Inorganica Chimica Acta, 12 (1975) 85–91

Complexes of Formamidines and Ethyl Formimidate

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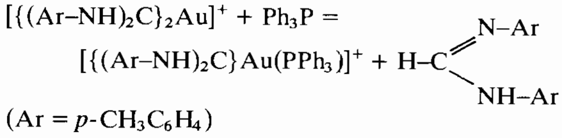
Received June 27, 1974

Formamidines and formimidates (L = (p-MeC$_6$H$_4$NH)(p-MeC$_6$H$_4$N=)CH; L' = (p-MeC$_6$H$_4$N=)(EtO)CH are shown to yield metal complexes, not obtained directly before. The following complexes were characterized through spectral and magnetic data: L_2Ag^+, L_2AgNO_3, L_2ZnBr_2, L_2CdBr_2, $L_3Cd_2Br_4$, $LHgCl_2$, L_2CoCl_2, $[LH]_2[CoCl_4]$, *cis-*$(CO)_2RhClL$ *as well as* L'_2Ag^+ *and cis-*$(CO)_2RhClL'$*. I.r. and n.m.r. spectra allow to distinguish these complexes from the derivatives of the isomer carbene ligands,* $(R{-}NH)_2C$: *and* $(R{-}NH)(R'O)C$:.

Introduction

During our investigations on the reactivity of coordinated isocyanides[1] it was found[2] that in same cases the "carbene" ligand, obtained by nucleophilic attack of an amine, could be displaced by excess triphenylphosphine affording a formamidine, a stable isomer of a carbene, :C(NH–Ar)$_2$, *i.e.,*



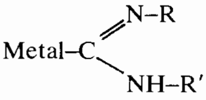
$$[\{(Ar{-}NH)_2C\}_2Au]^+ + Ph_3P = [\{(Ar{-}NH)_2C\}Au(PPh_3)]^+ + H{-}C\begin{matrix}\nearrow\!\!\!\!\!= N{-}Ar\\ \searrow NH{-}Ar\end{matrix}$$

$$(Ar = p\text{-}CH_3C_6H_4)$$

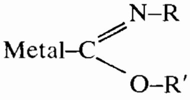
the free existence of which has not been reported[3]. Therefore it was decided to investigate whether a formamidine could yield complexes. The informations available in the literature on the donor character of formamidines and of formimidate esters[4] are very scarce, the unstable Cu(OAc)$_2$(N,N'-diarylformamidine)$_2$ being the only complex reported.[5]

A few complexes[6,7], deriving from related molecules, ReCl$_4$(N-aryl-acetamidine)$_2$ and ReCl$_4$(ethyl acetiamidate)$_2$, are known; they were obtained only indirectly by addition of an amine or alcohol on coordinated acetonitrile, but direct addition to give the adducts reported was not found possible. The same reaction[6] was also employed to prepare (C$_6$F$_5$)(CH$_3$O)C=NH complexes of platinum and iridium from C$_6$F$_5$C≡N.

In addition, C-metalated formamidine or C-metalated alkyl formimidates



$$Metal{-}C\begin{matrix}= N{-}R\\ NH{-}R'\end{matrix}$$



$$Metal{-}C\begin{matrix}= N{-}R\\ O{-}R'\end{matrix}$$

are known to be basic and donor.

Indeed sometime such molecules can form autocomplexes, *e.g.* [Au–C(OR)=NAr]$_3$[8], [Ag–C(OR)=NAr]$_3$[9], [Au–C(NHR)=NR']$_n$[10], or can be protonated[11], yielding *e.g.* [(Ph$_3$P)Au–C(OR)=NHAr]$^+$, or afford complexes[11] upon reaction with suitable acceptor species: [D$_2$Ag]$^+$, [D'Ag]$^+$, (CO)$_2$RhClD and [(CO)$_2$RhCl]$_2$D', where D is (Ph$_3$P)Au–C(OR)=NAr and D' is Hg[C(OR)=NAr]$_2$.

