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DINUCLEAR COMPLEXES OF RHODIUM(I) CONTAINING DIISOCYANIDE LIGANDS AND SOME OF THEIR PHOSPHINE DERIVATIVES

P.V. YANEFF and J. POWELL *
Lash Miller Chemical Laboratories, University of Toronto, Toronto M5S 1A1 (Canada)

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Summary

A series of organic diisocyanides [(1,3-diisocyanopropane, 1,4-diisocyanobutane, 1,5-diisocyanopentane, 1,6-diisocyanohexane, 1,3-bis(isocyanomethyl)-benzene and 1,4-bis(isocyanomethyl)cyclohexane)] was found to rapidly react with $[RhCl(CO)_2]_2$ or $[RhCl(C_8H_{12})]_2$ to give the photosensitive complexes $[Rh_2(diisocyanide)_4]^{2+}$ (1—6). Reaction between 1,8-diisocyanooctane and $[RhCl(C_8H_{12})]_2$ produces the monomeric cation $[Rh(1,8\text{-diisocyanooctane})_2]^+$. Photochemical solvolysis reactions of complexes 1—2 are examined. Reaction of 1—7 with bis(diphenylphosphino)methane (DPM) displaces two diisocyanide ligands to give *trans*-$[Rh_2(diisocyanide)_2(DPM)_2]^{2+}$ (8—14), which may also be obtained from the reaction of the diisocyanide and *trans*-$[RhCl(CO)(DPM)]_2$. Similarly, $[Rh_2(diisocyanide)_2(PPh_3)_4]^{2+}$ (15—19) may be prepared from reaction between $[Rh_2(diisocyanide)_4]^{2+}$ and triphenylphosphine or from the reaction of *trans*-$[RhCl(CO)(PPh_3)_2]$ or $[RhCl(PPh_3)_3]$ with the diisocyanide ligand. Complex 7 also reacts with triphenylphosphine and bis(diphenylphosphino)ethane-(diphos) producing the complexes *cis*-$[Rh(1,8\text{-diisocyanooctane})(PPh_3)_2]^+$ (20) and *cis*-$[Rh(1,8\text{-diisocyanooctane})(diphos)]^+$ (21), respectively.

Introduction

A recent report [1] concerning the synthesis of some rhodium diisocyanide complexes prompts us to report our findings on the preparation and properties of some rhodium(I) complexes containing diisocyanide and phosphine ligands.

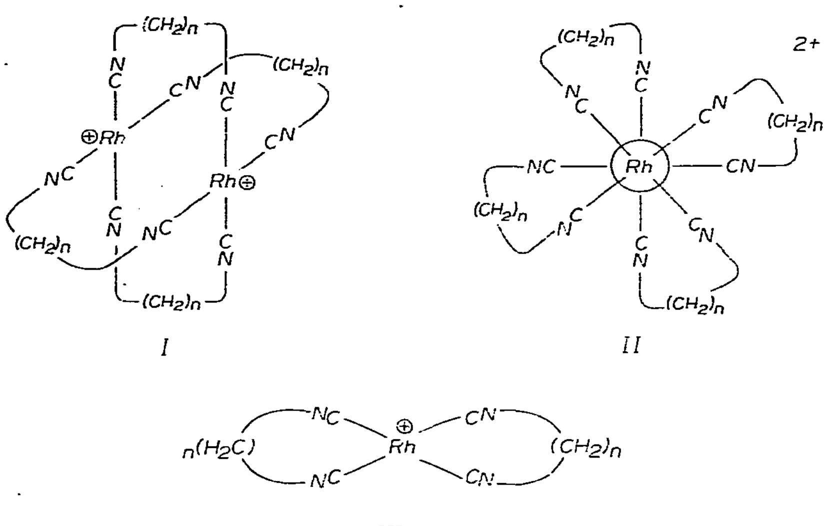
When we began this work, the only diisocyanide complexes previously reported in the literature were of the form $[Rh_2(diisocyanide)_4][X]_2$(I) (diisocyanide = 1,3-diisocyanopropane; X = Cl, BPh_4, BF_4), proposed to contain a weak rhodium—rhodium interaction [2,3]. The unusual spectroscopic and chemical properties reported for these complexes has led us to examine the effect of altering the structure of the bridging diisocyanide ligand and study this variation in terms of the chemical reactivity of their complexes. Initially, we synthesized a series of diisocyanide ligands and studied their reactions with rhodium(I) and iridium(I) complexes. In this paper we report the synthesis and spectroscopic characterization of diisocyanide complexes structurally similar to I for the ligands 1,4-diisocyanobutane, 1,5-diisocyanopentane, 1,6-diisocyanohexane, 1,3-bis(isocyanomethyl)benzene and 1,4-bis(isocyanomethyl)cyclohexane. Triphenylphosphine substituted derivatives and bis(diphenylphosphino)-methane (DPM) derivatives have also been prepared.

Results and discussion

The dimeric rhodium(I) complexes $[Rh_2(diisocyanide)_4][X]_2$ (1—6; diisocyanide = 1,3-diisocyanopropane, 1,4-diisocyanobutane, 1,5-diisocyanopentane, 1,6-diisocyanohexane, 1,4-bis(isocyanomethyl)cyclohexane and 1,3-bis(isocyanomethyl)benzene; X = Cl, BF_4, PF_6 or BPh_4) were conveniently synthesized from the addition of the appropriate diisocyanide in methanol to a methanolic suspension of $[RhCl(C_8H_{12})]_2$ [4]. The addition of $NaBPh_4$ in methanol precipitated the complexes as their tetraphenylborate salts. The tetrafluoroborate or hexafluorophosphate salts were prepared via the addition of $NaBF_4$ or $NaPF_6$ in water and the volume concentrated until the product separated. Alternatively, these latter two salts could be prepared by the reaction of $AgBF_4$ or $AgPF_6$ with $[RhCl(C_8H_{12})]_2$ in methanol. After the AgCl which precipitated was removed, addition of the diisocyanide gave the required product. Finally, $[RhCl(CO)_2]_2$ also reacts with diisocyanide yielding $[Rh_2(diisocyanide)_4]Cl_2$. 1,8-diisocyanooctane reacts with $[RhCl(C_8H_{12})]_2$ in methanol to give the monomeric species $[Rh(1,8\text{-diisocyanooctane})_2][BPh_4]$ (7) upon the addition of $NaBPh_4$ in methanol.

