Oxidation-addition Reactions of Some Isonitrile Complexes of Rhodium(I)

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Oxidative-addition of bromine or iodine to the complexes $[(RNC)_4Rh]^+$, *trans*-$[(RNC)_2(R'_3P)_2Rh]^+$, and *trans*-$(RNC)_2Rh(CO)X$ (R = *p*-$Me{\cdot}C_6H_4$, *p*-$MeO{\cdot}C_6H_4$, *p*-ClC_6H_4; R'_3 = Ph_3, Ph_2Me; X = Cl, Br) occurs by *trans*-addition. None of the complexes reacts with hydrogen chloride or bromide. The complexes $(MeOC_6H_4NC)_2Rh(CO)X_3$ are unstable to loss of carbon monoxide in solution. The complex $(MeOC_6H_4NC)_2Rh(CO)Cl$ reacts with methyl iodide to form the five-co-ordinate acetyl complex $(MeOC_6H_4NC)_2Rh(COMe)I_2$.

OXIDATION-ADDITION reactions have been extensively investigated to establish the stereochemistry of addition and the influence of the ligands, especially the neutral ligands.[1] Most studies have involved phosphine or carbonyl complexes, and it is generally found that increasing the σ-basicity and/or decreasing the π-acidity of the ligands leads to greater stability of the oxidised product, although an apparent exception to this trend has been found recently.[2] Isonitriles are moderate σ-donor ligands and are probably intermediate between tertiary phosphines and carbon monoxide as π-acceptors.[3] It was therefore of interest to examine the the behaviour of complexes containing these ligands. Some rhodium(I) complexes have been described,[4,5] but neither their stereochemistry nor their oxidation appears to have been examined.

The Complexes $[(RNC)_4Rh]X$.—Complexes of the type $[(RNC)_4Rh]X$ [R = *p*-$Me{\cdot}C_6H_4$ (tol), *p*-$MeO{\cdot}C_6H_4$ (anis); X = I, BPh_4] were obtained by reaction of di-μ-chloro-tetracarbonyldirhodium(I) with an excess of the appropriate isonitrile,[4] followed by precipitation as the tetraphenylborate or iodide. The i.r. spectra of these complexes (Table 1) show one strong C–N stretching band (slightly split for the *p*-anisyl derivative), consistent with the expected E_u mode for square-planar geometry. In both cases a weak band at higher frequency is also observed, presumably the theoretically inactive A_{1g} (or B_{1g}) mode.

These complexes react readily with iodine in chloroform to give the $[(RNC)_4RhI_2]^+$ cations, isolated initially as the tri-iodides; tetraphenylborates were obtained by metathesis. Reaction with bromine in chloroform gave only intractable products, but the slow addition of bromine to ethanol suspensions of the complexes gave clean reactions yielding products approximating to the composition $[(RNC)_4RhBr_2]Br_3$. Analysis indicated some variability in the composition of the anion.

These complexes were uni-univalent electrolytes in

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nitromethane solution (Table 1). The vibrational spectra in the C–N stretching region are consistent with *trans*-geometry for the cations; slight solid-state splitting is found for the tetraphenylborates.

The Complexes $[(RNC)_2(R'_3P)_2Rh]X$.—The complexes $[(RNC)_2(R'_3P)_2Rh]X$ (R = anis, $R'_3 = Ph_2Me$, X = BPh_4; R = p-ClC_6H_4, R = Ph, X = Cl, BPh_4) were obtained by reaction of the stoicheiometric amount of the appropriate isonitrile with the complex $[Rh(CO)_2Cl]_2$, followed by treatment with the phosphine.[5] The i.r. spectra of these complexes are consistent with *trans*-planar geometry, although $[(p\text{-}ClC_6H_4NC)_2(Ph_3P)_2Rh]BPh_4$ shows slight solid-state splitting of the N–C stretching band. The ^1H n.m.r. spectrum of $[(anisNC)_2(Ph_2MeP)_2Rh]BPh_4$ (dichloromethane) showed a broad singlet at τ 7·8 for the CH_3–P group and two signals, τ 6·23 and 6·33, for the MeO-group. These features are not consistent with a *trans* configuration, but may have been caused by dissociation of the complex.