Here we report complexes of formamidines and formimidate esters; together with a criterium for distinguishing them from isomeric bis(alkyl- or arylamino)carbene complexes.

Experimental

The compounds were analyzed (Table I) after drying at room temperature and *ca.* 0.1 torr till constant weight. All the evaporation or concentration were carried out under reduced pressure (water aspirator). I.R. spectra were recorded on Perkin–Elmer 137 and 457 instruments and N.M.R. spectra on a Varian NEVA 60 Mc machine, the most relevant data being reported in Table II.

Ligands

N,N'-di-p-tolylformamidine

The compound was prepared from *p*-toluidine and ethyl orthoformate according to the literature[12]; it was purified by crystallization from benzene/hexane or from hot ethanol. The hydrochloride was obtained as a colourless precipitate by addition of hydrochloric acid to an acetone solution of the formamidine. The perchlorate or the tetrafluoroborate, were prepared similarly and precipitated on addition of water.

N,N'-di-p-nitrophenylformamidine

The compound was prepared from *p*-nitroaniline and ethyl orthoformate according to the literature[13]; it was purified by crystallization from nitrobenzene.

TABLE I. Analytical Data. Found % and (Calcd %).

	Compound and Colour	m.p. (°C)	C%	H%	N%	M.w[a]
I	L[e]		80.04	6.49	12.6	–
	white	141	(80.04)	(7.15)	(12.5)	
II	$[LH]^+ Cl^-$	subl. from	68.2	6.35	10.86	–
	white	200	(69.1)	(6.55)	(10.74)	
III	$[LH]^+ ClO_4^-$		55.60	5.24	8.63	–
	white	190	(55.4)	(5.24)	(8.63)	
IV	L_2CoCl_2[d]		61.94	5.52	9.71	552[b]
	blue	148	(62.3)	(5.54)	(9.67)	(578)
V	$[LH_2][CoCl_4]$	dec. from	55.26	5.26	8.52	588[c]
	turquoise	200	(55.3)	(5.22)	(8.61)	(651)
VI	$(CO)_2RhClL$	see text	49.4	3.71	6.83	450[b]
	pale yellow	114–7	(48.9)	(3.82)	(6.70)	(418)
VII	L_2ZnBr_2		53.29	4.85	8.32	695[c]
	white	161	(53.5)	(4.75)	(8.33)	(673)
VIII	L_2CdBr_2		49.27	4.53	7.62	–
	white	168	(50.0)	(4.45)	(7.78)	
IX	$L_3Cd_2Br_4$		44.32	4.11	6.81	–
	white	174	(44.5)	(3.95)	(6.91)	
X	$LHgCl_2$	dec.	36.8	3.03	5.73	–
	yellow	158	(36.3)	(3.20)	(5.66)	
XI	$[L_2Ag]^+ BF_4^-$		55.98	5.00	8.79	–
	white	152	(56.0)	(4.99)	(8.72)	
XII	L_2AgNO_3	see text	58.06	5.11	11.24	623[c]
	white	157	(58.3)	(5.17)	(11.3)	(618)
XIII	L′[e]	113 b.p.	–	–	8.70	–
	colourless	at *ca.* 20 mmHg			(8.6)	
XIV	$[L'_2Ag]BF_4$	dec	46.30	5.00	5.36	558[c]
	white	104	(46.2)	(4.99)	(5.39)	(521)
XV	$(CO)_2RhClL'$	dec	40.68	3.73	3.88	394[c]
	pale yellow	106–7	(40.3)	(3.65)	(3.93)	(357.5)
XVI	L″[e]		54.89	3.48	19.82	–
	yellow	231	(54.6)	(3.48)	(19.6)	

[a] Found by osmometry at 37° C. [b] In benzene. [c] In chloroform. [d] Cobalt: 10.1 (10.2); chlorine 12.55 (12.25). [e] L is $HC(=NC_6H_4\text{-}p\text{-}Me)(NH\text{-}C_6H_4\text{-}p\text{-}Me)$; L′ is $HC(=NC_6H_4\text{-}p\text{-}Me)(OEt)$; L″ is $HC(=NC_6H_4\text{-}p\text{-}NO_2)(NH\text{-}C_6H_4\text{-}p\text{-}NO_2)$.

