Journal of Organometallic Chemistry, 179 (1979) 89—100

COMPLEXES OF *N,N'*-SUBSTITUTED FORMAMIDINES

I. COMPOUNDS $[M(RNC(H)NR')]_n$ (M = Cu^I, Ag^I; R = *p*-TOLYL; R' = ALKYL; *n* = 2,4); AND STUDY OF THE DIMER—DIMER AND DIMER—TETRAMER EQUILIBRIA IN SOLUTION

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(Received April 24th, 1979)

Summary

A series of complexes $[M(RNC(H)NR']_n$ (M = Cu^I, Ag^I; R = *p*-tolyl; R' = methyl, ethyl, i-propyl, t-butyl, cyclohexyl; *n* = 2,4) has been prepared. ^1H and ^{13}C NMR studies, as a function of temperature, concentration, metal atom and alkyl substituent, show the presence of dimeric and tetrameric isomers. Starting with the two possible dimers it requires only one metal—nitrogen bond in each dimer to be broken and two new metal—nitrogen bonds to be formed to give four tetrameric isomers. These studies show that; (i) the dimer/tetramer ratio increases at higher temperatures; (ii) the size of the alkyl substituents determines the relative ratio of the tetramers; (iii) the dimer/tetramer ratio increases with increasing bulkiness of the alkyl substitutents, and (iv) the dimer/tetramer ratio increases when Ag^I is replaced by Cu^I.

Introduction

In recent years much attention has been focussed on the chemistry and structural characteristics of triazenido- and amidino-metal compounds. In the triazenido compounds the triazenido group usually acts as a bridging ligand [1—7] or as a chelating ligand [7—10]. In some cases a chelating acyltriazenido group is formed by insertion of a CO group into a metal—nitrogen bond [6,7,13]. Much less is known about metal amidino complexes. Among the compounds reported in the literature the amidino ligand also acts mainly as a bridging ligand [15—19] or as a chelating ligand [17,20,21], and the amidino ligand is

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converted into a carbamoyl group by CO insertion into the metal—nitrogen bond [20—23]. Part of our research deals with IrM and RhM (M = Cu, Ag) triazenido compounds in which the metal-to-metal bond is stabilized by a bridging triazenido group [6]. At present we are attempting to prepare the analogous Ir^I (Rh^I) to Cu^I (Ag^I) bonded amidino complexes [24]. The amidino ligands RNC(H)NR′ are unsymmetrically substituted, and this, in principle, makes possible a studies of the influence of the electronic and steric properties of the N-substituents and the type of N—M bonds formed in the mixed metal dimers. It will be shown that even in these homo oligomeric amidino metal complexes the electronic and steric properties of the N-substituents determine the nature of the aggregates present in solution. In this article we present the preparation, structural, stereochemical and chemical properties of a number of Cu^I and Ag^I amidino complexes which are the starting materials for the preparation of the mixed amidino-metal compounds.

Experimental

Preparation of N-p-tolyl-N′-alkylformamidines, HRNC(H)NR′ (R = p-tolyl; R′ = methyl, ethyl, iso-propyl, t-butyl, cyclohexyl)

The preparation of *N*-aryl-*N*′-t-butylformamidine has been described before [20] but a better route, which leads to an almost quantitative yield, is reported here.

A flask containing ethyl-*N*-*p*-tolyl-formamidate (0.5 mol) and catalytic amounts of acetic acid (1 ml) and ethylorthoformate (1 ml) was fitted with a reflux condensor and heated to 165°C, and the alkylamine was introduced. In the case of methylamine or ethylamine a rapid stream of gas was passed through the mixture while in the case of isopropyl-, t-butyl- or cyclohexyl-amine 0.55 mol of the amine was added dropwise during 10 min. The mixture was then refluxed at 165°C for 30 min to one hour, depending on the alkylamine used. When the formamidate was completely converted into the formamidine (as checked by ^{1}H NMR) the ethanol was distilled off. The residue was dissolved in hexane. White crystals were obtained on cooling the hexane solution to —30°C (90% yield).

Preparation of the Cu and Ag formamidines $[M(RNC(H)NR')]_n$ (R = p-tolyl; R = methyl, ethyl, isopropyl, t-butyl, cyclohexyl; M = Cu^I, Ag^I)

To a solution of $AgNO_3$ or CuCl (30 mmol) in 25% NH_4OH (35 ml) was added a solution of the formamidine (30 mmol) in ethanol (50 ml) with rapid stirring, and a solution of KOH (33 mmol) in ethanol (50 ml) and water (25 ml) was added dropwise during 20 min. After completion of the reaction vigorous stirring was continued for 10 min, and the crude product was filtered off and dried in vacuo. The product was dissolved in dry CH_2Cl_2, and after filtration, concentration, and addition of hexane, white microcrystals were obtained at —30°C in 60—90% yield.

