Reaction of Ligand Ammonia in Hexaammineruthenium(III) with Aldehydes to Form Ruthenium(II) Nitriles

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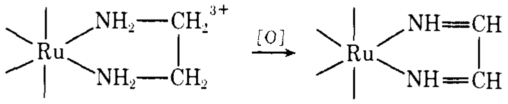
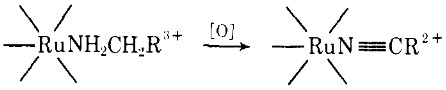
Abstract: $Ru(NH_3)_6^{3+}$ in alkaline solution reacts with aromatic and aliphatic aldehydes to form nitrilepentaammineruthenium(II) species, identified by infrared and ultraviolet-visible spectral properties and by analysis. The reaction is of general applicability, although rates and yields depend on the solubility and stability of the aldehyde in the aqueous alkaline medium. The net reaction under inert atmosphere produces equimolar amounts of Ru(II)-nitrile and Ru(II)-imine complex. In the presence of O_2 or H_2O_2 the imine is quantitatively converted to additional Ru(II)-nitrile. The proposed mechanism involves an intramolecular redox reaction of a Ru(III)-imine species to form the Ru(II)-nitrile.

Investigations into the reactions of ammine and amine ligands coordinated to Ru(III) have revealed two characteristic reactions. The first is the oxidative dehydrogenation of diamine[1,2] and amine[3,4] ligands to yield diimine and nitrile ruthenium(II) complexes respectively: e.g.,

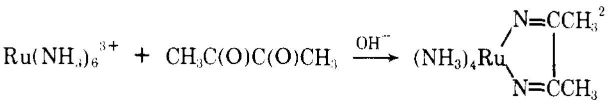


(1)



$$—RuNH_2CH_2R^{3+} \xrightarrow{[O]} —RuN{\equiv}CR^{2+} \quad (2)$$

The second characteristic reaction involves nucleophilic attack of hexaammineruthenium(II) at electrophilic sites on another species.[5,6] Some examples of this reaction type are:



(3)

$$Ru(NH_3)_6^{3+} + NO \xrightarrow{OH^-} Ru(NH_3)_5N_2^{2+} \quad (4)$$

We have recently described[7] preliminary observations on a reaction which combines features of these two characteristic reactions in which hexaammineruthenium(III) reacts with aldehydes to form nitrilepentaammineruthenium(II) complexes. This paper reports on the further characterization of that reaction.

Experimental Section

Materials. Hexaammineruthenium(III) tribromide was prepared by the method of Fergusson and Love[8] and $(H_3N)_5Ru^{II}\text{-}NCC_6H_4\text{-}4\text{-}CHO^{2+}$ was prepared by reaction of $(H_3N)_5Ru^{II}(OH_2)^{2+}$ with $NCC_6H_4\text{-}4\text{-}CHO$.[10] Aldehydes were purchased from various suppliers (Eastman Organics, Aldrich) and used as received. Argon gas (purified) was purchased from the Matheson Company. The hydrogen peroxide (3%) used in stoichiometry experiments was purchased from J. T. Baker and Company and standardized by two methods.[9] Ru analyses were performed on a Varian 2100 atomic absorption unit using the Ru line at 349.9 nm.

Reaction of $Ru(NH_3)_6^{3+}$ with Aldehydes. In a typical reaction $[Ru(NH_3)_6]Br_3$ (~0.167 mmol) was dissolved in 1.5 mL of H_2O and excess aldehyde added. The solution was thoroughly mixed and 1.5 mL of 2 M NaOH was added. Oxygen was bubbled through the solution at a rate of 500 mL/min for approximately 20 min, then several drops of saturated $NaClO_4$ solution added to precipitate the product. *Warning:* Caution should be used in handling perchlorate salts of coordination compounds containing organic ligands as explosions have been reported. The precipitate was filtered off, recrystallized from warm H_2O (40 °C), washed with 4:1 mixture of ether:ethanol, and dried over P_2O_5.

The utility of this reaction as a synthetic method is affected by the aqueous solubility of the aldehyde and its stability in basic solution. For example, perfluorobenzaldehyde undergoes a haloform type cleavage in 1 M OH^-;[17] however, by lowering the base concentration to 0.10 M, the reaction yielded the desired nitrile product. The problem of solubility was overcome by the use of methanol-water mixtures (10–15 vol % methanol) in several cases (3-nitrobenzaldehyde, 4-nitrobenzaldehyde, and 4-chlorobenzaldehyde) in which aqueous solubility of the aldehyde was low. This procedure resulted in faster reactions and higher yields of the nitrile complexes.