The physical properties, spectroscopic data and analytical data for the complexes prepared are listed in Table 1. All of the diisocyanide complexes 1—7 display a single isocyanide stretching frequency in their infrared spectra in the 2190—2170 cm^{-1} region. Relative to the free ligand, $\nu(C\equiv N)$ increases slightly (ca. 20—30 cm^{-1}) upon coordination. The presence of only one $\nu(C\equiv N)$ absorption implies that all four diisocyanide ligands are equivalent in their coordination to the rhodium atoms. We assume the structure of 1—6 is as proposed for I by Gray and co-workers [2] and that of 7 as recently suggested for $[Rh(1,8\text{-diisocyanooctane})_2][PF_6]$ [1] (i.e., structure III). However, it should be noted that whilst the complex cations $[Rh_2\{CN(CH_2)_nNC\}_4]^{2+}$ will adopt a structure that will be close to an eclipsed conformation for $n = 3$ (i.e., structure I), the complexes containing α,ω-diisocyanides with higher chain lengths ($n = 4$—6) may adopt either an eclipsed conformation similar to I or a staggered conformation (structure II) similar to that observed for $[Rh_2(CNPh)_8]^{2+}$ in the crystalline state [5] (Fig. 1).

The exceedingly dark blue and purple colours of the tetrakis(diisocyanide) complexes (1—6) may be attributed to weak metal—metal interactions as has been previously observed and discussed for both monoisocyanide and diisocyanide complexes of rhodium(I) and iridium(I) [1,2,6]. Gray and co-workers [5] have observed that mononuclear rhodium(I) isocyanide complexes (i.e., $Rh(CNR)_4^+$) display absorptions in their electronic spectra around 415—380 nm and have assigned this absorption to a spin allowed $a_{1g} \rightarrow a_{2u}$ transition. More-



I

II

III

Fig. 1. Structures proposed for the diisocyanide complexes $Rh_2\{CN(CH_2)_nNC\}_4^{2+}$ and $Rh\{CN(CH_2)_nNC\}_2^{+}$. For n = 3, type I is proposed but as n increases from 4—6, a configurational rearrangement from an eclipsed towards a staggered configuration may occur such that structure II is also a possibility. For n = 8, chelation at a single rhodium centre is assumed.

over, in concentrated solutions, new absorptions occur around 550 nm and 715 nm; these have been attributed to a $1b_2 \rightarrow 2a_1$ transition in the dimer, $[Rh_2(CNR)_8]^{2+}$, and to a $2a_{1g} \rightarrow 2a_{2u}$ transition in the trimer, $[Rh_3(CNR)_{12}]^{3+}$, respectively.

Our electronic data (Table 1), in agreement with previous results [1,2] indicate that the dinuclear rhodium(I) diisocyanide complexes may aggregate in solution to give oligomeric species and that the steric nature of the diisocyanide ligand is responsible, in part, for determining the extent of this oligomerization. Thus, for example, $[Rh_2(CNC_3H_6NC)_4][Cl]_2$ readily oligomerizes from the dimer to the tetramer, hexamer, octamer and decamer. For $[Rh_2(CNC_4H_8NC)_4][PF_6]_2$ some oligomerization to the tetramer is possible whilst for $[Rh_2(CNC_6H_{12}NC)_4][PF_6]_2$ no evidence of oligomerization, even in concentrated solution, is observed. Also indicated from the electronic data is a shift to higher energy of the absorption assigned to the $1a_{2u} \rightarrow 2a_{1g}$ transition as the chain length of the alkyl diisocyanide ligands increases from 1,3-diisocyanopropane (555 nm) to 1,6-diisocyanohexane (505 nm). Assuming previous assignments and interpretations relating to the absorptions in the 600—500 nm region to be correct, this observation suggests that the rhodium-rhodium interaction in $[Rh_2\{CN(CH_2)_nNC\}_4]^{2+}$ is weakened as the alkyl chain length n, increases from 3 to 6. Certainly as the chain length increases the bridging diisocyanide ligands become more flexible being capable of bridging two metals at an increased metal—metal separation, and capable of accommodating a twisted (staggered) conformation of the two planar coordination planes.

Two structural isomers are observed for $[Rh(1,8\text{-diisocyanooctane})_2][BPh_4]$ (7). At low concentrations in solution and also in the solid state 7 is believed to be a monomeric species suggested from the presence of a strong 387 nm absorp-

(Continued on p. 106)