Reactions of $[M(RNC(H)NR')]_n$ with L (L = CO, MeNC, $C_6H_{11}NC$, Ph_3P, $Ph_2P(CH_2)_2PPh_2$)

Mixtures of these compounds in CH_2Cl_2 did not give any observable reaction (checked by ^{1}H NMR).

TABLE 1

ANALYTICAL DATA

Compound [a]	Mol. wt. [b] (found (calcd.))	Analysis (found (calcd.)(%))		
		C	H	N
HMpTF		72.54 (72.94)	8.27 (8.16)	18.98 (18.19)
HEpTF		73.71 (74.03)	8.69 (8.70)	17.41 (17.27)
HiPpTF		74.70 (74.96)	9.10 (9.15)	15.77 (15.89)
HtBpTF		75.56 (75.74)	9.47 (9.53)	14.52 (14.72)
HcHpTF		77.45 (77.78)	9.33 (9.26)	13.06 (12.96)
CuEpTF	668 (225)	53.63 (53.44)	5.99 (5.83)	12.61 (12.46)
CuiPpTF	457 (239)	55.26 (55.33)	6.38 (6.33)	11.70 (11.73)
CutBpTF	490 (253)	56.67 (57.01)	6.75 (6.78)	11.44 (11.08)
CucHpTF	531 (279)	59.98 (60.33)	6.98 (6.82)	10.22 (10.05)
AgMpTF	814 (255)	43.83 (42.38)	4.86 (4.35)	10.89 (10.98)
AgEpTF	880 (269)	44.78 (44.63)	5.00 (4.87)	10.35 (10.41)
AgiPpTF	567 (283)	46.46 (46.66)	5.24 (5.34)	9.95 (9.89)
AgtBpTF	571 (297)	48.75 (48.50)	5.84 (5.77)	9.73 (9.43)
AgcHpTF	604 (324)	51.66 (51.89)	5.96 (6.18)	8.94 (8.64)

[a] MpTF = methyl-*p*-tolylformamidine; EpTF = ethyl-*p*-tolylformamidine; iPpTF = isopropyl-*p*-tolylformamidine; tBpTF = *t*-butyl-*p*-tolylformamidine; cHpTF = cyclohexyl-*p*-tolylformamidine. [b] The solvent was CH_2Cl_2 (at 26.3°C); concentrations were about 0.04 *M* and the experimental error is ±10%.

Reactions of the formamidino copper and silver compounds with triazenes were studied in ^{1}H NMR experiments.

^{1}H NMR spectra were recorded on a A60-D and HA-100 Varian spectrometer and ^{13}C NMR spectra were recorded on a WP 80 Bruker spectrometer. Molecular weights were measured with a Hewlett Packard vapour pressure osmometer Mode 320 B. Microanalyses were carried out at the Organic Laboratory of the T.N.O. in Utrect (Table 1).

Results and discussions

Formamidino compounds of the composition $[M(RNC(H)NR')]_n$ (M = Cu^I, Ag^I; R = *p*-tolyl; R' = methyl, ethyl, isopropyl, t-butyl, cyclohexyl) were prepared by treatment of strongly basic solutions of the appropriate formamidine with CuCl and $AgNO_3$. Molecular weight measurements (Table 1) indicate the presence in solution of both dimers, probably analogous to $[Cu(PhN_3Ph)]_2$ [2], and tetramers, analogous to $[Cu(MeN_3Me)]_4$ [3]. The compounds are remarkably

stable towards CO, RNC, Ph_3P and $Ph_2P(CH_2)_2PPh_2$. The formamidino groups may, however, be replaced by triazenido groups by treating the complexes with triazenes such as $HMeN_3$-*p*-tolyl and H-*p*-tolyl-N_3-*p*-tolyl. The reactivity of the complexes towards ligand exchange with triazenes decreased with increasing size of the alkyl substituent on the formamidino ligand.

