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The Reaction of Rhodiumdicarbonylhalides with Nitriles

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The reaction

$$[Rh(CO)_2X]_2+2RCN \rightleftharpoons 2\mathrm{cis}[Rh(CO)_2(RCN)X]$$

has been studied and the thermodynamic data of the above equilibrium, obtained by infrared spectroscopy, have been correlated with the properties of the nitriles.

Introduction

The splitting of halide bridges of metal complexes and particularly of rhodiumdicarbonylhalides with bases such as halides[1] or amines[2] is a well known reaction. We have studied now the reaction of $[\mathrm{Rh(CO)_2X}]_2$ (X=Cl,Br) with weak Lewis bases such as aromatic or aliphatic nitriles[3]

$$[\mathrm{Rh(CO)_2X}]_2+2\mathrm{RCN} \rightarrow 2[\mathrm{Rh(CO)_2(RCN)X}]$$

Results

The isolation of the monomeric crystalline complex compounds $[\mathrm{Rh(CO)_2(RCN)X}]$ was easy in the case of aryl nitriles (Table I) on account of their insolubility in petroleum ether and stability in the solid state.

All the isolated compounds (Table I) are intensely coloured from green to red or violet and sometimes pleochroic. Some of these compounds were obtained in two different crystalline forms; the first one (α form) yellow, the other (β form) deeply coloured.

The generally more stable α form usually obtained directly from the reaction mixture while the β form could be obtained by the rapid evaporation *in vacuo* of the yellow benzene solutions.

The α and β forms differ in their infrared spectra in nujol mull in the region of carbonyl stretchings (Table II), the β form showing a more complex pattern than the α form. Generally the β form showed two, or more, weaker absorptions at frequencies lower

Table I. Analyses and properties of compounds of formula $[\mathrm{Rh(CO)_2(nitrile)X}]$

X	Nitrile	Colour	m.p.°C	C%		H%		N%		X%	
				calc.	found.	calc.	found.	calc.	found.	calc.	found.
Cl	C_6H_5CN	yellow(α)	93	36.3	36.8	1.7	1.5	4.7	4.6	11.9	12.1
		copper-red(β)	—	36:3	36.7	1.7	1.6	4.7	4.6	11.9	11.8
Br	C_6H_5CN	copper-red	94-96	31.6	31.9	1.5	1.7	4.1	4.2	—	—
Cl	p-ClC_6H_4CN	green	91	32.6	32.8	1.2	1.3	4.2	4.3	—	—
Br	p-ClC_6H_4CN	green	89	28.7	28.4	1.1	1.0	3.7	3.7	—	—
Cl	p-$CH_3C_6H_4CN$	brown-violet	67	38.5	38.6	2.3	2.5	4.5	4.4	—	—
Br	p-$CH_3C_6H_4CN$	brown-violet	72	33.7	33.7	2.0	1.7	3.9	3.8	—	—
Cl	m-$CH_3C_6H_4CN$	copper-red	83	38.5	38.7	2.3	2.5	4.5	4.4	11.4	11.5
Br	m-$CH_3C_6H_4CN$	brown-red	77	33.7	34.0	2.0	2.1	3.9	4.0	—	—
Cl	o-$CH_3C_6H_4CN$	green(γ)	(unst.)								
		violet(β)	58	38.5	38.5	2.3	2.4	4.5	4.7	11.4	11.5
Br	o-$CH_3C_6H_4CN$	copper-red	64	33.7	33.2	2.0	1.8	3.9	3.8	—	—
Cl	α-$C_{10}H_7CN$	brown-red(β)	(unst.)								
		yellow(α)	77	44.9	44.9	2.0	1.9	4.0	4.1	—	—
Br	α-$C_{10}H_7CN$	brown-red(β)	(unst.)								
		yellow(α)	96	39.8	39.5	1.8	1.6	3.6	3.7	—	—
Cl	β-$C_{10}H_7CN$	brown-red(β)	(unst.)								
		yellow(α)	99	44.9	45.3	2.0	2.1	4.0	4.0	—	—
Br	β-$C_{10}H_7CN$	brown-red(β)	(unst.)								
		yellow(α)	98	39.8	39.2	1.8	1.9	3.6	3.6	20.4	21
Cl	p-FC_6H_4CN	deep-red	83	34.3	34.4	1.3	1.3	4.4	4.3	—	—
Cl	o-ClC_6H_4CN	deep-red	76	32.6	32.7	1.2	1.3	4.2	4.1	—	—
Cl	p-$CH_3CONHC_6H_4CN$	yellow	125	37.1	38.0	2.3	2.5	7.9	8.0	—	—
Cl	$C_6H_5CH_2CN$	copper-red(β)	(unst.)								
		yellow(α)	67-70	38.5	38.8	2.3	2.4	4.5	4.7	11.4	11.5
Br	$C_6H_5CH_2CN$	yellow	65	33.7	34.0	2.0	2.0	4.0	41	—	—
Cl	p-$ClC_6H_4CH_2CN$	yellow	89-91	34.7	35.2	1.7	2.0	4.0	4.2	—	—
Cl	CH_3OOCCH_2CN	brown-red	65	24.5	25.1	1.7	2.1	4.8	4.6	—	—