TABLE 1

ANALYTICAL, PHYSICAL, INFRARED AND ELECTRONIC DATA OBTAINED FROM RHODIUM ISOCYANIDE COMPLEXES

	Compound	Elemental Analyses (Found (Calcd.) (%))		
		C	H	N
1a	$[Rh_2(CNC_3H_6NC)_4][BPh_4]_2 \cdot 2\,CH_3CN$ [b,c]	66.59 (66.37)	5.49 (5.41)	10.24 (10.75)
1b	$[Rh_2(CNC_3H_6NC)_4][PF_6]_2$			
2a	$[Rh_2(CNC_4H_8NC)_4][BPh_4]_2 \cdot 2\,CH_2Cl_2$ [c]	61.79 (61.43)	6.24 (5.30)	7.71 (7.74)
2b	$[Rh_2(CNC_4H_8NC)_4][BF_4]_2$			
3a	$[Rh_2(CNC_5H_{10}NC)_4][BPh_4]_2 \cdot 2\,CH_2Cl_2$ [c]	62.93 (62.34)	5.91 (5.63)	7.26 (7.45)
3b	$[Rh_2(CNC_5H_{10}NC)_4][PF_6]_2$			
4	$[Rh_2(CNC_6H_{12}NC)_4][BPh_4]_2 \cdot 2\,CH_2Cl_2$ [c]	64.45 (63.17)	5.99 (5.95)	7.21 (7.19)
5a	$[Rh_2(CNC_8H_8NC)_4][BPh_4]_2$ [c]			
5b	$[Rh_2(CNC_8H_8NC)_4][BF_4]_2 \cdot 2\,MeOH$	47.20 (47.27)	4.30 (3.78)	10.51 (10.49)
6	$[Rh_2(CNC_8H_{14}NC)_4][BPh_4]_2 \cdot CH_2Cl_2$ [c]	68.23 (67.73)	6.43 (6.26)	8.81 (7.10)
7	$[Rh(CNC_8H_{16}NC)_2][BPh_4] \cdot CH_2Cl_2$ [c]	65.00 (64.68)	7.38 (7.76)	6.58 (6.70)
8	$[Rh_2(CNC_3H_6NC)_2(Ph_2PCH_2PPh_2)_2][BPh_4]_2$ [e]	70.66 (72.00)	5.53 (5.37)	2.75 (3.11)
9	$[Rh_2(CNC_4H_8NC)_2(Ph_2PCH_2PPh_2)_2][BPh_4]_2$ [e]	71.35 (72.21)	5.76 (5.51)	3.46 (3.06)
10	$[Rh_2(CNC_5H_{10}NC)_2(Ph_2PCH_2PPh_2)_2][BPh_4]_2$ [e]	71.45 (72.41)	6.26 (5.65)	3.92 (3.01)
11	$[Rh_2(CNC_6H_{12}NC)_2(Ph_2PCH_2PPh_2)_2][BPh_4]_2$ [e]	72.60 (72.71)	6.38 (6.10)	3.25 (3.00)
12	$[Rh_2(CNC_8H_8NC)_2(Ph_2PCH_2PPh_2)_2][BPh_4]_2$ [e]	72.88 (73.60)	5.71 (5.24)	3.26 (2.91)
13	$[Rh_2(CNC_8H_{14}NC)_2(Ph_2PCH_2PPh_2)_2][BPh_4]_2$ [e]	73.79 (73.14)	6.56 (5.82)	3.94 (2.90)
14	$[Rh_2(CNC_8H_{16}NC)_2(Ph_2PCH_2PPh_2)_2][BPh_4]_2$ [e]	72.92 (72.99)	6.81 (6.02)	3.72 (2.89)
15	$[Rh_2(CNC_3H_6NC)_2(PPh_3)_4][BPh_4]_2$ [e]	73.17 (74.85)	6.21 (5.42)	3.39 (2.69)
16	$[Rh_2(CNC_4H_8NC)_2(PPh_3)_4][BPh_4]_2$ [d]	72.96 (75.14)	5.92 (5.53)	4.82 (2.66)
17	$[Rh_2(CNC_5H_{10}NC)_2(PPh_3)_4][BPh_4]_2$ [d]	72.10 (75.28)	6.13 (5.66)	3.60 (2.64)
18	$[Rh_2(CNC_6H_{12}NC)_2(PPh_3)_4][BPh_4]_2$ [d]	73.91 (75.41)	6.57 (6.32)	3.82 (2.59)
19	$[Rh_2(CNC_8H_{14}NC)_2(PPh_3)_4][BPh_4]_2$ [d]	75.68 (75.88)	6.69 (5.83)	3.68 (2.53)
20	$[Rh(CNC_8H_{16}NC)(PPh_3)_2][BPh_4] \cdot CH_2Cl_2$	67.53 (70.18)	7.17 (5.55)	4.36 (2.36)
21	$[Rh(CNC_8H_{16}NC)(Ph_2PC_2H_4PPh_2)][BPh_4] \cdot CH_2Cl_2$	66.19 (67.36)	6.98 (5.84)	4.41 (2.62)

[a] Nujol Mulls. [b] Taken from ref. [2]. [c] Determined at room temperature in acetonitrile solution. [d] Determined at room temperature in dimethyl sulphoxide solution. [e] Determined at room temperature in acetone solution. [f] Observable only in concentrated solution. [g] Green form of 16; Anal. Found C, 72.41; H, 6.15; N, 5.04. [h] Analysis indicate a slight amount of excess ligand present. Also previously observed for complexes as $[Rh(CNR)_2(PPh_3)_2]^+$ ref. [6]. [i] Green form also includes a 588 nm (4.3) absorption.

P	Colour	Infrared data [a] $\nu(C\equiv N)$ (cm^{-1})	Electronic data λ (nm) ($\epsilon \times 10^{-3}$ (±10%))
	Purple	2178vs	555(22.5) 340(6.1) 315(33.8)
	Blue-black	2178vs	
	Purple	2182vs	526(19.7) 380(sh) 340(2.0) 313(42.0)
	Green-black	2179vs	
	Brown	2177s	508(17.2) 379(sh) 338(12.1) 314(69.2)
	Green-black	2175s	
	Pink	2180s	505(15.6) 386(sh) 338(3.3) 314(47.0)
	Blue-green	2190vs	625 [f], 413(12.8) 388(5.3) 330(55.0)
	Blue-green	2184vs	
	Orange	2164vs	518 [f], 442(2.1) 387(9.6) 338(sh) 319(31.5)
	Yellow	2178m	387(13.0) 338(sh) 313(28.0)
	Green	2149vs	621(13.2) 344(6.6) 327(14.2)
	Purple	2150vs	604(8.4) 386(2.2) 327(10.2)
6.01 (6.67)	Purple	2145s	580(8.1) 378(2.0) 327(9.3)
	Purple	2132s	570(3.5) 416(1.5) 327(7.7)
	Green	2146s	
	Purple	2123s	556(5.0) 387(1.9) 326(6.6)
5.96 (6.38)	Purple	2130s	557(10.8) 343(2.4) 327(12.9)
	Orange	2182s	394(8.6) 360(sh) [i]
	Yellow	2143s	397(8.2) 315(21.2) 270(23.9)
	Yellow	2150s	400(4.8) 315(15.8) 252(31.8)
	Yellow	2148s	400(6.4) 317(21.8) 254(24.6)
	Yellow	2149s	401(8.1) 318(24.9) 260(31.3)
	Yellow	2147s	
5.10 (5.44)	Yellow	2170s	404(2.3) 276(sh) 254(15.8)