In only one case, with 2,5-hydroxybenzaldehyde, were we unable to isolate a solid product. The visible color changes, however, indicate that the normal condensation and oxidation reactions occur. The product of the 2-hydroxybenzaldehyde reaction is also highly soluble and was consequently obtained in small yield.

Reactions under argon atmosphere were carried out using standard serum cap and syringe techniques.

The aldehydes used in this reaction are listed in Table I. Reaction yields of previously reported compounds are reported in Table II; yields and analyses of new compounds are in Table III.

Stoichiometric Measurements. (a) $Ru(NH_3)_6^{3+}$/benzaldehyde stoichiometry was determined by mixing equimolar amounts of the two reactants in 1 M NaOH. Excess oxidant (O_2) was bubbled through the solution and the formation of $Ru(NH_3)_5NCC_6H_5^{2+}$ was monitored by removing aliquots, diluting, and running the electronic spectrum. (b) Oxidant stoichiometry was determined by dissolving $[Ru(NH_3)_6]Br_3$ and benzaldehyde in 1.5 mL of H_2O in 10-mL reaction vials equipped with rubber septum caps. The solution was flushed with argon and an equal volume of previously deaerated 2 M NaOH added. Microliter quantities of standardized H_2O_2 corresponding to various $Ru\text{-}H_2O_2$ molar ratios were injected into the vials, and the reactions allowed to proceed for 60 min at 30 °C. Product formation was monitored by withdrawing aliquots, with minimum air contact, and running the electronic spectrum in a 0.05-cm path length cell.

Spectrophotometric Measurements. Infrared spectra were run on a Perkin-Elmer 257 spectrophotometer and electronic spectra on Cary Models 14 and 15 spectrophotometers.

Results

Reaction with No Added Oxidant. Several experiments were performed with benzaldehyde using solutions flushed with argon and carried out under an argon atmosphere. Upon addition of the aqueous alkali to the pale yellow solution containing $Ru(NH_3)_6^{3+}$ and C_6H_5CHO (final concentration ca. 0.005 M in Ru), the solution immediately turned deep red and remained visually unchanged for several hours. The spectral properties (described below) of these solutions and of the perchlorate and fluoborate salts obtained from them are those expected for an equimolar mixture of the nitrile,

Table I. Aldehydes Used for Reaction with Hexaammineruthenium(III) in Base

Name	Formula
Acetaldehyde	CH_3CHO
Acrolein	$CH_2{=}CHCHO$
Propionaldehyde	CH_3CH_2CHO
Crotonaldehyde	$CH_3CH{=}CHCHO$
Furaldehyde	2-$CHOC_4H_3O$
2-Pyridinecarboxaldehyde	2-C_5H_4NCHO
Perfluorobenzaldehyde	C_6F_5CHO
Chlorobenzaldehyde	4-ClC_6H_4CHO
Benzaldehyde	C_6H_5CHO
Nitrobenzaldehydes	3-$NO_2C_6H_4CHO$ 4-$NO_2C_6H_4CHO$
4-Hydroxybenzaldehyde	4-HOC_6H_4CHO
Salicylaldehyde	2-HOC_6H_4CHO
2,5-Dihydroxybenzaldehyde	2,5-$(HO)_2C_6H_3CHO$
Cyanobenzaldehyde	4-NCC_6H_4CHO
Terephthalaldehyde	4-$CHOC_6H_4CHO$
Tolualdehydes	2-$CH_3C_6H_4CHO$ 4-$CH_3C_6H_4CHO$
Anisaldehyde	4-$CH_3OC_6H_4CHO$
4-Carboxaldehydebenzonitrile-pentaammineruthenium(II)	4-$OHCC_6H_4CNRu(NH_3)_5^{2+}$

$(H_3N)_5RuNCC_6H_5^{2+}$, and imine, $(H_3N)_5RuNH{=}CH{-}C_6H_5^{2+}$, complexes of Ru(II). Attempts to separate the imine and nitrile reaction products by fractional precipitation (using perchlorate and fluoborate anions) were unsuccessful.

Reaction with Added Oxidant. In the presence of excess oxygen or hydrogen peroxide the reaction of $Ru(NH_3)_6^{3+}$ with benzaldehyde (or other aldehydes containing an unsaturated α-carbon atom) in one molar base produces an immediate deep red color which changes to a brownish yellow. The second color change occurs within seconds with a 100-fold excess of H_2O_2, in 10-20 min with a vigorous stream of O_2, and over a period of several hours if the solution is exposed to the atmosphere without stirring. The spectral properties of these solutions and of the solids obtained from them (described below) are those expected for the corresponding nitrile complexes.