These complexes reacted smoothly, in ethanol suspension, with bromine or iodine to give $[(RNC)_2(R'_3P)_2RhX_2]X_3$ (X = Br, I). Use of chlorinated solvents gave very soluble, tarry products which could not be purified. Consistent analyses were again difficult to achieve due, presumably, to variable halogen-content of the anions. The complexes $[(anisNC)_2(Ph_2MeP)_2RhX_2]X_3$ showed a single strong C–N stretching mode in the i.r., and the ^1H n.m.r. spectra (deuteriochloroform) showed 1 : 2 : 1 triplets for the H_3C–P resonance (X = Br, τ 7·18, 'J' 3·5 Hz; X = I, τ 7·45, 'J' 4 Hz). The H_3C–O resonance was a singlet at τ 6·11 in both cases. These observations are consistent with *trans* arrangements for both pairs of neutral ligands. The i.r. spectra of the complexes $[(p\text{-}ClC_6H_4NC)_2(Ph_3P)_2RhX_2]X_3$ showed one strong N–C stretching mode and a second, less intense band at higher frequency. The appearance of two peaks could be ascribed to solid-state splitting but the separation seems rather large (16—34 cm^{-1}). The separation is similar to that observed between the symmetric and antisymmetric modes of some of the other complexes, and it seems possible that the isonitrile groups are *trans* but not exactly collinear, thus allowing some intensity for the higher-frequency, symmetric mode. A *cis* configuration cannot be definitely excluded, however.

TABLE 1

Infrared stretching frequencies (Nujol) and molar conductivities (nitromethane)

Rhodium(I) complexes	ν_{C-N} /cm^{-1}	$\nu_{^{13}C-N}$/cm^{-1}	Λ_M [a]
$[(tolNC)_4Rh]BPh_4$	2154vs, 2193w	2119vw	64
$[(anisNC)_4Rh]BPh_4$	[c] 2150vs, 2156vs, 2202vw	2126vw	16·3 [b]
$[(anisNC)_2(Ph_2MeP)_2Rh]BPh_4$	2128vs, 2171w, 2190vw,sh		
$[(ClC_6H_4NC)_2(Ph_3P)_2Rh]BPh_4$	2125vs, 2135vs	2098w, 2107vw,sh	
$[(ClC_6H_4NC)_2(Ph_3P)_2Rh]Cl$	2128vs	2104vw	
$(anisNC)_2Rh(CO)Cl$ [d]	2166vs, 2195vw	2136w,sh	non
$(anisNC)_2Rh(CO)Br$ [e]	2166vs, 2195w	2137w,sh	non
Rhodium(III) complexes			
$[(tolNC)_4RhI_2]I_3$ [f]	2211m,sh, 2222vs	2187vvw	121
$[(tolNC)_4RhI_2]BPh_4$	[h] 2212vw,sh, 2222vs, 2243vw	2187vvw	
$[(tolNC)_4RhBr_2]Br_3$ [g]	2212vw,sh, 2227vs, 2252vw	2195vw,sh	98
$[(anisNC)_4RhI_2]I_3$	[h] 222vs, 2246vw	2186vw	144
$[(anisNC)_4RhI_2]BPh_4$	2212vs, 2224vs, 2243vvw	2185w	66
$[(anisNC)_2(Ph_2MeP)_2RhI_2]I_3$	2200vs	2168vw	125
$[(anisNC)_4RhBr_2]Br_3$	2230vs, 2240s,sh		
$[(anisNC)_2(Ph_2MeP)_2RhBr_2]Br_3$	2208vs, 2233w	2176w	125
$[(ClC_6H_4NC)_2(Ph_3P)_2RhI_2]I_3$	2189vs, 2205m	2170w,sh	
$[(ClC_6H_4NC)_2(Ph_3P)_2RhBr_2]Br_3$	2195s, 2229m		96
$(anisNC)_2Rh(CO)Br_2Cl$ [i]	2231s, 2247w,sh	2206m,sh	
$(anisNC)_2Rh(CO)Br_3$ [j]	2223s, 2242w,sh	2205m,sh	
$(anisNC)_2Rh(COMe)I_2$ [k]	2180vs, 2205w,sh	2148w,sh	non