We directed our attention to the structural and dynamic characteristics about which, even for the related triazenido compounds, nothing is known. The use of unsymmetric formamidino ligands provided us with an opportunity to gain greater insight into these systems. For the unsymmetric formamidines one may expect, in the case of the dimeric compounds, two geometrical isomers, i.e. IA (a = c = alkyl; b = d = *p*-tolyl) and IB (a = d = alkyl; c = b = *p*-tolyl) (Fig. 1). Combination of these two dimeric forms results in the formation of four different tetrameric isomers. If, for example the tetramers are assumed to be directly formed from the dimers, the occurrence of the following five equilibria can be postulated.

$$\mathrm{IA} + \mathrm{IA} \overset{(1)}{\rightleftharpoons} \mathrm{IIAA} \begin{bmatrix} 1 = 3 = 6 = 8 = \text{alkyl} \\ 2 = 4 = 5 = 7 = p\text{-tolyl} \end{bmatrix}$$

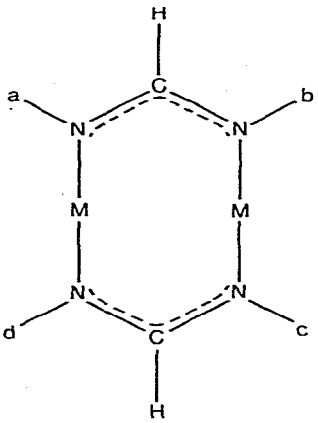
$$\mathrm{IA} + \mathrm{IB} \overset{(2)}{\rightleftharpoons} \mathrm{IIBB} \begin{bmatrix} 1 = 2 = 5 = 8 = \text{alkyl} \\ 3 = 4 = 6 = 7 = p\text{-tolyl} \end{bmatrix}$$

$$\mathrm{IB} + \mathrm{IB} \overset{(3)}{\rightleftharpoons} \mathrm{IIA'A'} \begin{bmatrix} 1 = 3 = 5 = 7 = \text{alkyl} \\ 2 = 4 = 6 = 8 = p\text{-tolyl} \end{bmatrix}$$

$$\mathrm{IA} + \mathrm{IB} \overset{(4)}{\rightleftharpoons} \mathrm{IIAB} \begin{bmatrix} 1 = 2 = 5 = 7 = \text{alkyl} \\ 3 = 4 = 6 = 8 = p\text{-tolyl} \end{bmatrix}$$

In Fig. 2 the various tetrameric forms are shown. The isomers IIAA and IIA′A′ each contain four equivalent formamidines. The isomer IIBB possesses two pairs of equivalent formamidines, while IIAB has four inequivalent formamidines. Models show that for the tetramers to form it is sufficient that the two reacting dimers each undergo breaking of one metal—nitrogen bond, after which the dimers can combine to give a tetramer by forming two new metal—nitrogen bonds. The type of tetrameric isomer formed depends on which metal—nitrogen bonds are broken and which metal—nitrogen bonds are formed. The situation in this case is relatively simple, since IIAA, IIA′A′ and IIAB can only be formed in one way i.e. from two molecules of IA, two molecules of IB and from one molecule of IA and one molecule of IB, respectively. In contrast, IIBB can be formed by combining two molecules of IA or two molecules of IB. The same tetrameric isomers may in principle be formed by starting with the monomers. Since a reaction of four monomers seems highly unlikely, and since no evidence was found for the existence of such monomers we can assume that the tetramers are formed by a binuclear reaction of two dimers. Furthermore, examination of models indicates that the isomer IA should be slightly more stable than isomer IB, while IIAA and IIA′A′ should be much more stable than IIAB and IIBB, in that order. This is in particular so for large alkyl substituents.

Detailed information about the structural and dynamic characteristics was ob-



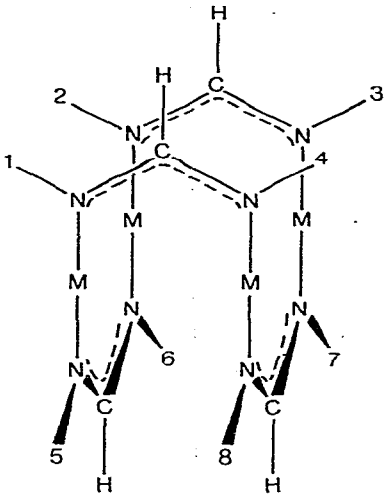


Fig. 1. Structure for the dimers $[M(RNC(H)NR')]_2$. IA, a = c = alkyl; b = d = *p*-tolyl, IB, a = d = alkyl; c = b = *p*-tolyl.