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(2) D. N. Lawson and G. Wilkinson, *J. Chem. Soc.*, 1950 (1965).

Table II. Some infrared absorptions of compounds of formula $[Rh(CO)_2(nitrile)X]$ [a]

X	Nitrile	Medium	$\nu_{C\equiv N}$	$\nu_{C\equiv N}$ [b]	$\nu_{C=O}$ [c]
Cl	C_6H_5CN (β)	Nujol	2295	2231	2103, 2098, 2071, 2038, 2016
Cl	C_6H_5CN (β)	CH_2Cl_2	2278	—	2093, 2038
Cl	C_6H_5CN (α)	nujol	2283	—	2085, 2042
Cl	*p*-$CH_3C_6H_4CN$	nujol	2268	2229	2081, 2023
Cl	*p*-$CH_3C_6H_4CN$	hexane	—	—	2080, 2031
Cl	*p*-ClC_6H_4CN	nujol	2270	2230	2081, 2023
Cl	*p*-ClC_6H_4CN	hexane	—	—	2098(sh), 2086, 2031
Cl	*m*-$CH_3C_6H_4CN$	nujol	2275	2229	2095, 2067, 2015, 1985(sh)
Cl	*m*-$CH_3C_6H_4CN$	hexane	—	—	2085, 2030
Cl	*o*-$CH_3C_6H_4CN$ (α)	nujol	2263	2226	2070, 2023
Cl	*o*-$CH_3C_6H_4CN$ (α)	hexane	—	—	2085, 2030
Cl	*p*-FC_6H_4CN	nujol	2280	2230	2095, 2080, 2040, 2018
Cl	*p*-$CH_3CONHC_6H_4CN$	nujol	2260	2217	2080, 2040
Cl	α-$C_{10}H_7CN$ (α)	nujol	2260	2222	2083, 2018
Cl	β-$C_{10}H_7CN$ (α)	nujol	2282	2227	2080, 2040
Cl	*o*-ClC_6H_4CN	nujol	2278	2235	2093, 2081, 2038, 2028, 2013
Cl	$C_6H_5CH_2CN$ (α)	nujol	2309	2253	2090, 2007, 1985(sh)
Cl	$C_6H_5CH_2CN$ (β)	nujol	2308	—	2098, 2093, 2080, 2030, 2010, 1975(w)
Cl	$C_6H_5CH_2CN$ (β)	CH_2Cl_2	2306	—	2090, 2080(sh), 2038
Br	C_6H_5CN	nujol	2270	2231	2080, 2060, 2025, 2005, 1995
Br	*p*-$CH_3C_6H_4CN$	nujol	2261	2230	2083, 2070, 2026, 1998
Br	*m*-$CH_3C_6H_4CN$	nujol	2281	2229	2095, 2081(sh), 2066, 2013
Br	*m*-$CH_3C_6H_4CN$	hexane	—	—	2100(w), 2085, 2030
Br	*o*-$CH_3C_6H_4CN$	CH_2Cl_2	2260	2226	2096(sh), 2085, 2030
Br	*p*-ClC_6H_4CN	nujol	2261	2230	2083, 2070, 2026, 1998
Br	*p*-ClC_6H_4CN	CH_2Cl_2	2268	—	2085, 2030
Br	α-$C_{10}H_7CN$	nujol	2265	2222	2083, 2073, 2083, 2000
Br	β$C_{10}H_7CN$	nujol	2260	2227	2088, 2070, 2015, 2005
Br	$C_6H_5CH_2CN$	nujol	2300	2253	2083, 2003
Cl	CH_3OOCCH_2CN	nujol	2310	2235	2090, 2070, 2025, 2013

[a] All the frequencies are given in cm^{1-}. [b] Frequency of the free nitrile in film or nujol mull. [c] All the absorptions are strong unless stated otherwise.