Aldehydes with saturated α-carbon atoms show no noticeable color change, but again yield products which have been identified as the nitrile complexes.

Infrared Spectra. The infrared spectra of the solid reaction products show strong peaks in the $\nu(C{\equiv}N)$ region at lower frequencies than the free nitriles. This behavior, characteristic of Ru(II) nitrile complexes, has been attributed to $d\pi$-$p\pi^*$ back-bonding.[10] Further confirmation that the products contain Ru(II) is provided by the low frequency (~1280 cm^{-1}) positions of the NH_3 symmetrical deformation modes.[10,11] Spectra of reaction products were in good agreement with those previously obtained[10,12] from the direct substitution of a nitrile ligand for H_2O in $Ru(NH_3)_5H_2O^{2+}$ except for the 4-cyanobenzonitrilo complex for which we found a second peak in the $C{\equiv}N$ stretch region as expected from the presence of both bound and free nitrile groups. This apparent discrepancy is discussed in a separate section below. Nitrile stretching frequencies of the reaction products are listed in Tables II and III.

When the reaction with benzaldehyde was carried out under an argon atmosphere, the infrared spectrum of the solids recovered shows the peak expected for the $Ru(NH_3)_5NCC_6H_5^{2+}$ species plus one additional peak at 1440 cm^{-1}. Upon redissolving, oxidation, and reprecipitation this peak disappears, producing a spectrum indistinguishable from the pure benzonitrile complex. We attribute the 1440-cm^{-1} peak to a $\nu(C{=}N)$ vibration (shifted to lower frequencies by back-bonding to the Ru(II) metal center) due to the presence of a $Ru(NH_3)_5NH{=}CHR^{2+}$ species containing coordinated imine. Oxidative dehydrogenation of this species yields the nitrile complex.

Electronic Spectra. In the reaction of an unsaturated aldehyde with $Ru(NH_3)_6^{3+}$ in the presence of air, an absorption by the product in the visible region of the spectrum (600-350 nm) is evidence of a ruthenium(II) species having a coordinated unsaturated nitrile ligand.[14] This visible absorption peak has been attributed to a metal to ligand ($d\pi$-π^*) charge transfer (MLCT) band.[10,13] The spectra also contain bands in the UV region which have been assigned to ligand π-π^* transitions. Products from the reactions of saturated aldehydes show no visible absorption but do exhibit a band in the UV region of the spectrum which has been attributed to a MLCT. The electronic spectral data for previously unreported nitrile complexes are presented in Table IV. For products in which the complex was previously prepared via direct ligand substitution good agreement with literature values[14] was generally found (see Table II). The exceptions to this are the 2-pyridinecarbonitrile complex and its conjugate acid for which we obtained ϵ values significantly larger than those reported previously and the 4-cyanobenzonitrilo product which gave a different peak. Our results have been carefully rechecked and are believed to be reliable. We believe the preparative method employed by us to prepare the pyridine-nitrile complex is more likely to produce a single product than the direct substitution method. The 4-cyanobenzonitrile case is discussed below.

In the absence of O_2, the $Ru(NH_3)_6^{3+}$-benzaldehyde reaction solutions showed an absorption peak at 376 nm, attributable to $Ru(NH_3)_5NCC_6H_5^{2+}$, and a shoulder at 450 nm. The yield of $Ru(NH_3)_5$-$NCC_6H_5^{2+}$ species was 50 ± 5% as determined by the absorption at 376 nm. Upon oxidation of this solution by O_2 or H_2O_2 the peak at 450 nm disappears and the peak at 376 nm increases to 100 ± 5% of that expected for

Table II. Reaction Yields and Comparison of Spectral Data of Nitrile Complexes $Ru(NH_3)_5NCR^{2+}$ with Previous Studies

R =	% yield[h]	$\nu(C{\equiv}N)$, cm^{-1}		λ_{max} (ϵ), nm	
		Lit.[a]	Found[d]	Lit.[a]	Found
CH_3	33	2239[f]	2250	229 (15400)[c]	229 (15400)
$CH_2{=}CH$	20	2184[g,d]	2180	372 (5250)[g] 356 sh (4570)	372 (5700) 356 sh (4820)
2-C_5H_4N	76	2179[d]	2180	408 (6600)[b]	408 (10120)
2-$C_5H_4NH^+$	—	2153[d]	2155	505 (8130)[b]	505 (12100)
C_6F_5	50	2189[e]	2180	408 (7800)	408 (7860)
C_6H_4-4-Cl	42	2192[e]	2180	380 (8140)	383 (8100)
C_6H_5	53	2188[d]	2185	376 (8500)	376 (8100)
C_6H_4-4-CH_3	81	2198[e]	2190	367 (7400)	367 (7840)
C_6H_4-4-OCH_3	58	2194[f]	2190	365 (9550)	365 (9500)

[a] From ref 10 except as noted. [b] From ref 12. [c] From ref 22. [d] ClO_4^- salt. [e] Br^- salt. [f] BF_4^- salt. [g] From ref 13. [h] As isolated solids.