Fig. 2. Structure for the tetramers $[M(RNC(H)NR')]_4$. IIAA, 1 = 3 = 6 = 8 = alkyl; 2 = 4 = 5 = 7 = *p*-tolyl; IIA'A', 1 = 3 = 5 = 7 = alkyl; 2 = 4 = 6 = 8 = *p*-tolyl; IIBB, 1 = 2 = 5 = 8 = alkyl; 3 = 4 = 6 = 7 = *p*-tolyl; IIAB, 1 = 2 = 5 = 7 = alkyl; 3 = 4 = 6 = 8 = *p*-tolyl.

tained by measuring the ^{1}H NMR spectra at various concentrations in a temperature range of —80°C to +40°C. Above 40°C decomposition occurred. The relevant data are recorded in Table 2. These data were used in conjunction with ^{13}C NMR spectra. The details of ^{13}C NMR measured at —30°C, are given in Table 3.

The NMR data show that, depending on the metal atom and on the alkyl substituent, three classes of oligomer can be distinguished, viz.:

A. Solutions containing mainly the two dimers:
   copper(I)-*N*-*p*-tolyl,-*N'*-cyclohexylformamidine (CucHpTF)
   copper(I)-*N*-*p*-tolyl,-*N'*-isopropylformamidine (CuiPpTF)
   copper(I)-*N*-*p*-tolyl,-*N'*-t-butylformamidine (CutBpTF)
B. Solutions containing two dimers and two tetramers:
   silver(I)-*N*-*p*-tolyl,-*N'*-t-butylformamidine (AgtBpTF)
C. Solutions containing two dimers and more than two tetramers:
   copper(I)-*N*-*p*-tolyl,-*N'*-ethylformamidine (CuEpTF)
   silver(I)-*N*-*p*-tolyl,-*N'*-methylformamidine (AgMpTF)
   silver(I)-*N*-*p*-tolyl,-*N'*-ethylformamidine (AgEpTF)
   silver(I)-*N*-*p*-tolyl,-*N'*-isopropylformamidine (AgiPpTF)
   silver(I)-*N*-*p*-tolyl,-*N'*-cyclohexylformamidine (AgcHpTF)

A. Solutions containing mainly two dimers.

The molecular weights of CuiPpTF, CutBpTF and CucHTF measured at 26.3°C in CH_2Cl_2 show that at this temperature the dimeric forms dominate. This is confirmed by the ^{1}H NMR spectra, measured from —50°C to +40°C, which show the presence of two different isomers each with two equivalent for-

(Continued on p. 96)

TABLE 2

^{1}H NMR DATA [a]

Compound	*p*-Tolyl		CH	Alkyl		
	CH_3	aryl		CH	CH_2	CH_3
MpTF	2.21	6.73; 6.97	7.42			2.80
EpTF	2.23	6.74; 7.00	7.47		3.28q [b]	1.15t [b]
iPpTF	2.26	6.76; 7.02	7.46	3.77s [c]		1.19d [c]
tBpTF	2.27	6.77; 7.03	7.63			1.23
cHpTF	2.27	6.76; 7.02	7.49	3.51(vbr)	1.60(vbr)	
AgMpTF	2.25	6.98(br);	7.95(vbr); 7.78(vbr); 7.62(vbr)			3.27(br); 3.25(br); 3.22(br);
+30°C	2.14(br)	6.74(br);				2.95(br); 2.94(br); 2.91(br)
AgMpTF	2.27(br)	7.00(br);	8.02(br); 7.94(br); 7.85(br);			3.29(br); 3.26(br); 3.22(br);
−30°C	2.17(br); 2.14(br)	6.76(br);6.68(br)	7.79(br); 7.69(br); 7.61(br); 7.54(br)			3.00(br); 2.96(br); 2.92(br); 2.89(br)
AgEpTF	2.25(br)	6.69(br);	8.01(vbr); 7.75(vbr); 7.69(vbr)		3.34(vbr)	1.02(vbr);
0°C	2.14(br)	6.72(br)			2.99(vbr)	1.29(vbr)
AgiPpTF	2.29(br)	6.89(br); 6.72(br);	7.92(vbr); 7.82(vbr); 7.67(vbr)	3.56(vbr);		1.20(vbr);
0°C	2.13(br)	6.52(br); 6.04(br)		3.07(vbr)		0.94(vbr)
AgtBpTF	2.27(br)	6.95(br)	8.23(vbr); 8.02(vbr)			1.34(vbr);
+30°C		6.82(vbr)				1.13(vbr)
AgtBpTF	2.28(br)	6.97(br);	8.10(vbr); 7.94(vbr); 7.77(vbr)			1.36; 1.32; 1.10; 1.01
−30°C	2.20(br)	6.75(br)				
AgCHpTF	2.28(br)	6.98(br); 6.69(br)	8.08(vbr); 7.83(vbr); 7.60(vbr)	2.73(vbr)	1.59(vbr);	
0°C					1.17(vbr)	
CuEpTF	2.28(br)	7.03(br); 6.78(br);	7.89(vbr); 7.76(vbr); 7.56(vbr)		3.31(vbr)	1.29(vbr);
0°C	2.14(br)	6.70(br)			2.91(vbr)	1.16(vbr)
CuIPpTF	2.27	6.97(br)	7.97; 7.95	3.42s [d]		1.22d [d];
0°C						1.21d [d]
CutBpTF	2.28	6.92; 7.03	8.02; 7.98			1.34;
0°C						1.32
CucHpTF	2.28	7.96	7.94; 7.91	2.93(vbr)	1.73(vbr);	
0°C	2.14				1.31(vbr)	