Table III. Properties of compounds with alifatic nitriles of formula $[Rh(CO)_2(nitrile)Cl]$

Nitrile	Colour	Approximate Temperature of decomposition °C	Solvent of reaction
CH_3CN	Violet	−10	Hexane
C_2H_5CN	Green	0	Petr. Ether
$CH_2=CH-CN$	Green	0	Petr. Ether
$C_5H_{11}CN$	Red-brown	−30	Petr. Ether

than those of the symmetrical and antisymmetrical stretchings of the two *cis* carbonyl groups.

A similar pattern was found in analogous d^8 dichroic iridium(I) and rhodium(I) dicarbonyl amine compounds[2,4] which have weak intermetallic interactions.

The β forms probably have similar intermetallic interactions while the α forms should have a simple square planar coordination of the metal without any metal-metal interaction. Compounds with aliphatic nitriles RCN were formed in solution and were isolated in the solid state at −78°C only with $R=CH_3$ and CH_3CH_2 (Table III).

However, owing to the high volatility of these nitriles the solid compounds transformed again in the rhodiumdicarbonylhalide when the temperature was raised.

With aliphatic nitriles of lower volatility, as caprilic nitrile, only intractable oils have been obtained.

Both complexes with aliphatic and aromatic nitriles showed two C≡N stretchings in their infrared spectra in solution with Δν around 40-50 cm^{-1}.

The absorption at higher frequency (which corresponds to the unique ν C≡N band in the nujol spectra) could be attributed to the coordinated nitrile[5] while the one at lower frequency must be attributed to the presence in solution of the free nitrile. Moreover the infrared spectra in solution showed, in the region of the carbonyl stretchings, the presence of variable amounts of $[Rh(CO)_2X]_2$. This fact can be explained by a dissociation and condensation, in solution, of the nitrile complexes confirming that the reaction of formation of nitrile complexes is an equilibrium reaction.

The existence of an equilibrium between mononuclear nitrile complexes and rhodiumdicarbonylhalide and free nitriles was also confirmed by the reactivity of the monomeric compounds. Indeed they showed the same reactivity of the rhodiumdicarbonylhalide (see experimental).

Moreover the low values of the molecular weights found for the nitrile compounds in benzene or chloroform solutions confirmed again the existence of a dissociative equilibrium studies.

Equilibrium Studies

The equilibrium

$$2[Rh(CO)_2(nitrile)X] \rightleftarrows [Rh(CO)_2X]+2\ \text{nitrile}$$

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(4) M. Angoletta, *Gazz. Chim. Ital.*, *89*, 2359 (1959).

(5) B. L. Ross, J. G. Grasselli, W. C. Ritchey and H. D. Kaesz, *Inorg. Chem.*, *2*, 1025 (1963).

Table IV. Equilibrium Constants 2 $Rh(CO)_2(nitrile)X \rightleftharpoons [Rh(CO)_2X]_2 + 2nitrile$ for (K_{eq} mole/l)

X	Nitrile	Solvent	20°	30°	40°
Cl	p-ClC_6H_4CN	$CHCl_3$	$2.60 \pm 0.10 \times 10^{-1}$	$3.26 \pm 0.20 \times 10^{-1}$	$3.86 \pm 0.20 \times 10^{-1}$
Cl	p-ClC_6H_4CN	C_6H_6	—	$9.11 \pm 0.20 \times 10^{-1}$	—
Cl	p-$CH_3C_6H_4CN$	$CHCl_3$	$2.50 \pm 0.20 \times 10^{-2}$	$2.90 \pm 0.10 \times 10^{-2}$	$3.40 \pm 0.10 \times 10^{-2}$
Cl	m-$CH_3C_6H_4CN$	$CHCl_3$	$7.30 \pm 0.20 \times 10^{-2}$	$7.90 \pm 0.20 \times 10^{-2}$	$8.60 \pm 0.30 \times 10^{-2}$
Cl	p-FC_6H_4CN	$CHCl_3$	$1.70 \pm 0.10 \times 10^{-1}$	$1.90 \pm 0.20 \times 10^{-1}$	$2.11 \pm 0.20 \times 10^{-1}$
Cl	p-$CH_3OC_6H_4CN$	$CHCl_3$	$8.60 \pm 0.10 \times 10^{-3}$	$1.10 \pm 0.10 \times 10^{-3}$	$15.00 \pm 0.80 \times 10^{-3}$
Cl	p-$CH_3CONHC_6H_4CN$	$CHCl_3$	$1.40 \pm 0.10 \times 10^{-2}$	$1.80 \pm 0.20 \times 10^{-2}$	$2.30 \pm 0.20 \times 10^{-2}$
Cl	p-$NO_2C_6H_4CN$	$CHCl_3$	25.3 ± 2.5	59.6 ± 7.9	94.6 ± 7.7
Cl	C_6H_5CN	$CHCl_3$	$1.07 \pm 0.10 \times 10^{-1}$	$1.12 \pm 0.10 \times 10^{-1}$	$1.14 \pm 0.10 \times 10^{-1}$
Cl	C_6H_5CN	C_6H_6	$5.14 \pm 0.10 \times 10^{-1}$	$6.28 \pm 0.10 \times 10^{-1}$	$7.32 \pm 0.10 \times 10^{-1}$
Br	C_6H_5CN	$CHCl_3$	$9.70 \pm 0.20 \times 10^{-2}$	$1.10 \pm 0.20 \times 10^{-1}$	$1.30 \pm 0.10 \times 10^{-1}$
Cl	C_2H_6CN	$CHCl_3$	$2.40 \pm 0.20 \times 10^{-2}$	$4.60 \pm 0.20 \times 10^{-2}$	$8.50 \pm 0.70 \times 10^{-2}$
Cl	$C_5H_{11}CN$	$CHCl_3$	$1.70 \pm 0.10 \times 10^{-2}$	$2.90 \pm 0.10 \times 10^{-2}$	$4.11 \pm 0.20 \times 10^{-2}$
Cl	$C_6H_5CH_2CN$	$CHCl_3$	$1.30 \pm 0.10 \times 10^{-1}$	$1.90 \pm 0.10 \times 10^{-1}$	$2.60 \pm 0.10 \times 10^{-1}$

