform solution was then introduced on to an alumina column, and by elution with $CHCl_3$, colourless needles were isolated which, after crystallisation from hexane, were identified as ethyl N -benzoyl carbamate.

The IR spectrum in nujol mull showed the following characteristic absorption peaks (cm^{-1}): $\nu(N-H)$ 3275 m, $\nu(C=O)$ 1770 s, 1750 vs, 1680 w, $\nu(C-O)$ 1210 vs, 1190 s.

The NMR spectrum in $CDCl_3$ showed a triplet at τ 8.73, and a quartet at 5.7 assignable to the OCH_2CH_3 group, a multiplet in the range 2.1-2.75, assignable to the monosubstituted phenyl group, and a broad singlet at 1.95, due to $N-H$ proton. The ratio of the integrals was: 3/2/5/1, as expected. Analysis: found: C, 60.32; H, 5.30; N, 7.20. Calcd.: C, 62.2; H, 5.70; N, 7.25%. By elution with $CHCl_3/EtOH$ (90/10) a white solid also separated, which was identified as benzamide.

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