[a] In $CDCl_3$; ppm relative to TMS. [b] *J* 7 Hz. [c] *J* 7 Hz. [d] *J* 7 Hz.

TABLE 3

^{13}C NMR DATA [a]

Compound	p-Tolyl [b]					CH	Alkyl [c]			
	CH_3	C(1)	C(2)	C(3)	C(4)		C(1)	C(2)	(C3)	C(4)
MpTF	20.30	148.94	120.59	129.33	131.61	151.18	28.20			
EpTF	20.34	148.90	120.49	129.33	131.61	150.79	37.24	15.05		
iPpTF	20.39	148.80	120.54	129.38	131.61	150.16	44.36	23.20		
tBpTF	20.39	148.75	120.59	129.43	131.76	150.16	50.34	30.34		
cHpTF	20.43	148.94	120.54	129.38	131.66	150.21	51.65	33.74	24.56	25.29
AgMpTF	20.36	149.38(br)	119.78(br)	129.05(br)	129.72(br); 129.39(br)	161.92(br)	44.92(br)			
AgEpTF	20.48	149.28(br); 148.70(br)	120.69(br)	129.33	130.58 129.04	162.78(br); 162.39(br)	49.90(br)	19.80; 19.46		
AgiPpTF	20.43	149.72(br); 149.28; 148.89	121.22(br)	129.36(br)	129.14(br)	161.81(br)	54.71(br); 54.32(br)	27.56(br); 27.18(br); 26.21(br); 25.87(br)		
AgtBTF	20.43	150.45(br); 150.11(br)	121.13(br); 120.64; 120.30	129.18(br)	129.62(br)	162.39(br); 160.45(br); 159.96(br); 159.53(br)	54.61(br);	33.45; 33.25; 32.72; 32.43		
AgcHpTF	20.44	149.96(br)	121.32(br)	129.14(br)	129.96(br)	161.42(br)	62.53(br); 62.19(br)	37.96(br); 37.33(br)	25.14(br)	25.73(br)
CuEpTF	20.34	148.46; 147.78(br)	120.59(br); 120.45(br)	128.78(br); 128.86(br)	130.54(br); 129.86(br); 129.52(br)	166.81; 164.14(br); 164.51(br); 163.80(br)	49.22(br); 49.03(br)	19.27(br); 18.93(br)		
CuiPpTF	20.48	147.97; 147.83	120.20; 119.91	129.52	130.74	165.31(br)	54.13(br)	26.29		
CutBpTF	20.48	148.65; 148.36	120.45	129.52	130.86	167.93; 165.45	54.52; 54.08	32.48		
CucHpTF	20.48	148.07; 147.88	120.15; 119.96	129.48	130.64	165.49; 165.40	61.99	38.01; 37.81	25.05	25.29

[a] In $CDCl_3$; ppm relative to TMS at −30°C. [b] The C(1) atom is bound to nitrogen. [c] The C(1) atom is bound to nitrogen.

mamidino groups (IA and IB). A representative ^{1}H NMR spectrum is shown in Fig. 3a for CutBpTF at 0°C.

The ^{13}C NMR spectra measured at −30°C provide further evidence that the dimeric forms predominate (Fig. 4a). Nevertheless, there are indications that tetramers may be formed at very low temperatures, since, for example, the ^{1}H NMR resonances of CutBpTF are broadened and a new t-butyl signal forms (Fig. 3b). Since the spectrum at −80°C is analogous to that of AgtBpTF (vide infra), we tentatively conclude that at this temperature dimer/tetramer equilibria become apparent. Furthermore it is of interest that ^{1}H NMR measurements carried out at various concentrations and temperatures show that the dimer IA/dimer IB ratio is temperature but not concentration dependent. Since no assignment of the NMR resonances is possible no further conclusions could be reached.