Ethyl N-p-tolylformimidate

It was prepared according to the literature[14], and purified by distillation, and kept at –80° C. Its purity was checked by nmr immediately before use.

Complexes of Ethyl N-p-tolylformimidate

Bis(ethyl N-p-tolylformimidate)silver(I) tetrafluoroborate

A stirred benzene suspension of silver(I) fluoroborate (218 mg; 1.12 m*M*) was treated with ethyl N-*p*-tolylformimidate (0.40 ml; 365 mg; 2.24 m*M*). The white precipitate (511 mg) was filtered, washed with ether, and crystallised immediately from CH_2Cl_2/Et_2O. The compound can be stored a few days *in vacuo* while it becomes coloured after a few hours in the air; it melts at 120° C after a decomposition at *ca.* 104° C. Conductance (acetone, 20° C, 1.1×10^{-3} molar): 154 ohm^{-1} cm^2 mol^{-1}. If the colourless compound is allowed to stand three days it becomes red.

Cis-dicarbonyl(ethyl N-p-tolylformimidate) chlororhodium(I)

The formimidate (0.22 ml; 200 mg; 1.23 m*M*) was added to a petroleum ether solution (50 ml) of tetracarbonyl-*μ*-dichloro-dirhodium(I) (220 mg; 0.567 m*M*). The yellow precipitate which formed immediately was filtered and washed with the same solvent (360 mg; 87%); it is a non-electrolyte in acetone.

Complexes of N,N′-di-p-tolylformamidine

Bis(N,N′-di-p-tolylformamidine)silver(I) tetrafluoroborate

The amidine (485 mg; 2.17 m*M*) was added to a stirred benzene suspension of silver(I) tetrafluoroborate (211 mg; 1.08 m*M*).

The white precipitate was stirred for 20 min, filtered (551 mg) and crystallized from CH_2Cl_2/petroleum ether to yield the compound (438 mg; 0.68 m*M*; 63%), soluble in $CHCl_3$ and acetone, insoluble in diethyl

TABLE II. Spectral and Other Data.