tion in its electronic spectrum (Table 1). We have mentioned above that for monoisocyanide complexes the $a_{1g} \rightarrow a_{2u}$ transition occurs in this region. Moreover, molecular models also show that both 1,7-diisocyanoheptane and 1,8-diisocyanooctane have the potential to chelate at a single metal centre (i.e., structure III) or span two metal atoms as in II. In concentrated solutions 7 exhibits a new absorption at 505 nm attributed to the dimeric cation $[Rh_2(1,8\text{-diisocyanooctane})_4]^{2+}$. The structure of this dimeric cation has been suggested to consist of face-to-face association of two molecules of 7 [1], however, molecular models indicate that a staggered structure similar to II is also a possibility and a simple differentiation between the two is not possible.

The ligands 1,3-bis(isocyanomethyl)benzene and 1,4-bis(isocyanomethyl)-cyclohexane differ slightly relative to their aliphatic alkyl counterparts in complexes 1—4 and 7 in that both involve ring systems. Consequently, both complexes 5 and 6 involving these ligands would be expected to exhibit a slightly different behaviour to complexes 1—4 and 7. Complexes 5 and 6 are expected to be dimeric in the solid state as molecular models indicate that neither ligand may chelate at a single metal centre. The green colour of 6a in DMSO is rapidly lost and the solution turns yellow. This green colour is attributed to the characteristic $1a_{2u} \rightarrow 2a_{1g}$ transition (λ_{max} 630 nm) in the dimer. The exceedingly low energy of this transition is in accord with the expected stabilization of the a_{1g} orbital via conjugation with the π-system of the benzene ring as previously observed for aromatic monoisocyanide ligands [5]. Similar results were obtained for 5a in DMSO, but for this complex the $1a_{2u} \rightarrow 2a_{1g}$ transition occurs in the 520 nm region characteristic of its non-aromatic nature. The changes observed in the electronic spectra of 5 and 6 in DMSO will be discussed and interpreted in the next section.

Photochemical solvolysis

Kawakami and co-workers have reported that $[Rh_2(CNC_4H_8NC)_4]^{2+}$ exhibits a weak absorption ($\epsilon = 2000$) at 383 nm and a more intense 564 nm ($\epsilon = 19\ 000$) absorption in DMSO [1]. The 383 nm band was assigned to the presence of a small amount of a solvent containing species, postulated to be $[Rh(CNC_4H_8NC)_2(DMSO)_2]^+$ containing unidentate diisocyanide ligand and coordinated solvent. Moreover, the 383 nm absorption (which is in the region characteristic of mononuclear isocyanide complexes) was reported to decrease upon the addition of free 1,4-diisocyanobutane.

We observe the intensity of this 383 nm absorption (observed in the electronic spectra of 1—6) to be a function of the coordinating ability of the solvent. Only the chloride salt of 1 was sufficiently soluble in a wide variety of solvents to allow a comparison in molar extinction coefficient values. The following were observed: methanol (100), acetonitrile (1000), dimethyl sulphoxide (2000). Also we observed that the addition of excess diisocyanide ligand to a methanolic solution of the chloride salt of 1 in room light could increase the 383 nm absorption at the expense of the visual absorption thus causing a colour change from dark blue to orange-yellow. The absorption spectrum for the addition of 1,3-diisocyanopropane to $[Rh_2(CNC_3H_6NC)_4][Cl]_2$ in methanol is presented in Fig. 2. However, if this addition is performed in the dark and the sample stored in the dark, several days are required before the blue colour is lost. This experiment