B. Solutions containing two dimers and two tetramers

Although the molecular weight of AgtBpTF at 26.3°C in CH_2Cl_2 indicates that the dimeric species dominate, it is clear from the ^{1}H NMR spectra that other species are present (e.g. Fig. 5a). Especially at higher concentration.

This spectrum is very similar to that of CutBpTF at −80°C and shows a large broad signal at 1.34 ppm and a smaller broad signal at 1.13 ppm which are both due to the t-butyl group. At lower temperatures the whole ^{1}H NMR spectrum changes, but the most informative changes involve the t-butyl signals. The signal at 1.34 ppm decreases, while the signal at 1.13 ppm increases in intensity, and the two peaks both start to sharpen. At −30°C (Fig. 5b) the signal at 1.35

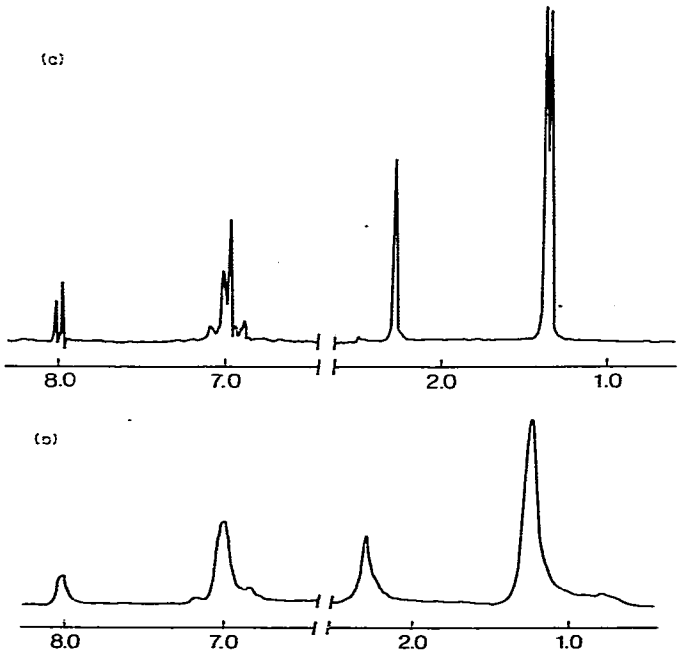


Fig. 3. (a) ^{1}H NMR spectrum of CutBpTF at 0°C (in $CDCl_3$); (b) ^{1}H NMR spectrum of CutBpTF at −80°C (in CD_2Cl_2).

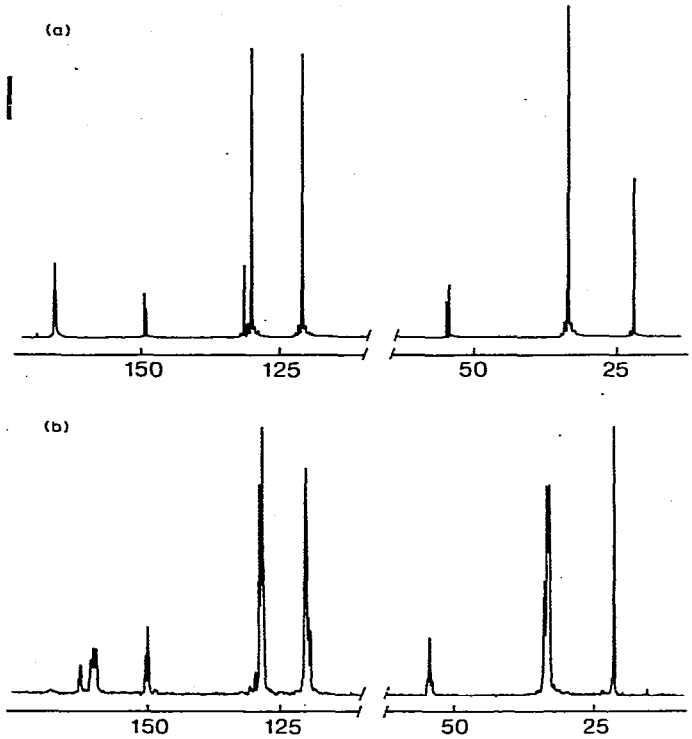


Fig. 4. (a) ^{13}C NMR spectrum of CutBpTF at −30°C (in $CDCl_3$); (b) ^{13}C NMR spectrum of AgtBpTF at −30°C (in $CDCl_3$).