Table III. Yields and Analytical Data for Previously Uncharacterized $Ru(NH_3)_5NCR^{2+}$ Complexes Prepared by the $Ru(NH_3)_6^{3+}$–RCHO Reaction (Perchlorate Salts)

R =	ν(C≡N) in cm^{-1}	% yield[b]	% Ru		% ClO_4^-	
			Calcd	Found	Calcd	Found
CH_3CH_2	2250 (s)	20	23.00	22.49		
$CH_3CH{=}CH$	2180 (s)	74	22.39	22.29		
2-C_4H_3O	2178 (s)	64	21.17	20.63	41.42	41.73
C_6H_4-3-NO_2	2195 (s)	73	18.98	18.31	37.21	38.00
C_6H_4-4-NO_2	2175 (s)	59	18.98	19.09	37.21	36.54
C_6H_4-4-OH	2240 (m) 2180 (m)	54	20.07	20.50		
C_6H_4-2-OH[a]	2180 (s)	5				
C_6H_4-2-CH_3	2180 (s)	74	20.16	19.86	39.52	39.00

[a] The low yields of this compound precluded analysis. [b] As isolated solids.

Table IV. Ultraviolet-Visible Spectral Data for Aqueous $Ru(NH_3)_5NCR^{2+}$ Complexes

R =	λ_{max} (ϵ)	λ_{max} (ϵ)[a]	λ_{max} (ϵ)	λ_{max} (ϵ)
CH_3CH_2				229 (15000)
$CH_3CH{=}CH$	355 (8400)	340 (8630)	245 (15700)	
2-C_4H_3O	365 (7213)	345 (7125)	268 (23500)	
C_6H_4-3-NO_2	390 (7750)		253 (18275)	218 (20500)
C_6H_4-4-NO_2	490 (10200)		255 (20337)	
C_6H_4-4-OH	360 (4090)	340 (4550)	255 (18181)	
C_6H_4-4-O^-	335 (11950)		268 (22767)	
C_6H_4-2-OH	360 (7900)		245 (13457)	
C_6H_4-2-CH_3	373 (8480)	350 (7335)	247 (17630)	233 sh (15128)

[a] λ_{max} in nm, ϵ in M^{-1} cm^{-1}.

$Ru(NH_3)_5NCC_6H_5^{2+}$, with an isosbestic point at 408 nm. We attribute the absorption at 450 nm to the $Ru(NH_3)_5NH{=}CHC_6H_5^{2+}$ species containing coordinated benzylimine.

Stoichiometry. Several experiments were conducted with the $Ru(NH_3)_6^{3+}$/benzaldehyde reaction to establish stoichiometric features of the reaction: (a) *Aldehyde.* When equimolar amounts of $Ru(NH_3)_6Br_3$ and C_6H_5CHO reacted in the presence of excess oxidant, the apparent yield of $Ru(NH_3)_5NCC_6H_5^{2+}$, as determined by the electronic spectrum, was 100 ± 5%; (b) *Oxidant.* When $[Ru(NH_3)_6]Br_3$ reacted with C_6H_5CHO in the presence of known amounts of oxidant (30 °C, 1 h), 100% yield was obtained when the H_2O_2 to Ru molar ratio was 1:2. Larger amounts of peroxide resulted in decreased yields, probably due to oxidation of Ru(II) to Ru(III).[15]