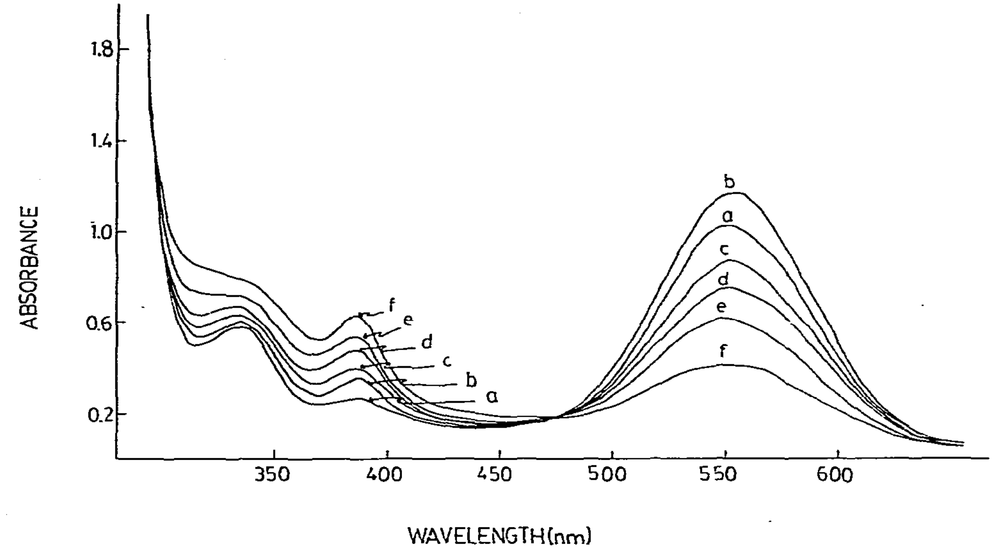
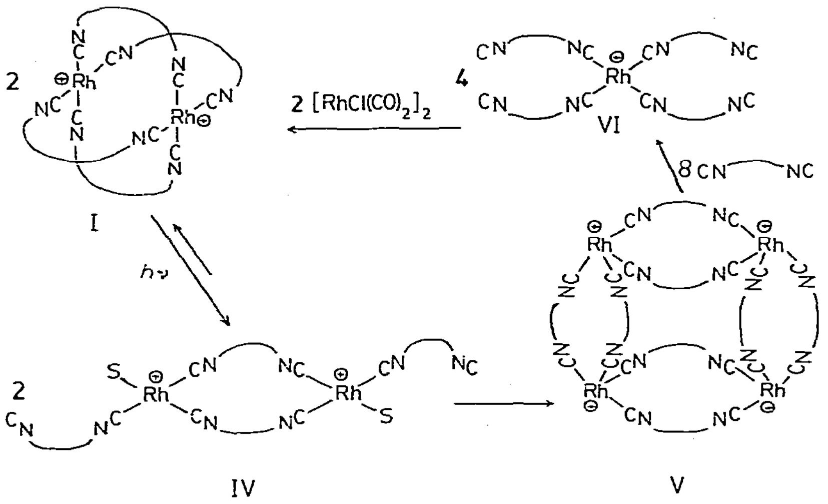


Fig. 2. Electronic absorption spectral changes during the addition of 1,3-diisocyanopropane to a 4.35×10^{-5} *M* MeOH solution of $[Rh_2\{CN(CH_2)_3NC\}_4][Cl]_2$ at 25°C. Amount of 1,3-diisocyanopropane added: (a) none, (b) 1.08×10^{-4} mol, (c) 2.17×10^{-4} mol, (d) 4.35×10^{-4} mol, (e) 8.71×10^{-4} mol, (f) 1.74×10^{-3} mol.

would suggest that the dimeric diisocyanide rhodium cations $[Rh_2(CN\{R\}NC)_4]^{2+}$ in the presence of excess diisocyanide ligand, dissociate photochemically to give the mononuclear complex $[Rh(CN\{R\}NC)_4]^+$ containing both coordinated and uncoordinated diisocyanide ligand (see VI, Scheme 1).

SCHEME 1. Proposed intermediates in the photochemical solvolysis reactions ($\lambda > 524$ nm) of $[Rh_2(CN{-}NC)_4]^{2+}$ and its subsequent regeneration ($CN{-}NC = CN(CH_2)_{3,4}NC$). (See Fig. 3.)



Further experiments clearly established that $[Rh_2(\text{diisocyanide})_4]^{2+}$ is extremely photosensitive but stable when prepared and stored in the dark. No change was observed in a sample of 1 or 2 in acetonitrile even after two months.

However, dilute solutions (10^{-4}—10^{-5} M) change from purple (or red) to yellow-orange upon irridiation. This transformation may be induced by bright sunlight, fluorescent room light or by photolysis at wavelengths between 520—560 nm. Specifically, photolysis of 2 in acetonitrile results in the complete loss of the 525 nm absorption and the generation of a new band at 383 nm. Photoexcitation of 1 at 555 nm caused a similar transformation. If these photochemical products were of the form $[Rh(diisocyanide)_2(solvent)_2]^+$ as suggested by Kawakami et al. then two absorptions due to coordinated and uncoordinated isocyanide should be observable in their IR spectra. Concentration of the photolysed solution and the slow addition of diethyl ether resulted in the formation of a yellow powder. The IR spectra of this solid exhibited a single $\nu(C{\equiv}N)$ absorption at 2220 cm^{-1} (Nujol) or 2222 cm^{-1} (MeCN). This is a slight increase in $\nu(C{\equiv}N)$ to that of 2 which occurs at 2182 cm^{-1}.

Storage of the photolysed solutions in the dark does not result in a reversal to the dimeric species. However, photogeneration of the yellow species from 2 followed by the addition of two moles of diisocyanide ligand per rhodium caused the absorption at 383 nm (ϵ = 2000) to increase in intensity with a maximum intensity (ϵ = 8000) being reached when the Rh/diisocyanide ratio is 1/4 (see Fig. 3). The IR spectrum of this product (nujol) now exhibits $\nu(C{\equiv}N)$ absorptions at 2220 vs and 2140 m cm^{-1} attributed to coordinated and uncoordinated isocyanide, respectively and is consistent with the formation of $[Rh(CNC_4H_8NC)_4]^+$ species. The addition of excess diisocyanide to the photochemically generated species also resulted in a small amount of reassociation to give some of the dimer $[Rh_2(diisocyanide)_4]^{2+}$ characterized by the absorption at 524 nm (see Fig. 3). Addition of a stoichiometric quantity of $[RhCl(CO)_2]_2$ to a solution containing $[Rh(CNC_4H_8NC)_4]^+$ produces two moles of 2 according to the electronic spectrum (see Fig. 3 and scheme 1).