[a] Molar conductivity in Ω^{-1} cm^2 mol^{-1}, extrapolated to infinite dilution: non = non-conducting. [b] 10^{-4}M in nitrobenzene. [c] 2154 cm^{-1} in $CHCl_3$. [d] ν_{CO} = 2005vs. [e] ν_{CO} = 2009vs. [f] Raman: 2228, 2244 cm^{-1}. [g] Raman: 2234, 2249 cm^{-1}. [h] 2219 in $CHCl_3$. [i] ν_{CO} = 2136vs. [j] ν_{CO} = 2121vs. [k] ν_{CO} = 1688vs.

The Complexes $(RNC)_2Rh(CO)X$.—The complexes $(anisNC)_2Rh(CO)X$ (X = Cl, Br) were prepared by treating the appropriate rhodium(I) carbonyl halide dimer with the stoicheiometric amount of the isonitrile at 0 °C.[5] No such derivatives could be isolated using p-tolyl isonitrile under a variety of conditions, although reaction of the carbonyl had always occurred. The i.r. spectra of the anisyl complexes indicate the usual *trans*-planar geometry.

The carbonyl complexes react rapidly with bromine in chloroform, but no tractable products could be obtained. Tars were precipitated, the i.r. spectra of which showed no carbonyl absorptions. A pure product, $(anisNC)_2Rh(CO)Br_3$, was obtained by the reaction of the solid bromo-carbonyl complex with bromine vapour. A similar product was obtained from the chloro-complex and bromine vapour. Both products were stable as solids, but decomposed immediately on dissolution in all solvents tried, with loss of carbon monoxide and formation of tars similar to those obtained by direct reaction. Slow reactions also occurred between the rhodium(I) carbonyl complexes and iodine vapour, but did not go to completion. The i.r. spectra of the complexes $(anisNC)_2Rh(CO)Br_2X$ (X = Cl, Br) showed that the *trans*-configuration of the isonitriles is retained. The single C–O stretching mode had the higher frequency for the chloro-complex, which suggests that the chlorine is *trans* to the carbonyl group, *i.e.* *trans*-addition has occurred.

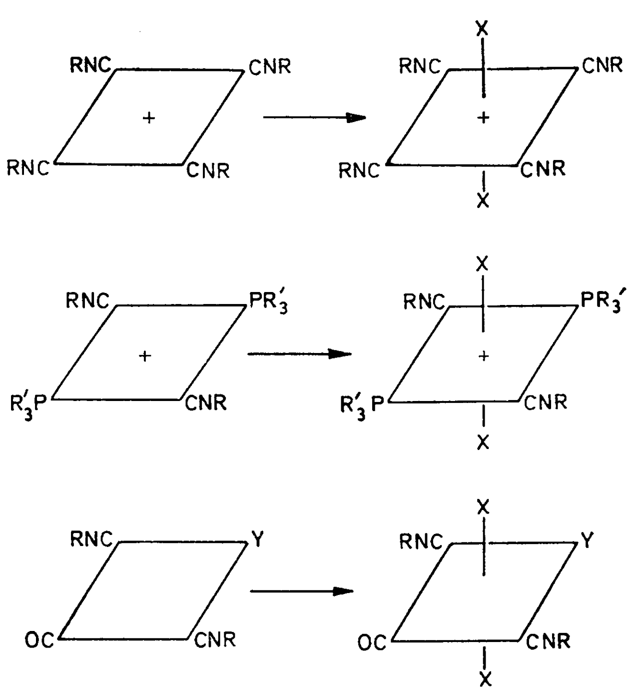
The complex $(anisNC)_2Rh(CO)Cl$ reacted with an excess of methyl iodide to give a low yield of a stable, crystalline complex of composition $(anisNC)_2Rh(CO)MeI_2$. The yield was considerably increased by carrying out the reaction under carbon monoxide. The product was non-conducting in nitromethane or nitrobenzene, and was monomeric in chloroform. The ^1H n.m.r. spectrum (chloroform) showed the $H_3C{-}O$ resonance at τ 6·17 and a further resonance, of similar intensity, at τ 8·40. The latter signal is attributed to an acetyl group, $H_3C{\cdot}CO{\cdot}Rh$, the presence of which is also indicated by absorption at 1688 cm^{-1} in the i.r. spectrum. No bands attributable to terminal or bridging carbonyl groups were found. The single strong N–C stretching frequency indicates that the isonitrile ligands are mutually *trans*, and a trigonal-bipyramidal configuration seems likely. Square-pyramidal geometry is also possible, but the metal atom would be expected to lie above the basal plane, which should result in appreciable intensity for the symmetric N–C stretching mode.