The 4-Cyanobenzonitrile Complexes. The 4-$CNC_6H_4CNRu(NH_3)_5^{2+}$ ion is of special interest because it contains both coordinated and uncoordinated nitrile groups within the same molecule and thus provides a direct comparison of vibrational and electronic effects of Ru(II) coordination to the nitrile group. Our attempts to prepare this species by reaction of hexaammineruthenium(III) ion with 4-cyanobenzaldehyde, however, gave a product, I, with different spectral properties than previously reported for a compound, II, prepared by the direct substitution reaction between $(H_2O)Ru^{II}(NH_3)_5^{2+}$ and 4-cyanobenzonitrile which had been identified as the monomer.[10] We repeated the substitution reaction as previously described[10] (addition of the dinitrile to dilute aqueous $Ru(NH_3)_5OH_2^{2+}$) and obtained the same results. However, when we changed the reaction conditions by adding aqueous $Ru(NH_3)_5OH_2^{2+}$ dropwise to a saturated solution of the 4-cyanobenzonitrile in ethanol, the perchlorate product had the same spectral properties as I, the product of the $Ru(NH_3)_6^{3+}$ reaction with 4-cyanobenzaldehyde. These results are summarized in lines A and B of Table V. To resolve this discrepancy, we first mixed $(H_3N)_5Ru(OH_2)^{2+}$ with excess 4-cyanobenzaldehyde to form 4-$OHCC_6H_4CN$–$Ru^{II}(NH_3)_5^{2+}$ (line C, Table V), then allowed this Ru(II) complex to react with $Ru^{III}(NH_3)_6^{3+}$ in alkaline solution to obtain a product indistinguishable from II. As expected, the carbonyl peak at 1680 cm^{-1} disappeared during this reaction. We also reacted $Ru(NH_3)_5OH_2^{2+}$ with I and obtained a product essentially identical with II. The unequivocal conclusions are (1) that our Ru(III)/aldehyde reaction yields the expected mononuclear product:

$$Ru(NH_3)_6^{3+} + 4\text{-}OHCC_6H_4CN \xrightarrow{OH^-} (H_3N)_5RuNCC_6H_4CN^{2+} \quad (5)$$

and (2) that the Ru(II)/nitrile reaction (under conditions previously reported[10]) produces the bridged dimer:

$$2Ru(NH_3)_5OH_2^{2+} + 4\text{-}NCC_6H_4CN \rightarrow (H_3N)_5RuNCC_6H_4CNRu(NH_3)_5^{4+} \quad (6)$$

The monomer clearly shows two sharp peaks in the ν(CN) region with a shift of 50 cm^{-1} to lower energy clearly attributed to the effect of Ru(II) coordination. There is also a significant shift of both electronic peaks to higher energy.

Discussion

The reported pK_a of 12.4[16] for $Ru(NH_3)_6^{3+}$ suggests that in 1 M aqueous base, the complex exists nearly completely in the amidopentaammineruthenium(III) form. It has been shown[6] that in 1 M OH^- the complex acts as a nucleophile toward the carbonyl groups in diones to form diimine complexes; similar diimine complexes are formed by the oxidative dehydrogenation of bidentate Ru(III) diamine complexes.[1,2] Furthermore, the oxidative dehydrogenation of monoamine ligands on Ru(III) produces nitrilepentaammineruthenium complexes in an analogous reaction.[3]

The reaction of $Ru(NH_3)_6^{3+}$ with aldehydes in the presence of base and oxidant appears to combine these two characteristic reactions of ruthenium(III) to yield nitrilepentaammineruthenium(II) complexes, identifiable by their characteristic infrared and UV-visible spectral properties.

The driving force for the $Ru(NH_3)_6^{3+}$-RCHO reaction is probably the formation of a ruthenium complex in which the metal is stabilized in its +2 oxidation state by back-bonding with the nitrile ligand. Evidence for back-bonding is provided by the decreased C≡N stretching frequencies of the complexed vs. free nitrile. The increased stability of the nitrilepentaammineruthenium(II) complex is also reflected in the Ru(II)-Ru(III) reduction potentials.[18] The $Ru(NH_3)_6^{3+}$-$Ru(NH_3)_6^{2+}$ reduction potential is 0.05 V, as compared to 0.485 V for the $Ru(NH_3)_5NCC_6H_5^{3+}$-$Ru(NH_3)_5NCC_6H_5^{2+}$ reduction. This represents a stabilization energy of approximately 10 kcal/mol. Similar stabilization has been found for other Ru(II) complexes containing π acceptor ligands.[18,19]

In the presence of excess oxygen, the experimental results established a 1:1 stoichiometric ratio of aldehyde to $Ru(NH_3)_6^{3+}$; the balanced equation is almost certainly

$$Ru^{III}(NH_3)_6^{3+} + RCHO + OH^- + \tfrac{1}{4}O_2 \rightarrow Ru^{II}(NH_3)_5NCR^{2+} + \tfrac{5}{2}H_2O \quad (7)$$

Even when a large molar excess (100-fold) of aldehyde was used no evidence for bisnitrile complexes of ruthenium(II) was obtained. Two explanations seem reasonable:[20] First, the maximum stability of back-bonding may be obtained when there are five saturated and one unsaturated ligand coordinated to ruthenium(II) because of lack of competition for the metal π electrons by other π acceptor ligands. Second, protons on a ruthenium(II) species are certainly less acidic than those on Ru(III) and deprotonation of the initial ruthenium(II) product to form a second nucleophilic species is unlikely. A "direct route" to the dinitrile complexes via oxidation of the $Ru^{II}(NH_3)_5NCR$ to the Ru(III) complex followed by treatment with additional aldehyde is precluded by the extremely rapid base hydrolysis of Ru(III)-nitriles.[15]