Compound	IR	UV[a]	NMR[c]
I	C_6H_{12}: 1667s, 1650sh Nujol: 3300–3100m, unresolved; 1660br, 1610s, 1585s	285 (19,500) 307 (16,500)	$CDCl_3$: 7.67s Me; 3.19–2.75m Ar; 1.89s CH[b]
II	Nujol: 3340w, 3180w, 3130m, 3080m; *ca.* 1695vs,br, 1612m, 1590w	286(15,400) 310.5(16,700)	–
III	Nujol: 3260m, 3210m, 3150m; 1695vs,br	–	$CDCl_3$: 7.69s Me; 2.87–2.42 Ar; 0.89t(J = 13); –1.08s broad[d]
IV	$CHCl_3$: 3180w; 1645s, 1600m, 1590m Nujol: 3200m, 3180m, 3100w; *ca.* 1645vs, 1605s, 1590s; 321m, 283m, (Co–Cl)	281(47,900),296sh(32,000) 308sh, 592sh(500) 632(750)	paramagnetic
V	Nujol: 3230m, 3170m, 3120m, 3100m; 1690s, 1610m, 1590w; 370s, 342m (Co–Cl)	596sh(197),632sh(322), 673(428)	paramagnetic
VI	$CHCl_3$: 2075s, 2005s; 1645s, 1603m. Nujol: 3230m, 2075s, 2055sh, 2005s, 1945w, 1915w; *ca.* 1650vs, 1610m, 1590m; 300m (Rh–Cl)	275(22,600) 304(18,200)	$CDCl_3$: 7.67s Me; 2.87s Ar; 2.04s CH; *ca.* 1.2 (40 cps, broad)
VII	$CHCl_3$: 3180w; 1640s, 1598m Nujol: 3190m, 3100w; 1640s,br, 1605m; 1590m	284.5(37,100) 304(33,700)	$CDCl_3$: 7.71s Me; 3.04q Ar; 2.13s CH; *ca.* –0.16 (30 cps, br) NH
VIII	Nujol: 3210m, 3100w, 1665sh, 1645s, 1610m, 1595m	–	–
IX	Nujol: 3230w, 3200m, 3100w, 1688s, 1662w, 1642s, 1610w, 1590m	–	–
X	Nujol: 3290w, 3200m, 3100w; 1690w, 1645s, 1590m	285(17,500) 308(17,200)	$(CD_3)_2CO$: 7.67s Me; 2.75s Ar; 1.22s CH;
XI	$CHCl_3$: 3300m; 1648s, 1603s, 1590s Nujol: 3330m; *ca.* 1650vs,br, 1610s, 1590s	285(42,000) *ca.* 305(35,000)	$CDCl_3$: 7.69s Me, 2.93s Ar; 1.93 CH, C_6D_6: 7.94s Me; 2.85s Ar; 2.4s CH[b]
XII	$CHCl_3$: 3170w; 1660s, 1605m, 1593m Nujol: 3200m, 3100w; *ca.* 1650vs,br, 1610s, 1590s	287(23,000) 308(21,150)	$CDCl_3$: 7.73s Me; 3.0s Ar; 1.95s CH[b]
XIII	Film: *ca.* 1650vs, br	–	CCl_4: 8.74t,(J 7 cps) Me; 7.75s Me; 5.75q CH_2; 3.42–2.97q Ar; 2.47s CH
XIV	Nujol: 1648vs,br, 1610s	–	$CDCl_3$: 8.59t Me; 7.72s Me; 5.45q CH_2; 2.84s Ar; 1.95s and 1.66s CH
XV	$CHCl_3$: 2080s, 2015s; 1640s, 1605m Nujol: 2080s, 2000vs, 1950sh; 1640vs, 1605s	–	8.82t, 8.49t Me; 7.62s*p*-Me; 5.74q, 5.55q CH_2; 2.95s, 2.90s Ar; 2.29s, 2.09s CH[b]

[a] In $CHCl_3$. [b] No NH signal was detected. [c] s = singlet, t = triplet, q = quartet, m = multiplet; coupling constant of ethyl group was *ca.* 7 cps. [d] NH, it disappeared on deuteratiom with D_2O.

ether. The compound is light-sensitive and cannot be stored undecomposed. Electrical conductance (1.2 and 0.6 × 10^{-3} molar acetone solution at 25 °C): 144 and 156 ohm^{-1} cm^2 mol^{-1}, respectively.

Bis(N,N'-di-p-tolylformamidine)(nitrato)silver(I)

To a stirred suspension of $(CH_3)_2S \cdot AgNO_3$ (352 mg; 1.52 m*M*) in benzene (150 ml) the amidine (365 mg; 1.63 m*M*) in the same solvent (50 ml) was added. After 45 min the suspension was filtered and the residue was washed with benzene. The combined solutions were concentrated and the white precipitate was filtered (488 mg; 0.79 m*M*; 52%) and crystallised from benzene/ether. The compound is soluble in benzene, CH_2Cl_2, $CHCl_3$, CH_3NO_2 and acetone; on heating the sample becomes grey at *ca.* 85 °C and melts with decomposition at 157 °C. Electrical conductance (1.2 × 10^{-3} molar acetone solution at 21 °C): 13.5 ohm^{-1} cm^2 mol^{-1}.