The exact nature of the photochemically produced yellow species has not as yet been determined, but a solvated species containing unidentate diisocyanides seems unlikely on the basis of the above IR data. The electronic data (383 nm absorption) and IR data ($\nu C{\equiv}N$ 2220 cm^{-1}) are consistent with the yellow species containing the "$Rh(CNR)_4^+$" chromophore (cf. for $Rh(CNMe)_4^+$ 383 nm absorption and $\nu(C{\equiv}N)$ 2222 cm^{-1}). Consequently a probable structure for this species is a tetramer such as V. A likely reaction scheme for the formation of V is shown in Scheme 1. Irridiation of the dimer I results in a photochemical solvolysis reaction to give a dimeric species such as IV containing both bridging and unidentate diisocyanides and coordinated solvent. The coordinated solvent can then be displaced by "free" isocyanide in one of two ways to either regenerate the original dimer or to give the tetrameric species V. Addition of excess diisocyanide to V regenerates some of the original dimer but predominantly gives the monomeric species VI with four free isocyanide groups which, on addition of $[RhCl(CO)_2]_2$, regenerates the original dimer.

Phosphine derivatives

The tetraphenylborate salts 1—7 readily react in acetone with bis(diphenylphosphino)methane (DPM) to give *trans*-$[Rh_2(diisocyanide)_2(DPM)_2][BPh_4]_2$ as the dark green or purple complexes 8—14. An alternative synthetic route whereby yields are significantly increased is to add the diisocyanide to *trans*-

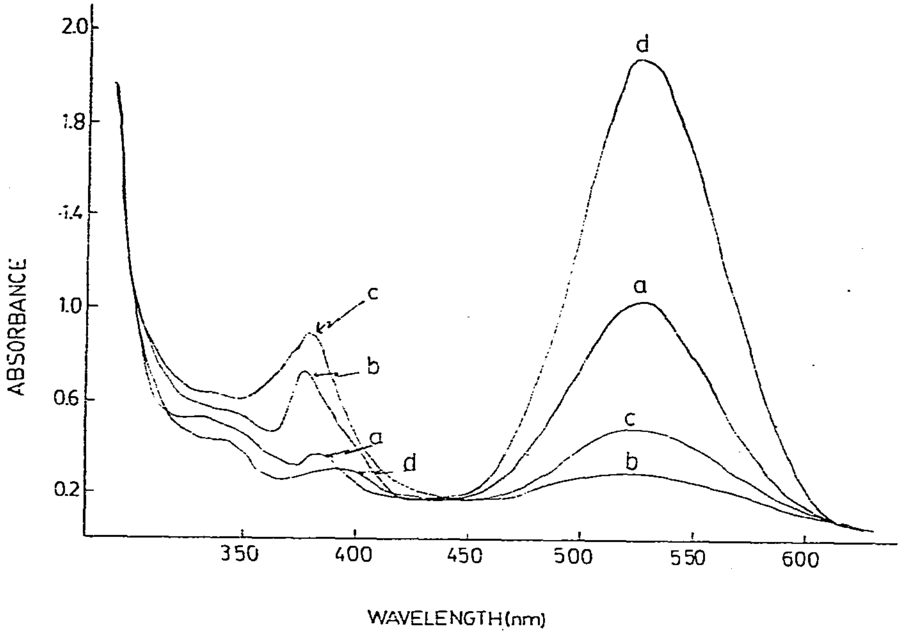
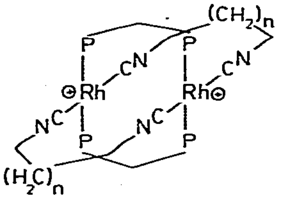


Fig. 3. Electronic absorption spectral changes observed during λ524 nm photolysis of a 5.12 X 10^{-5} *M* solution of $[Rh_2\{CN(CH_2)_4NC\}_4][BPh_4]_2$ in DMSO at 20°C and subsequent regeneration of the dimer: (a) original spectrum of the dimer, (b) immediately following 524 nm irradiation, (c) upon the addition of 1,4-diisocyanobutane (1.02 X 10^{-4} mol), (d) upon the addition of $[RhCl(CO)_2]_2$ (5.12 X 10^{-5}) (see Scheme 1).

$[RhCl(CO)(DPM)]_2$ in methanol followed by the addition of sodium tetraphenylborate to precipitate the required complex. The range of complexes obtained and their spectroscopic data are presented in Table 1. These complexes (8—14; VII) are proposed to be structurally similar to *trans*-$[Rh_2(CNR)_4(DPM)_2][BPh_4]_2$ (R = Me, n-Bu, t-Bu, cyclohexyl) prepared from the reaction between $[Rh(CNR)_4][BPh_4]$ and bis(diphenylphosphino)methane [7]. Their IR spectra all display a single $\nu(C{\equiv}N)$ absorption in the region 2150—2123 cm^{-1} which is a slight decrease relative to $\nu(C{\equiv}N)$ in $[Rh_2(diisocyanide)_4][BPh_4]_2$. A similar decrease has been observed in monoisocyanide—phosphine complexes; for example in $[Rh(CNMe)_4]^+$, $\nu(C{\equiv}N)$ occurs at 2197 cm^{-1} [8] while in *trans*-$[Rh_2(CNMe)_4(DPM)_2]^{2+}$, $\nu(C{\equiv}N)$ occurs at 2174 cm^{-1} [7].

The electronic spectral data are compiled in Table 1. The complexes 8—14 all exhibit absorptions in the visible region of their spectra (λ_{max} 621—555 nm; ϵ = 3500—13 200) which is a red shift of 50—60 nm relative to the tetrakis species 1—7. The origin of this low energy absorption may be assigned on the basis of previous studies of isocyanide—phosphine complexes [7] and is thought to be due to a metal—ligand charge transfer transition from the metal occupied d_{z^2} orbitals to the lowest empty π^* orbitals on the diisocyanide ligands. A qualitative molecular orbital diagram has been proposed by Balch for the interaction of two planar $Rh(CNR)_2(PR_3)_2$ units [7] which agrees with the suggestion that the low energy transitions in 8—14 are due to the spin allowed transitions $1b_{1u} \rightarrow 2a_g$. Balch also reported that this low energy transition moves to higher energy as the physical size of the isocyanide ligand increases, implying probable increase in the rhodium—rhodium distance. We observe a shift to higher energy in $[Rh_2\{CN(CH_2)_nNC\}_2(DPM)_2]^{2+}$ as the size of the alkyl chain increases from $n = 3$ (621 nm) to $n = 8$ (557 nm).