Table V. Thermodynamic Values[a]

X	Nitrile	Solvent	ΔG Kcal/mol	ΔH Kcal/mol	ΔS cal/°Kmol
Cl	C_6H_5CN	$CHCl_3$	1.3	—0.6	—6.3
Cl	C_6H_5CN	C_6H_6	~0.4	—3.0	—11.4
Cl	p-$CH_3C_6H_4CN$	$CHCl_3$	2.1	—2.9	—16.7
Cl	m-$CH_3C_6H_4CN$	$CHCl_3$	1.5	—1.5	—10.1
Cl	p-ClC_6H_4CN	$CHCl_3$	0.7	—3.6	—14.7
Cl	p-FC_6H_4CN	$CHCl_3$	1.0	—2.20	—10.7
Cl	p-$CH_3CONHC_6H_4CN$	$CHCl_3$	2.4	—4.6	—23.6
Cl	p-$CH_3OC_6H_4CN$	$CHCl_3$	2.8	—3.8	—21.9
Br	C_6H_5CN	$CHCl_3$	1.3	—2.8	—14.2
Cl	$C_6H_5CH_2CN$	$CHCl_3$	1.1	—6.3	—24.9
Cl	C_2H_5CN	$CHCl_3$	2.0	—11.4	—45.2
Cl	$C_5H_{11}CN$	$CHCl_3$	2.2	—8.1	—34.8

[a] All the thermodynamic data are at 25°C.

has been investigated in chloroform or benzene solution by i.r. spectroscopy (see experimental).

The equilibrium constants (which are reported in Table IV) clearly showed that with aliphatic nitriles, which are more basic, the nitrile complexes are much more stable than with aromatic nitriles.

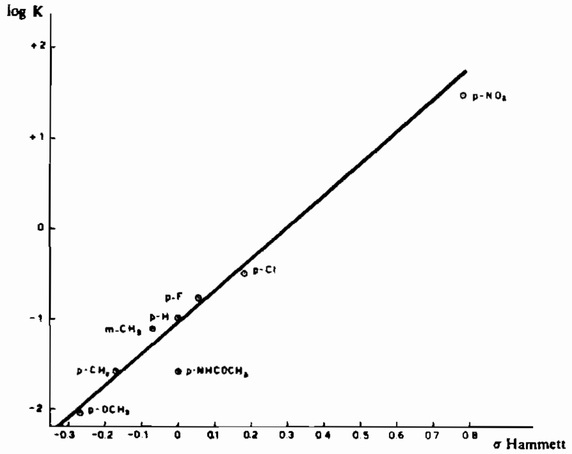

Figure 1.

With aromatic nitriles the stability of the nitrile complexes decreased by increasing the electron withdrawing power of the substituents in the phenyl ring. This means that there is a very close relationship between the stabilities of the nitrile complexes and the Lewis basicity of the donor nitrogen atom of the nitrile ligands.

Indeed an almost linear correlation was obtained for the substituted phenylnitriles between log K_{eq} and Hammett's σ constants of the substituents in the ring (Figure 1). The only nitrile complex which did not fit into this linear correlation was the one with *para*-acetylamido substituted phenyl nitrile.