Bis(N,N'-di-p-tolylformamidine)dibromozinc(II)

The amidine (680 mg; 3.0 m*M*) was dissolved in ether (60 ml) and added to a stirred suspension of $ZnBr_2 \cdot 4H_2O$ (473 mg; 1.60 m*M*) in the same solvent. After stirring for 10 min the resulting solution was concentrated to a small volume and the colourless precipitate was crystallised from ether to yield the compound (413 mg; 0.61 m*M*; 40%), soluble in CH_2Cl_2, $CHCl_3$, and acetone, insoluble in benzene. It could be crystallised from acetone/ether. Electrical conductance (9.6×10^{-4} molar nitromethane solution at 21 °C): 37.1 $ohm^{-1}\ cm^2\ mol^{-1}$.

Bis(N,N'-di-p-tolylformamidine)dibromocadmium (II)

An acetone solution of the amidine (400 mg; 1.78 m*M*) was added to $CdBr_2 \cdot 4H_2O$ (289 mg; 0.84 m*M*) partially dissolved in the same solvent. After filtration and addition of petroleum ether the solution was concentrated to a small volume; upon addition of more petroleum ether and scratching a dirty-white solid precipitated. After an unsuccessfull attempt to crystallize it from CH_2Cl_2/petroleum ether, the precipitate was dissolved in CH_2Cl_2 and diethyl ether was added. Upon vacuum concentration a crystalline compound separated, which analyzed as $L_3Cd_2Br_4$. On further concentration a white crystalline solid separated, which was crystallised again from the same solvent to yield L_2CdBr_2. Both compounds were obtained in low yield (*ca.* < 50 mg) and are non-electrolytes in nitromethane and in acetone, respectively.

(N,N'-di-p-tolylformamidine)dichloromercury(II)

(A) An ether (70 ml) suspension of the amidine (1.61 g; 7.2 m*M*) was added to an ether solution (30 ml) of mercury(II) chloride (1.01 g; 3.6 m*M*). The yellow precipitate which formed immediately was stirred for 20 min and filtered (1.56 g; 87%); on concentration of the mother liquor, colourless unreacted amidine was recovered (0.77 g).

The yellow compound was crystallised twice by concentration of the acetone solution (100 ml) in the presence of diethyl ether.

(B) An ethereal solution of ethyl *N*-*p*-tolylformimidate (1.2 ml; 1.09 g; 6.7 m*M*) was added to an ethereal solution (30 ml) of mercury(II) chloride (827 mg; 3.05 m*M*). After *ca.* 2 hr additional ethyl *N*-p-tolylformimidate was added, and the clear solution was evaporated to dryness. Additional ethyl *N*-p-tolylformimidate (1.0 ml) and ether (100 ml) were added; after stirring for 0.5 hr the suspension was evaporated to dryness and the residue was stirred under petroleum ether. The white powder (1.04 g) was filtered; its ir spectrum showed C–O–Et absorption at *ca.* 1030 cm^{-1} and other bands which all disappeared after crystallization from CH_2Cl_2/petroleum ether (or from much diethyl ether). The compound was identified as (*N,N'*-di-*p*-tolylformamidine)dichloromercury(II) by C, H, N analysis, m.p. and infrared spectrum.

Bis(N,N'-di-p-tolylformamidine)dichlorocobalt(II) and N,N'-di-p-tolylformamidinium tetrachloro-cobaltate(II)

(A) An acetone solution of $CoCl_2 \cdot 6H_2O$ (830 mg; 3.5 m*M*) and of the amidine (1.560 g; 6.96 m*M*) was concentrated under vacuum. Petroleum ether was added and the pale green precipitate was removed. On evaporating to dryness a sticky greenish product was obtained; this was stirred under petroleum ether to yield a blue powder (1.196 g), which was crystallized by concentration of the ethereal solution; another crystallization afforded the analytical sample of L_2CoCl_2. The compound is a non-electrolyte in acetone; it has a magnetic moment of 4.7 B.M. (the value of diamagnetic correction was calculated according to the literature) in the solid state at 300 °K and is paramagnetic in $CDCl_3$ solution.