ppm split into two signals at 1.32 and 1.36 ppm, and the signal at 1.13 ppm split into signals at 1.15 and 1.01 ppm. It is noteworthy that the last two signals are of about equal intensity and remain so as concentration and temperature are

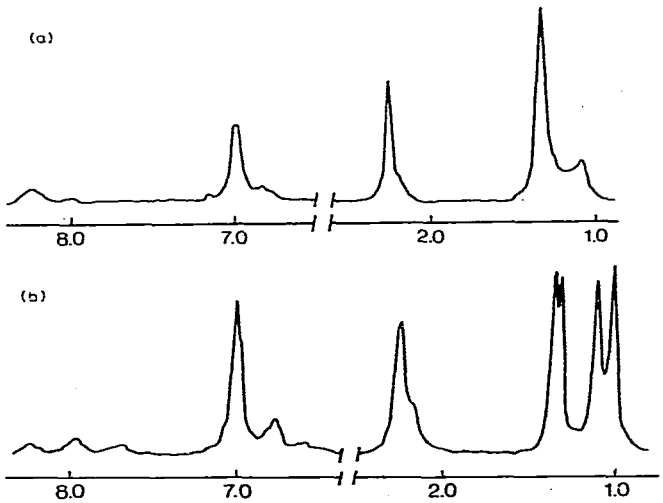


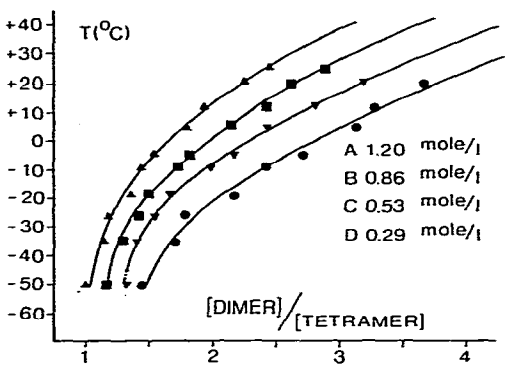
Fig. 5. (a) ^{1}H NMR spectrum of AgtBpTF at +30°C (in $CDCl_3$); (b) ^{1}H NMR spectrum of AgtBpTF at −30°C (in $CDCl_3$).

varied. However, the signal at 1.32 ppm increases relative to that at 1.36 ppm with increasing temperature and increasing concentration. It is evident that the signals at 1.32 and 1.36 ppm must be assigned to the two isomeric froms IA and and IB, and the signals at 1.01 and 1.15 ppm to the tetrameric isomers IIAA and IIA′A′, each with four equivalent formamidino groups. There is no evidence for the presence of isomers IIBB and IIAB, which is understandable in view of the bulkiness of the t-butyl groups. The ^{13}C NMR spectrum of AgtBpTF at −30°C (Fig. 4b) is also in complete agreement with the ^{1}H NMR spectra. Figure 6 shows that the relative amounts of the tetrameric species increases with increasing concentration and with decreasing temperatures, which can be understood in terms of the equilibria 1—5.

If it is assumed that no monomeric forms are involved, these equilibria reveal that interconversion of the dimers IA and IB can only occur via an intermediate tetrameric species IIBB. In the light of these observations it would be of interest to consider why the ratio of the concentrations of IA and IB changes with increasing temperature, while the ratio IIAA/IIA′A′ does not, but this would not be very fruitful at present since we were unable to assign the two peaks of the dimers and the two peaks of the tetramers.

C. Solution containing two dimers and more than two tetramers

The ^{1}H NMR spectra of CuEpTF, AgMpTF, AgEpTF, AgiPpTF and AgcHpTF indicate the presence of two dimers and more than two tetramers. For the first three compounds, the molecular weights at 26.3°C in CH_2Cl_2 clearly show that at this temperature a large percentage of tetrameric species is present, while for the last two the dimeric form seems dominant (Table 1). The ^{1}H NMR spectra of the ethyl, isopropyl and cyclohexyl derivatives are very complicated because the hydrogen—hydrogen couplings and exchange processes. However, the general line shapes of the C—^{1}H resonances and *p*-tolyl signals in the range of −50°C to +40°C are very similar to that of AgtBpTF in this range, which indicates that the solutions mainly contain the dimers IA and IB and the tetramers IIAA and IIA′A′. The ^{13}C NMR spectra confirm these findings, although both ^{1}H and ^{13}C NMR spectra indicates that further species are present. More information is



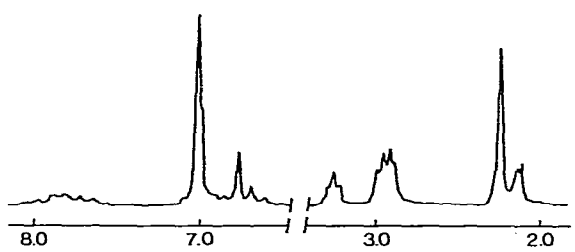


Fig. 6. The ratio dimer tetramer versus temperature (concentrations are given for the monomeric form).