Without added oxidant the electronic and infrared spectral evidence points to a mixture of ruthenium(II) species, with the probable reaction stoichiometry:

$$Ru^{III}(NH_3)_6^{3+} + RCHO + OH^- \rightarrow \tfrac{1}{2}Ru^{II}(NH_3)_5NCR^{2+} + \tfrac{1}{2}Ru^{II}(NH_3)_5\text{-}NH{=}CHR^{2+} + 2H_2O \quad (8)$$

Upon addition of external oxidant the infrared and visible spectral features change to those characteristic of $Ru(NH_3)_5NCC_6H_5^{2+}$ species. The presence of an isosbestic point at 408 nm is evidence for a direct conversion of the imine to the nitrile. An intermediate with similar visible spectral properties was found in the oxidation of $Ru(NH_3)_5NH_2CH_2C_6H_5^{3+}$ which was also assigned to a $Ru(NH_3)_5NH{=}CHC_6H_5^{2+}$ species.[3]

When H_2O_2 was used as the external oxidant the maximum yield is obtained when there is 0.50 mol of H_2O_2 per mole of $Ru(NH_3)_6^{3+}$. This leads to the following equation for the overall reaction:

$$Ru(NH_3)_6^{3+} + RCHO + \tfrac{1}{2}H_2O_2 + OH^- \rightarrow Ru(NH_3)_5NCR^{2+} + 3H_2O \quad (9)$$

This observation supports the 1:4 oxygen to hexaammineruthenium(III) stoichiometry with oxygen as the external oxidant shown in eq 7. Attempts at direct experimental verification of the O_2 stoichiometry by O_2 uptake experiments were unsuccessful, possibly due to side reactions which lead to the decomposition of the complex in alkaline solution.

The hexaammineruthenium(III)-aldehyde reaction represents a two-electron redox process in which the ruthenium is reduced and the ligand oxidized. In the absence of an external oxidant, ruthenium(III) acts as a one-electron oxidant accounting for the 50% yield of the nitrile product. In the presence of an external oxidant, the monoimine complex is oxidatively dehydrogenated to yield the nitrile species.

Table V. Characterization of Ru(II) Complexes of 4-Cyanobenzonitrile

Reactants[a]	λ_{max} (ϵ) aq	ν(C≡N) ClO_4^- salt	Ref
(A) Ru^{III}, 4-NCC_6H_4CHO	428 (12000)	2232	*b*
	245 (25060)	2182	
(B) Ru^{II}, 4-NCC_6H_4CN	462 (—)	2180	10
	462 (19800)	2180	*b*
	252 (25600)		
	429 (—)	2220 (sh)	*b*, *c*
		2185	
(C) Ru^{II}, 4-NCC_6H_4CHO	446 (8320)	2177	10
	448 (8070)	2178	*b*
		1680 (C=O)	
(D) Ru^{II}, 1[d]	462 (—)	2180	*b*
(E) Ru^{III}, 4-$OCHC_6H_4CHO$	457 (broad)	2180	*b*
	252 (—)		

[a] Ru^{III} = alkaline $Ru(NH_3)_6^{3+}$; Ru^{II} = $Ru(NH_3)_5OH_2^{2+}$. [b] Present study. [c] Ru^{II} added to ethanolic solution of the dinitrile (see text). [d] 1 = product of reaction (A).

Although our observations do not provide the basis for a detailed mechanism, some general statements can be made: (1) The base dependence and the plausibility of a nucleophilic attack at the carbonyl group both suggest that the pentaammineruthenium(III) amido complex is the reactive form of the original ruthenium species. (2) It is unlikely that a Ru(III) nitrile species is an intermediate because of the known rapid base hydrolysis of the nitrile ligand to the amido; e.g., $t_{1/2}$ for $Ru(NH_3)_5NCC_6H_5$ at 25 °C in 1 M OH^- is 0.0003 s.[15] (3) Somewhere in the overall reaction Ru(III) is reduced to Ru(II) and the ligand (possible the imine) is oxidized to the nitrile (a two-electron oxidation). When Ru(III) is the only oxidant this results in a 50% yield. Whether this ligand redox reaction is intramolecular, intermolecular, or solvent mediated is undetermined.