(B) The pale green precipitate removed from the solution (see A) was washed with diethyl ether till colourless washings (532 mg); it was then crystallized twice from CH_2Cl_2/Et_2O, to yield the turquoise green $[LH]_2[CoCl_4]$ insoluble in benzene. Conductance: (acetone, 25 °C, 0.91×10^{-3} molar), (nitromethane, 25 °C, 1.0×10^{-3} molar) 92 and 73 $ohm^{-1}\ cm^2\ mol^{-1}$ respectively.

(C) $[LH]_2[CoCl_4]$ could be obtained also by treatment of L_2CoCl_2 with dry hydrogen chloride in dichloromethane. It was identified by ir spectrum, dec. point and analysis.

Dicarbonyl(N,N'-di-p-tolylformamidine) chlororhodium(I)

A saturated petroleum ether solution of tetracarbonyl-μ-dichloro-dirhodium(I) (292 mg; 0.73 m*M*) was mixed with a solution of the amidine (347 mg; 1.55 m*M*) in the same solvent (50 ml). A yellow precipitate (340 mg; 0.81 m*M*; 56%) formed nearly immediately and was filtered after 10 min; upon concentration of the mother liquor a brown product separated which was not investigated. Electrical conductance (1.4×10^{-3} molar acetone solution, 21 °C): 6.1 $ohm^{-1}\ cm^2\ mol^{-1}$.

Results

N,N'-Diarylformamidines as Ligands

Two N,N'-diarylformamidines were prepared and investigated, *i.e.* H–C(=NAr)(NH–Ar) where Ar was *p*-nitrophenyl or *p*-tolyl. The *p*-nitro compound having two strong electron withdrawing groups, was found to be quite unsuitable as a ligand because attempts with cadmium bromide, zinc bromide, cobalt chloride, $[(CO)_2RhCl]_2$ or silver fluoroborate afforded no complex derivative. On the other hand the *p*-tolyl compound (L) was more suitable and gave all the complexes reported in the table, *i.e.* with elements of the I, II and VIII group of the periodic system. They were identified through chemical analyses, molecular weight determinations, spectral evidence, conductance data and, in the case of the cobalt complex, through magnetism. In the same conditions other reactions were tried unsuccessfully with many halides of the first row transition metals, with Na_2PtCl_6, Na_2PtCl_4 and with Me_2SAuCl. In the last case the compound could not be purified, even after addition of a perchlorate or of a tetrafluoroborate ion at various ligand/gold ratios. No attempts were carried out with other transition metal perchlorates or fluoroborates.

In the case of the halides of the first row transition elements the crude reaction product gave diarylformamidinium hydrochloride upon purification. In one case a polyhalometallate $[LH]_2[CoCl_4]$ was isolated amongst the by-products of the reaction leading to L_2CoCl_2. The identity of the compound was supported also by the reaction of hydrogen chloride with the covalent cobalt complex:

$$L_2CoCl_2 + 2\,HCl = [LH]_2[CoCl_4]$$

Infrared Spectra

The ligand showed the required absorptions: amongst them a medium and broad band in the 3300–3100 cm^{-1} region and a strong band at *ca.* 1600 cm^{-1} are due to the stretching and bending of N–H, a very strong and rather broad band at 1660 cm^{-1} is due to the C=N stretching. These bands were found also in the metal complexes, but the $\nu(C{=}N)$ was displaced to lower wavenumber (*ca.* 1640–1650 cm^{-1}, very strong and broad), as required by complex formation. The same $\nu(C{=}N)$ was displaced to higher wavenumber (*ca.* 1695 cm^{-1}) when the nitrogen atom was protonated, as in the formamidinium chloride, perchlorate or tetrachlorocobaltate(II). In any case the $\nu(C{=}N)$ absorption was found in a range (1640–1695 cm^{-1}) which is quite different from that ($\leqq$ 1600 cm^{-1}) where the isomeric carbene ligands absorb, owing to the contribution of the canonical form $Ar{-}\overset{\oplus}{N}H{=}\overset{\ominus}{C}{-}NH{-}Ar$.