No reaction was observed between methyl iodide and the complex $(anisNC)_2Rh(CO)Br$, nor between the chloro- or bromo-complexes and ethyl or n-propyl iodide or acetyl iodide or bromide.

DISCUSSION

The rhodium(I) complexes $[(RNC)_4Rh]^+$, $[(RNC)_3(R'_3P)Rh]^+$, and $(RNC)_2Rh(CO)X$ have the normal square-planar configurations with the isonitrile groups mutually *trans* in the mixed-ligand complexes. These configurations are retained on oxidation by bromine or iodine, the halogen adding *trans* in each case (Scheme). *trans*-Addition of halogens has been observed for the complexes $(Ph_3P)Rh(CO)_2Cl$,[6] $(Et_2E)_2(CO)Cl$ (E = S, Se, Te),[7] and $L_2Ir(CO)Cl$ ($L = Ph_3P$, Ph_2MeP),[8,9] although *cis*-addition has also been claimed for $L_2M(CO)Cl$ ($L = Et_3P$, Et_3As, Ph_3P; M = Rh, Ir).[10] *trans*-Addition of gaseous bromine to the solid complexes $(anisNC)_2Rh(CO)X$ (X = Cl, Br) is somewhat surprising [*cf.* *cis*-addition[11] of gaseous HX to $(Ph_3P)_2Ir(CO)Cl$]; the evidence in this case is based only on the C–O stretching frequency, and *cis*-addition cannot be completely ruled out. No reaction occurred between any of the rhodium(I) isonitrile complexes and hydrogen chloride.

The ease of oxidation of a given d^8 metal is largely a function of the neutral ligands,[1] although a case in which the strength of the newly formed metal–ligand bond is critical has recently been observed.[2] Complexes containing three or four P- or As-donor ligands are oxidised readily by hydrogen, hydrogen halides, and halogens, the reaction becoming easier as the ligand becomes more σ-basic (and/or less π-acidic). The complex $(Ph_3P)_2Rh(CO)Cl$ does not react with hydrogen chloride, but $(Ph_3P)_3RhCl$ forms an unstable adduct (with loss of a mole of the phosphine).[12] The stability of the adducts of other tertiary phosphine complexes, L_3RhCl, is related to the basicity of the phosphine.[13] The complexes $L_2Rh(CO)Cl$ ($L = PhEt_2P$, Et_2S, Et_2Se, Et_2Te) react to form trichloro-complexes.[7,14] An apparent exception to this general trend is the formation of $(Ph_3P)Rh(CO)Cl_3$ from the monochloro-complex and hydrogen chloride.[6] The lack of reaction of the isonitrile complexes with hydrogen chloride is consistent with the relatively high π-acidity of these ligands.