The addition of an external oxidant such as H_2O_2 or O_2 converts the imine to the nitrile via oxidative dehydrogenation:

$$\tfrac{1}{2}(H_3N)_5Ru^{II}(NH{=}CHR)^{2+} + \tfrac{1}{2}H_2O_2 \rightarrow \tfrac{1}{2}(H_3N)_5Ru^{II}NCR^{2+} + H_2O \quad (10)$$

or with O_2:

$$\tfrac{1}{2}(H_3N)_5Ru^{II}(NH{=}CHR)^{2+} + \tfrac{1}{4}O_2 \rightarrow \tfrac{1}{2}(H_3N)_5Ru^{II}NCR^{2+} + \tfrac{1}{2}H_2O \quad (11)$$

Addition of reaction 10 to reaction 8 yields the overall equation for the reaction which is in agreement with the experimentally determined stoichiometry shown above (reaction 9).

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References and Notes

(1) F. Basolo, J. E. Lester, and B. C. Lane, *Chem. Commun.*, 1618 (1971).
(2) T. J. Meyer, G. M. Brown, T. R. Weaver, and F. R. Keene, *Inorg. Chem.*, **15**, 190–196 (1976).
(3) H. Taube, G. Tom, and S. E. Diamond, *J. Am. Chem. Soc.*, **92**, 2661–2664 (1975).
(4) T. J. Meyer, D. J. Salmon, and F. R. Keene, *J. Am. Chem. Soc.*, **98**,

1884–1889 (1976).
(5) J. N. Armor and S. D. Pell, *J. Am. Chem. Soc.*, **95**, 7625–7633 (1973).
(6) A. M. Sargeson, I. P. Evans, and G. W. Everett, Jr., *J. Chem. Soc., Chem. Commun.*, 139–140 (1975).
(7) K. Schug and C. P. Guengerich, *J. Am. Chem. Soc.*, **97**, 4135 (1975).
(8) J. E. Fergusson and J. L. Love, *Inorg. Synth.*, **13**, 208–211 (1972).
(9) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis", 3rd ed, The MacMillian Company, New York, N.Y., 1961.
(10) P. C. Ford and R. E. Clarke, *Inorg. Chem.*, **9**, 227–235 (1970).
(11) A. D. Allen and C. V. Senoff, *Can. J. Chem.*, **45**, 1337–1341 (1967).
(12) P. C. Ford and R. E. Clarke, *Inorg. Chem.*, **9**, 495–499 (1970).
(13) P. C. Ford, R. D. Foust, Jr., and R. E. Clarke, *Inorg. Chem.*, **9**, 1933–1935 (1970).
(14) P. C. Ford, *Coord. Chem. Rev.*, **5**, 77–99 (1970).
(15) P. C. Ford and A. W. Zanella, *Inorg. Chem.*, **14**, 42–47 (1975).
(16) G. Navon and D. Waysbort, *Chem. Commun.*, 1410–1411 (1971). The validity of the pK value reported in this paper has been the subject of continuing discussion in the literature. See J. N. Armor, *J. Inorg. Nucl. Chem.*, **35**, 2067 (1973), and G. Navon, D. Waysbort, and M. Evenor, *Inorg. Chem.*, **14**, 514 (1975). The precise value of the pK_a is not material to the purposes of the paper.
(17) R. Filler, V. D. Beaucaire, and H. H. Kang, *J. Org. Chem.*, **40**, 935–939 (1975).
(18) P. C. Ford and T. Matsubara, *Inorg. Chem.*, **15**, 1107–1110 (1976).
(19) J. A. Page and I. J. Itzkovitch, *Can. J. Chem.*, **46**, 2743–2247 (1968).
(20) H. Taube, Kilpatrick Honorary Lectures, Illinois Institute of Technology, Chicago, 1975.
(21) J. D. Miller, Ph.D. Thesis, Cambridge University, as cited in G. Nord and O. Wernberg, *J. Chem. Soc. Dalton Trans.*, 845–849 (1975).
(22) P. C. Ford and R. E. Hintze, *J. Am. Chem. Soc.*, **97**, 2664–2671 (1975).