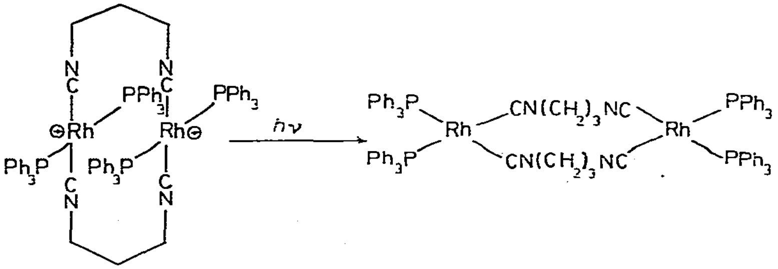


(VII)

The complex $[Rh_2(1,8\text{-diisocyanooctane})_2(DPM)_2]^{2+}$ is believed to have the diisocyanide ligand bridging between the two metal centres such that it is structurally similar to complexes 8—13 implying a rearrangement from the chelating nature of the ligand as in 7. This is based on the evidence that it is similar to complexes 8—13 in colour, IR and electronic spectra. Attempts to prepare complexes of stoichiometry $[Rh_2(\text{diisocyanide})_x(DPM)_y]^{2+}$ ($x = 1, 3$; $y = 3, 1$) failed from the reaction between $[Rh_2(\text{diisocyanide})_4]^{2+}$ and DPM. Also noteworthy in contrast to complexes 1—3 which only contain diisocyanide ligands, is that none of the isocyanide-phosphine complexes show any tendency to aggregate further even in concentrated solution as no evidence of any low energy absorptions greater than 650 nm were observed.

Balch and co-workers have recently noted that the dimeric cations *trans*-$[Rh_2(CN\text{-}t\text{-}Bu)_4(Ph_2ACH_2APh_2)_2]^{2+}$ (A = P, As) are very air sensitive in dilute acetonitrile solution and change from their purple colour to yellow fairly rapidly [14]. We have observed that our dinuclear rhodium(I) phosphine complexes 8—14 turn yellow-orange in the presence of air and light. However, no change occurs upon exposure to air in the dark. Thus oxidation of 8—14 by molecular oxygen involves photochemical activation. It may be that the oxygen sensitivity of Balch's monoisocyanide analogues of 8—14 also requires photochemical initiation.

Triphenylphosphine reacts with $[Rh_2(\text{diisocyanide})_4]^{2+}$ to give the complexes *trans*-$[Rh_2(\text{diisocyanide})_2(PPh_3)_4]^{2+}$ (15—19) isolated as their tetraphenylborate salts. Alternatively, the yields of 15—19 may be substantially increased when the free diisocyanide ligand is treated with either *trans*-$[RhCl(CO)(PPh_3)_2]$ or $[RhCl(PPh_3)_3]$. When prepared in the absence of light, complexes 15—19 are dark green or blue in solution and in the solid state. Upon exposure to light or upon recrystallization the dark colours are lost and the complexes become light yellow-orange. The IR data of the yellow-orange compounds are included in Table 1 and their $\nu(C{\equiv}N)$ absorptions have decreased relative to complexes 1—7. The electronic spectrum of 15a exhibits an absorption at 630 nm ($\epsilon = 8100$) which is very close to that observed in $[Rh_2(CNC_3H_6NC)_2(DPM)_2][BPh_4]_2$ implying a similar type of structure and metal—metal interaction in both types of complexes. A yellow sample of 15b exhibits no absorptions above 450 nm but does display a 397 nm absorption ($\epsilon = 3700$) which is very close to that reported for $[Rh(CNMe)_2(PPh_3)_2][PF_6]$ [7] which was identified as a $d_{z^2} \rightarrow \pi$ metal—ligand charge transfer transition. This observed colour change and hence loss of the metal—metal interaction could be explained by a *trans* → *cis* isomerization of the triphenylphosphine ligands which is not possible with the bidentate bis(diphenylphosphino)methane ligands.



(VIII) (IX)

The reactions of 7 with PPh_3 and diphos generate the monomeric complexes $[Rh(CNC_8H_{15}NC)(PPh_3)_2][BPh_4]$ (**20**) and $[Rh(CNC_8H_{16}NC)(diphos)][BPh_4]$ (**21**), respectively. Both **20** and **21** display typical ν(C≡N) absorptions in their IR spectra and the electronic data of **21** correlates well with the triphenylphosphine derivatives. The 1,8-diisocyanooctane complexes were found to be of such low solubility that no electronic data could be obtained for **20**.

Experimental

Infrared spectral data were recorded on a Perkin—Elmer 337 spectrophotometer and were calibrated against a polystyrene film. Absorption spectra were measured using a Unicam SP800 spectrophotometer using 1.00, 0.1 and 0.01 cm quartz cells. Photolyses were performed using a 1000 watt Xenon arc lamp (Oriel) and a Ferrand UV-visible Grating Monochromater with 50 nm slits (1/2 width). Elemental analyses were performed by Microanalysis Laboratory, Toronto, Ontario and Galbraith Laboratories, Knoxville, Tennessee.

The diisocyanide ligands were conveniently obtained as light yellow liquids from the corresponding diamines using a slightly modified version of a reported procedure and were used as a dichloromethane/diisocyanide mixture [9]. (Caution: Diisocyanide ligands have been observed to cause violent explosions upon vacuum distillations - this work and [2].) The rhodium complexes, $[RhCl(COD)]_2$ [3], *trans*-$RhCl(CO)(PPh_3)_2$ [10], $RhCl(PPh_3)$ [11], $[Rh(CO)_2]_2$ [12] and *trans*-$[RhCl(CO)(DPM)]_2$ [13] were all prepared according to the literature. Triphenylphosphine (BDH), bis(diphenylphosphino)methane (Strem) and bis(diphenylphosphino)ethane (Strem) were obtained from commercial sources and utilized without further purification.