This discrepancy can be due to an uncorrect value of Hammett's σ constant of the $pNHCOCH_3$ group or, more likely, to the donor properties of this substituent which could compete with the nitrile group.

The ρ values of the Hammett's equation is about 3.6, a rather high value indeed. This confirms that the reaction is very sensitive to small variation of the basicity of the nitriles and it could be used as a good indication of the relative donor properties of nitrile ligands.

We have also examined the thermodynamic parameters of the above equilibria. The results are rather interesting although, on account of the very low values of some reaction enthalpies, the data can not be always very accurate.

The reaction enthalpies seem to be the more important factor in determining the position of the equilibria. Indeed with more basic nitriles the reaction enthalpies are higher, although small variations of the basicity give differences too small to be surely discussed.

The change in the reaction entropy is important only with aliphatic nitriles, while with aromatic nitriles ΔS is always rather constant around 10-14 cal/°K mole. Only with aromatic nitriles having polar groups such as OCH_3 or $NHCOCH_3$ does the reaction entropy increase near to the values found for aliphatic nitriles.

Possibly these variations in the values of the reaction entropies are to be ascribed to solvation effects. We have found that the position of the equilibria is solvent dependent (Table IV), but it would be vain to try to discuss this fact only in terms of small variations of the ΔS values by changing the solvent.

Indeed we have found that both ΔH and ΔS changed on changing the solvent (Table V). However absolute values of ΔH of about 1-2 kcal/mole are rather unreliable and some doubts can be raised on small variations of ΔH.

Changing the halide bridge, *e.g.* Cl with Br, there is a small variation in the equilibrium constant which can be attributed mainly to variations in the ΔH values as expected by the fact that there is the cleavage of a bromine instead of a chlorine bridge.

Conclusion

The more interesting conclusion which can be reached from the above results is that the splitting of the halogen bridges of rhodiumdicarbonylhalides is affected mainly by the basicity of the entering ligand when the ligands are structurally similar.

Indeed the correlation found with the Hammett's constants suggests that, if there is any π-back-donation from the rhodium atom to the nitrile group, this effect must be in a linear correlation with Hammett's constants.

While it is reasonable to expect such a correlation for the σ donor bond, that is the basicity, it is very difficult to suppose a similar effect for the π bond.

It is then reasonable to suppose that there is no π bond between the rhodium atom and the nitrile.

It follows that the more basic is the ligand the easier is the splitting of the halogen bridge; this is confirmed by the fact that by reacting $[Rh(CO)_2Cl]_2$ with the *para*-aminophenylnitrile a compound is obtained in which only the nitrogen atom of the amino group is bound to the rhodium atom.

On changing the structure of the nitrile ligand the changes in the equilibrium positions are affected not only by the ΔH of the reaction, that is by the basicity, but also by the ΔS, probably by solvation effects.

It is interesting that some recent kinetic investigations on ligand substitution of a Rh^I compound have shown similarly that the rates are affected only by basicity of the entering « hard » amines[7]. In our case the nitrile ligands are rather « softer » than amines but it seems that still the basicity affects the position of the equibrium.

Experimental Section

All the nitriles used were those commercially available and were crystallized or distilled before the use. The complexes have been obtained by mixing a hexane solution of the rhodiumdicarbonylhalide with a hexane or benzene solution of the nitrile and by filtering off the obtained crystalline products.

The compounds which are stable on the air can be crystallized from benzene-petroleum ether, but usually they did not need any crystallization, being directly obtained in a very high purity.

All the melting points are uncorrected. With aliphatic nitriles crystalline compounds were obtained at low temperature (see Table III). These crystals are stable only at these temperatures.

C, H, N and halogens analyses have been carried out in the analytical laboratory of Milan University.

The equilibrium constants have been determined by mixing under nitrogen in a thermostated vessel solutions nearly 10^{-2} molar of the nitrile and of the rhodiumdicarbonylhalide. After nearly 20 minutes the infrared spectrum (Perkin-Elmer mod. 237) of the solution was recorded in the region 2300-2000 cm^{-1} and the concentration of the free nitrile determined spectroscopically.

The concentrations of the nitrile complex and of the unreacted rhodiumdicarbonylhalide were determined by difference.

At each temperature, five different starting concentrations were used; the reported equilibrium constants (Table IV) are the average values.

All the nitrile complexes reacted with acetylacetone to give place to rhodiumdicarbonyllacetylacetonate,[8] with tetraphenylarsoniumchloride to the tetraphenylarsonium salt of the rhodiumdicarbonyldichloride anion[1] and with triphenylphosphine to rhodiumbistriphenylphosphinecarbonylchloride.[9]

Acknowledgments. We wish to thank the Italian C. N.R. for financial support.

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