SCHEME

The π-acid character of the isonitriles is also reflected in the C–O stretching frequency of the complexes $(anisNC)_2Rh(CO)X$ (X = Cl, Br). Values greater than 2000 cm^{-1} do not seem to gave been observed previously for this type of complex. Coupling between the C–O and C–N stretching modes might be expected to give a frequency shift in the opposite direction, so that the high frequency probably indicates weak co-ordination of the CO-group. This may be attributed to effective competition by the isonitriles for the π-electron density on the metal atom. Our inability to prepare the corresponding *p*-tolylisonitrile complex may be related to the higher π-acid character expected for this ligand. The weak binding of the CO-group is shown in the ready loss of carbon monoxide from the oxidised products

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(anisNC)$_2$Rh(CO)Br$_2$X, which also have unusually high values for ν_{CO}. Similar loss of carbon monoxide has been observed on treatment of L$_2$Rh(CO)X$_3$ with aryl isonitriles.[15]

The reaction of (anisNC)$_2$Rh(CO)Cl with methyl iodide involves halogen exchange and the formation of an acetyl group (but not necessarily in that order). Presumably the first step is oxidative-addition of methyl iodide which may be followed either by loss of methyl chloride, giving halogen exchange, or by methyl migration, which might be facilitated by co-ordination of the solvent methyl iodide. The lack of reaction of the bromo-complex may indicate that the acetyl group is formed before halogen exchange occurs. The improved yield obtained in the presence of carbon monoxide might suggest a direct insertion step, but solvent-assisted methyl migration seems more likely, as in other systems.[16] The function of the carbon monoxide is then to inhibit loss of this ligand from the intermediate rhodium(III) methyl complex. Intramolecular formation of acyl complexes depends on the nature of the neutral ligands, becoming easier as these become more π-acidic, less σ-basic. Thus, complexes of the type (R$_3$P)$_2$Rh(CO)MeX$_2$ rearrange more readily for R = aryl than R = alkyl, and the complex (Ph$_3$P)Rh(CO)$_2$Cl reacts very readily.[6,17] These trends could result from a weakening of the rhodium–alkyl bond, or from reduced back-donation to the carbonyl group, which would render the carbonyl carbon atom more positive and more susceptible to nucleophilic attack by the alkyl group. The latter seems more likely in the present case.

TABLE 2

Analytical data

Complex	Decomp. pt. (°)	C (%)	H (%)	N (%)
[(tolNC)$_4$Rh]I		54·6 (55·0)	4·6 (4·0)	7·8 (8·0)
[(tolNC)$_4$Rh]BPh$_4$	95—105	73·3 (75·5)	5·6 (5·4)	6·2 (6·3)
[(tolNC)$_4$RhI$_2$]I$_3$ [a]	165—170	31·9 (31·9)	2·6 (2·3)	5·0 (4·7)
[(tolNC)$_4$RhI$_2$]BPh$_4$	110	58·6 (58·7)	4·5 (4·2)	5·1 (4·9)
[(tolNC)$_4$RhBr$_2$]Br$_3$ [b]	160	40·0 (39·6)	3·4 (2·9)	5·9 (5·8)
[(anisNC)$_4$Rh]BPh$_4$	120—125	70·4 (70·5)	5·1 (5·0)	6·0 (5·9)
[(anisNC)$_4$RhI$_2$]I$_3$ [c]	135—140	30·1 (30·2)	2·6 (2·2)	4·3 (4·3)
[(anisNC)$_4$RhI$_2$]BPh$_4$ [d]	105—109	55·3 (55·6)	3·7 (4·0)	4·6 (4·6)
[(anisNC)$_4$RhBr$_2$]Br$_3$ [e]	140—145	37·8 (37·1)	3·3 (2·7)	5·9 (5·4)
(anisNC)$_2$Rh(CO)Cl	140—150	47·5 (47·2)	3·4 (3·2)	7·2 (6·5)
(anisNC)$_2$Rh(CO)Br	165	42·7 (42·8)	3·0 (2·9)	6·0 (5·9)
(anisNC)$_2$Rh(CO)Br$_3$	125	32·3 (32·0)	2·4 (2·2)	4·7 (4·4)
(anisNC)$_2$Rh(COMe)I$_2$ [f]	150	32·2 (32·4)	2·7 (2·6)	4·4 (4·2)
[(ClC$_6$H$_4$NC)$_2$(Ph$_3$P)$_2$Rh]BPh$_4$	110	72·4 (72·5)	4·9 (4·7)	2·3 (2·3)
[(ClC$_6$H$_4$NC)$_2$(Ph$_3$P)$_2$RhBr$_2$]Br$_3$ [g]	120—125	46·5 (46·1)	2·6 (2·9)	2·3 (2·2)
[(ClC$_6$H$_4$NC)$_2$(Ph$_3$P)$_2$RhI$_2$]I$_3$	140—144	39·3 (39·0)	2·6 (2·5)	1·9 (1·8)
[(anisNC)$_2$(Ph$_2$MeP)$_2$Rh]BPh$_4$	60	70·5 (72·8)	5·3 (5·5)	3·2 (2·6)
[(anisNC)$_2$(Ph$_2$MeP)$_2$RhBr$_2$]Br$_3$	165	43·3 (43·2)	3·8 (3·4)	2·8 (2·4)