Preparation of $[Rh_2(CNC_4H_8NC)_4][BPh_4]_2 \cdot 2\,CH_2Cl_2$ *(2a)*

1,4-diisocyanobutane (0.75 g; 6.6 mmol) in dichloromethane/methanol (10 cm^3) was added to a suspension of $[RhCl(COD)]_2$ (0.75 g; 1.5 mmol) in methanol (40 cm^3) under nitrogen. The dark red solution was filtered and sodium tetraphenylborate (2.0 g; 5.8 mmol) in methanol (10 cm^3) was added to give a purple solid which was filtered, washed with methanol, diethyl ether and dried under vacuum. Yield 1.6 g (73%).

The related compounds $[Rh_2(diisocyanide)_4][BPh_4]_2 \cdot 2\ CH_2Cl_2$ (diisocyanide = 1,5-diisocyanopentane, 1,6-diisocyanohexane, 1,4-bis(isocyanomethyl)cyclohexane and 1,3-bis(isocyanomethyl)benzene) were all prepared similarly. Yields were 62, 71, 83 and 65%, respectively.

Preparation of $[Rh(CNC_8H_{16}NC)_2][BPh_4]$ *(7)*

1,8-diisocyanooctane (0.36 g; 2.35 mmol) in methanol (10 cm^3) was added to a suspension of $[RhCl(COD)]_2$ (0.58 g; 1.17 mmol) in methanol (30 cm^3). The solution slowly turned orange and after 10 minutes sodium tetraphenylborate (0.6 g; 1.75 mmol) in methanol (10 cm^3) was added to precipitate a yellow powder. Yield 1.3 g (67%).

Preparation of $[Rh_2(CNC_4H_8NC)_4][PF_6]_2$ *(2b)*

To a stirred suspension of $[RhCl(COD)]_2$ (1.0 g; 2.03 mmol) in methanol (30 cm^3) was added silver hexafluorophosphate (1.01 g; 4.0 mmol). The AgCl precipitate which was formed was filtered off and then 1,4-diisocyanobutane (0.86 g; 8.0 mmol) in methanol (10 cm^3) was added. The solution turned green and a dark green precipitate was isolated, washed with methanol, diethyl ether and dried under vacuum. Yield 1.35 g (67%).

Preparation of $[Rh_2(CNC_8H_8NC)_4][BF_4]_2$ *(5a)*

To acetonitrile (50 cm^3) containing $[RhCl(COD)]_2$ (1.6 g; 3.25 mmol) was added silver tetrafluoroborate. (1.26 g; 6.50 mmol) 1,3-Bis(isocyanomethyl)-benzene (2.0 g; 13.0 mmol) was added to the filtrate to immediately precipitate a dark blue solid which was filtered, washed with acetonitrile and diethyl ether and dried in vacuum. Yield 1.3 g (40%).

Preparation of $[Rh_2(CNC_3H_6NC)_2(Ph_2PCH_2PPh_2)_2][BPh_4]_2$ *(8)*

Method 1: To a solution of *trans*-$[RhCl(CO)(DPM)]_2$ (1.0 g; 0.9 mmol) in methanol (40 cm^3) was added 1,3-diisocyanopropane (0.17 g; 1.8 mmol) in methanol (5 cm^3). The solution immediately turned dark green and a green precipitate was obtained upon the addition of sodium tetraphenylborate (1.02 g; 2.7 mmol) in methanol (10 cm^3) which was filtered and washed with methanol. The green solid was reprecipitated from acetone/1-propanol. Yield 1.1 g (67%).

Method 2: A solution of bis(diphenylphosphino)methane (0.32 g; 0.83 mmol) in acetone (10 cm^3) was added to a suspension of $[Rh_2(CNC_3H_6NC)_4][BPh_4]_2$ (0.5 g; 0.41 mmol) in acetone (20 cm^3). The blue-green solution was filtered and 1-propanol (40 cm^3) added to the filtrate. The solvent was removed through the use of a rotary evaporator. Evaporation was stopped when the green solid began to separate. The product was suction filtered, washed with 1-propanol and dried in vacuum. Yield 0.31 g (42%).

Complexes 9—13 could be prepared by either method. Using Method 1, the yields were 9 (65%), 10 (61%), 11 (72%), 12 (58%) and 13 (49%).

Similarly, complexes 15—19 could be prepared by either procedure substituting triphenylphosphine for bis(diphenylphosphino)methane. The yields were 15 (76%), 16 (77%), 17 (71%), 18 (66%) and 19 (63%).

Preparation of $[Rh(CNC_8H_{16}NC)(PPh_3)_2][BPh_4]$ *(20)*

To $[Rh(1,8\text{-diisocyanooctane})_2][BPh_4]$ (0.2 g; 0.27 mmol) in acetone (40 cm^3) was added triphenylphosphine (0.14 g; 0.54 mmol) in acetone (5 cm^3). The solution turned dark yellow and methanol (30 cm^3) was added and the solution concentrated under vacuum to 10 cm^3 at which point more methanol (50 cm^3) was added to precipitate the yellow product which was collected by filtration, washed with methanol and dried under vacuum. Yield 0.21 g (70%).

Preparation of $[Rh(CNC_8H_{16}NC)(Ph_2PCH_2CH_2PPh_2)][BPh_4]$ *(21)*

This compound was prepared using the procedure as described above except that bis(diphenylphosphino)ethane (0.27 mmol) was substituted for triphenylphosphine. Yield 67%.

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