Two additional bands were found in the 2000 cm^{-1} region in the case of $(CO)_2RhClL$, in agreement with a *cis* configuration. They are in the same position as those found in other analogous complexes where L is a good σ-donor, such as amines or nitriles[15].

NMR Spectra

They support the formulae assigned. Although isomers are possible in principle, they were not detected in the spectra recorded. The *p*-tolyl protons are rather insensitive to change in the molecule, while the formyl hydrogen was found at rather different chemical shifts (from τ 1.89 to 2.13) in the same solvent, thus showing that the position attached to the formyl carbon atom is rather sensitive to environmental change. Investigations by ^{13}C NMR (chemical shift and heteronuclear coupling constants) on those compounds where a metal is attached to that carbon atom might be interesting, but are not possible now.

Electronic spectra

The electronic spectra of the complexes showed two strong bands in the ultraviolet region as in the ligand. In addition the cobalt compounds showed absorption in the visible part of the spectrum. In the ionic, turquoise-blue, derivative there is a band at 673 nm (with a shoulder at 632 nm) due to the $^4A_2 \rightarrow {}^4T_1(P)$ transition of the tetrachlorocobaltate(II) anion. In the covalent blue, cobalt derivative, L_2CoCl_2, the position and the intensity of the band (632 nm, $\varepsilon = 750$) suggest a tetrahedral arrangement of the ligands, in agreement also with the value of the magnetic moment (4.7 B.M.) at room temperature.

The combined available evidence suggest that zinc, cadmium, mercury and cobalt(II) complexes have a tetrahedral arrangement of ligand around the metal atom. The rhodium(I) complexes is square planar, the silver(I) complexes are likely to be linear, while no suggestion can be made now for the binuclear cadmium complex isolated as a by-product. The formamidine does not seem to be very powerful ligand; its basic nitrogen atom is protonated rather easily affording, in many cases, an ionic derivative instead of a metal complex.

Ethyl N-p-tolylformidate as Ligand

In order to see whether the formimidate esters can be ligands, we chose an ethyl N-arylformimidate as reagent. Indeed, if this term gives complexes, an N-alkyl homologue will also be a ligand, probably a better σ-donor ligand. Besides, an N-*p*-tolyl group was chosen, because the *p*-methyl protons are easily detected by NMR.

The $HC(OEt){=}NC_7H_7$ ligand, L′, reacted with silver(I) tetrafluoroborate and with tetracarbonyl-μ-dichloro-dirhodium(I) affording $[L'_2Ag]BF_4$ and *cis*-$(CO)_2RhClL'$ in good yields. The formulae were established through elemental analyses, molecular weight determinations, and spectral evidence on freshly prepared samples. During attempts to obtain other complexes with cobalt(II) chloride or zinc(II) bromide, in the same conditions employed successfully with di(N-*p*-tolyl)formamidine (L), no product was isolated. When ethereal mercury(II) chloride was reacted with L′ the crude product showed the infrared spectrum required by a coordinated formimidate, but, upon crystallization, the complex changed and the formamidine complex, $LHgCl_2$, was isolated in place of the expected formimidate complex, $L'HgCl_2$.

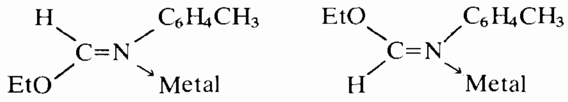
The reaction gives additional evidence for the instability of the complexes of L′ and is in agreement with the existence of the equilibrium

$$HC(OR){=}NR' + H_2N{-}R' \leftrightarrows R{-}OH + HC(NH{-}R'){=}NR'$$

The amine involved in the above equilibrium may come from *in situ* decomposition of the formimidate; although the sample used was stored at −80° C and was found to be pure according to its NMR spectrum carried out before the reaction.