[a] I, 53·1 (52·6). [b] Br, 39·5 (41·0). [c] I, 49·9 (50·0). [d] I, 20·8 (21·0). [e] Br, 36·5 (38·6). [f] I, 37·9 (38·1). [g] Cl, 5·7 (5·6); Br, 30·1 (30·7).

EXPERIMENTAL

Perkin-Elmer 521 and R10 and Varian HA100 spectrometers were used. The isonitriles and their rhodium(I) complexes were prepared by literature methods.[3-5] Analytical data are collected in Table 2. Most products were obtained with yields of 85% or better.

The Complexes [(RNC)$_4$RhX$_2$]Y (R = anis, tol; X = Br, I; Y = X$_3$,BPh$_4$).—An excess of iodine in chloroform was added slowly with stirring to a solution of the complex [(RNC)$_4$Rh]Z (Z = I, BPh$_4$) (1 mmol) in chloroform (20 ml). The addition of ether gave *brown crystals* of [(RNC)$_4$RhI$_2$]I$_3$. The corresponding *tetraphenylborates* were obtained by metathesis with sodium tetraphenylborate in acetone solution.

The corresponding *bromo-complexes* [(RNC)$_4$RhBr$_2$]Br$_3$ were obtained by adding an excess of bromine in ethanol to an ethanol solution of [(RNC)$_4$Rh]BPh$_4$, giving orange crystals. These complexes decompose in solution and could not be prepared in chloroform, neither could pure tetraphenylborates be prepared.

The Complexes [(RNC)$_2$(R'$_3$P)$_2$RhX$_2$]X$_3$ (R = *p*-ClC$_6$H$_4$, R' = Ph, X = Br, I; R = anis, R'$_3$ = Ph$_2$Me, X = Br, I).—The halogen in ethanol was added slowly to a stirred ethanol suspension of the complex [(RNC)$_2$(R'$_3$P)$_2$Rh]BPh$_4$. The complex dissolved during the reaction, but addition of an excess of the halogen gave yellow (X = Br) or brown (X = I) *crystalline precipitates* of the products. The anisNC-complexes were recrystallised from chloroform–ether.

The Complexes (anisNC)$_2$Rh(CO)Br$_2$X (X = Cl, Br).—The complex (anisNC)$_2$Rh(CO)X was exposed to bromine vapour in an evacuated system for 10—15 min. The golden-yellow *product* was washed with ether to remove adsorbed bromine. These complexes decompose rapidly in solution.

The Complex (anisNC)$_2$Rh(COMe)I$_2$.—An excess of methyl iodide was added to a chloroform solution of the complex (anisNC)$_2$Rh(CO)Cl and carbon monoxide was passed for *ca.* 30 min. After the addition of a little ether, passage of carbon monoxide was continued until precipitation of the red *product* was complete. The precipitate was recrystallised from chloroform–ether.

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