Facile Ortho Metalation of Triphenylphosphine in Five-Coordinated Methyliridium(III) Complexes

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Abstract: *trans*-$\{IrCl(N_2)[P(C_6H_5)_3]_2\}$ adds methyl sulfonates to give iridium(III)-dinitrogen complexes, $\{IrCl(O_3SY)(CH_3)(N_2)[P(C_6H_5)_3]_2\}$ ($Y = CF_3$ or F). These react with anions in methanol to give five-coordinated iridium(III) complexes having the formula $\{IrClX(CH_3)[P(C_6H_5)_3]_2\}$ (X = Cl, Br, I, NCO, CH_3CO_2, NO_3, or NO_2). These form 1:1 adducts with carbon monoxide. The dichloro complex reacts with an excess of dimethylphenylphosphine to give *mer*-$\{IrCl_2(CH_3)[P(CH_3)_2C_6H_5]_3\}$. The coordinatively unsaturated methyl complexes (X = Cl, Br, or NCO) undergo an ortho metalation of coordinated triphenylphosphine and eliminate methane. The process occurs in solution and in the solid state. In both cases the product is $\{\overline{IrC_6H_4P}(C_6H_5)_2ClX[P(C_6H_5)_3]\}$. The kinetics of the reaction have been studied for X = Cl or Br in 1,2-dichloroethane. The observed first-order rate constants are, at 40 °C, $(5.25 \pm 0.10) \times 10^{-4}\ s^{-1}$ for X = Cl and $(11.14 \pm 0.33) \times 10^{-4}\ s^{-1}$ for X = Br. Deuteration of the ortho positions of the triphenylphosphines gives an isotope effect, k_H/k_D, of 1.51, X = Cl, and 1.21, X = Br. Activation parameters were obtained from the temperature dependence of k_{obsd}. Differential scanning calorimetry was used to measure the enthalpy change for the ortho-metalation reaction of $\{IrCl_2CH_3[P(C_6H_5)_3]_2\}$ in the solid state, $\Delta H_0 = -2.6 \pm 0.1$ kcal mol^{-1}. The ortho-metalated product reacts with an excess of dimethylphenylphosphine to give $\{\overline{IrC_6H_4P}(C_6H_5)_2Cl[P(CH_3)_2C_6H_5]_3\}Cl\cdot CH_3OH$. The compounds have been characterized by IR, proton NMR, and electronic spectroscopy, elemental analyses, and molecular weight determinations.

Intramolecular substitution reactions by a metal on a coordinated ligand have attracted considerable interest because they represent the majority of examples of metal activation of carbon–hydrogen bonds in homogeneous solution. Recent reviews of the cyclometalation reaction have covered synthetic aspects and the very limited number of mechanistic studies.[1-4] Several examples of this type of reaction are found in tertiary phosphine and phosphite complexes of the platinum metals.[3] The majority involve a four-coordinate metal center with a d^8 configuration where the ortho metalation can be accounted for as an intramolecular oxidative addition reaction.[5] Examples are known for rhodium(I), iridium(I), palladium(II), and platinum(II).[3] Bennett and Milner have reported some kinetic data for ortho metalation in chlorotris(triphenylphosphine)iridium(I), but experimental difficulties prevented the determination of activation parameters.[6] This has been the only kinetic study of this type of reaction. Examples of the ortho metalation of phosphine and phosphite complexes of metals with d^6 configurations are less common. The best studied examples are ruthenium(II) complexes of triphenylphosphine or triphenyl phosphite.[7] In ruthenium(II) systems the reaction has also been postulated to be part of the mechanism for catalytic hydrogenation of olefins using $RuHCl(PPh_3)_3$[1] and must be involved in the stoichiometric hydrogenation of active olefins by this compound.[8] A mechanism proceeding via an internal oxidative addition reaction of a five-coordinated complex has been proposed.

Few examples of ortho metalation in six-coordinated iridium(III) complexes have been studied. Ortho metalation in $IrHX_2[P(OC_6H_5)_3]_3$ for X = Cl or Br apparently proceeds via a reductive elimination of HX to give $\{IrX[P(OC_6H_5)_3]_3\}$ followed by an internal oxidative addition. For the iodo analogue a mixture of H_2 and HI is eliminated (in boiling decalin) which might indicate that a pathway not involving prior generation of an iridium(I) species is possible.[9] Duff and Shaw have reported a study in which six-coordinated, dimethylnaphthylphosphine complexes of irdium(III) are ortho metalated under a variety of conditions. In general, high temperatures were required to bring about the reactions (e.g., refluxing in 2-methoxyethanol or fusing solid samples). In that paper, a 1,2-hydrometalation of coordinated ligand followed by H_2 elimination was suggested to account for ortho metalation in a coordinatively saturated complex.[10] A mechanism involving the formation of coordinatively unsaturated species may be an alternative in light of the high temperatures used to bring about reaction. Coordinatively unsaturated species are ubiquitous intermediates in reactions in organometallic systems[5] and are often suggested as intermediates in d^6 complex chemistry.

In this paper we report the synthesis and characterization of coordinatively unsaturated methyliridium(III) complexes which readily undergo ortho-metalation reactions under conditions which allow study of some of the important factors.