The infrared spectra showed all the absorptions required by the formimidate and by the other moieties composing the complex. The $\nu(C=N)$ of the coordinated formimidates was observed at *ca.* 1640 cm^{-1}, *i.e.* at a lower value than in the free ligand (1650 cm^{-1}), as expected. In the silver salt the B–F vibrations due to the fluoroborate anion were in agreement with tetrahedral coordination around the boron atom. In the rhodium derivative two $\nu(CO)$ vibrations were found, as required by a *cis* arrangement, at value which are typical of analogous complexes with other nitrogen ligands[15].

Although the NMR spectrum of the ligand in CCl_4 solution did not show the presence of isomers, more signals than expected for a single isomer were found in the spectra ($CDCl_3$ solution) of the two metal complexes. In the case of the $[AgL'_2]^+$ ion two singlets (τ 1.95 and 1.66; relative area *ca.* 3 : 10) were observed and assigned to the formyl hydrogen. In the case of $(CO)_2RhClL'$ not only the formyl hydrogen gave two singlets (τ 2.29 and 2.09; *ca.* 1 : 1), but also the ethyl protons gave two triplets and two quartets (each *ca.* 1 : 1), while the *p*-CH_3 group gave only one signal in both complexes. All these data suggest that two geometric isomers are present in the solutions:



of all the protons in the molecule the formyl proton, which is located right on the double bond, is the most sensitive to the change of environment around such a bond. On the other hand the *p*-methyl group, which contains the protons most remoted from the double bond, is not affected by the change (singlet at τ 7.72 and 7.62 for the Ag and Rh complex respectively). The ethoxy group is at an intermediate stage: two triplets at τ 8.82 and 8.49 and two quartets at τ 5.74 and 5.55 for the rhodium complex and one triplet plus one quartet at τ 8.59 and 5.45 for the silver salt (J being always *ca.* 7 cps).

An alternate explanation might be possible for the NMR spectra observed: the complexes might dissociate in solution, as follows:

$$[AgL'_2]^+ \leftrightarrows [AgL']^+ + L'$$
$$(CO)_2RhClL' \leftrightarrows 1/2\,[(CO)_2RhCl]_2 + L'$$

Then, the NMR spectrum might show one set of signals due to the complexed molecule and another set due to the uncoordinated ligand. The chemical shifts of the signals of the last set should be roughly the same in solution of each complex. Since this was not observed, the alternate explanation cannot be accepted. This conclusion is supported also by the infrared spectrum in $CHCl_3$ solution of the rhodium complex in the $\nu(CO)$ region: there is no evidence for the additional carbonyl stretching vibrations due to the dimer, $[Rh(CO)_2Cl]_2$.

Conclusions

The N,N′-disubstituted formamidines and the N-substituted alkyl formimidates are nitrogen donor molecules, if the N-substituents are not very strong electron withdrawing groups (*e.g.* *p*-NO_2–C_6H_4). They afford complexes, which are stable enough to be stored only in the case of the formamidines, but not in the case of $HC(OEt)=N–Ar$. Although both ligands might be able to give isomers, these were found only in the case of the formimidate complexes.

The spectral evidence allows formamidine or formimidate complexes to be distinguished from the derivatives of isomeric bis(alkylamino) or (alkylamino)(alkoxy)carbene ligands: (a) $\nu(C=N)$ in the former type of complexes is found at values higher than 1600 cm^{-1} (generally *ca.* 1640 cm^{-1}); (b) $\nu(C=N)$ in the carbene-type ligands is found generally at values not higher than *ca.* 1600 cm^{-1}; (c) in addition, in the case of $H–C(OR)=NAr$ complexes only, they do not show any N–H absorption while $:C(OR)(NH–Ar)$ derivatives do. Additional, but not decisive, support may come from the NMR spectra: the presence of a formyl proton excludes a carbene-type ligand. But, since this single proton may be found in a rather large zone of the spectrum where also the NH protons of carbene ligands appear, the corresponding signal may not be immediately detected or assigned.

Acknowledgements

Financial support by C.N.R. is acknowledged.

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