Fig. 7. ^{1}H NMR spectrum of AgMpTF at −30°C (in $CDCl_3$).

provided by the ^{1}H NMR spectrum of AgMpTF at −30°C (Fig. 7), which shows unambigously seven signals for the C—H proton and seven resonances for the hydrogen atoms of the CH_3 group, which are all in an intermediate exchange. If all the dimers and tetramers were present one would expect ten resonances for each group of protons. Accidental degeneracy, small concentrations of some isomers, and/or coalescence of some signals could be the reason that seven instead of ten signals are observed. This hypothesis is supported by the ^{13}C NMR spectrum of AgMpTF at −30°C, which shows that at this temperature most signals have already coalesced or are in the intermediate exchange region.

Concluding remarks

It has been shown for $[MCRNC(H)NR']_n$ that the ratio of dimer to tetramer increases generally with increasing bulk of the substituents. This is clearly shown in the series of the Cu and Ag compounds in which R remains constant (*p*-tol) while R′ is varied from ethyl to cyclohexyl. Furthermore, the tendency to form tetramers is greater for silver than for analogous copper complexes. It is tentatively proposed that the tetramers are probably formed by a bimolecular reaction of two dimers which involves metal—nitrogen bond breaking and bond formation. The dimer—dimer reactions must be considered in the light of analogous reactions of dimeric π-allyl palladium complexes which involve cubane type tetrameric intermediates [25]. Moreover, in view of the results it is unlikely that direct tetramer—tetramer equilibria exist. The observation that the metal IB complexes do not react with basic ligands is another illustration of the preference of the Group IB metals for linear coordination and of the special requirements of the formamidino ligand, which has its N-lone pairs favorably positioned for bridging two metals. Linear coordination and bridging formamidino ligands, are basic structural elements in both dimeric and tetrameric structures, and would be absent in the complexes formed by degradation of the aggregates with basic ligands. These conclusions, as well as the proposed mechanism for the dimer—tetramer and dimer—dimer interconversion, may shed light on the reactions of these metal IB complexes with Rh or Ir complexes [24].

Acknowledgements

We thank Mr. J. Berke and Mr. J. Ernsting for technical assistance.

References

1 M. Corbett and B.F. Hoskins, J. Chem. Soc. Chem. Commun., (1968) 1602.
2 J.E. O'Connor, G.A. Janusonis and E.R. Corey, J. Chem. Soc. Chem. Commun., (1968) 445.
3 I.D. Brown and J.A. Dunitz, Acta Cryst., 14 (1961) 480.
4 P. Hendriks, J. Kuyper and K. Vrieze, J. Organometal. Chem., 120 (1976) 285 and ref. therein.
5 S. Condeloro de Sanctis, N.V. Pavel and L. Toniolo, J. Organometal. Chem., 108 (1976) 409.
6 J. Kuyper, P.I. van Vliet and K. Vrieze, J. Organometal. Chem., 105 (1976) 379 and ref. therein.
7 P.I. van Vliet, J. Kuyper and K. Vrieze, J. Organometal. Chem., 122 (1976) 99.
8 L.D. Brown and J.A. Ibers, J. Amer. Chem. Soc., 98 (1976) 1597.
9 E. Pfeiffer, J. Kuyper and K. Vrieze, J. Organometal. Chem., 105 (1976) 371 and ref. therein.
10 M. Corbett and B.F. Hoskins, J. Amer. Chem. Soc., 89 (1967) 1530.
11 L.D. Brown and J.A. Ibers, Inorg. Chem., 15 (1976) 2794.
12 L. Toniolo, A. Immirzi, U. Croatto and G. Bombieri, Inorg. Chim. Acta, 19 (1976) 209.

13 E. Pfeiffer, A. Oskam and K. Vrieze, Trans. Metal. Chem., 2 (1977) 240.
14 G. Bombieri, A. Immirzi and L. Toniolo, Inorg. Chem., 15 (1976) 2428.
15 F.A. Cotton, T. Inglis, M. Kilner and T.R. Webb, Inorg. Chem., 14 (1975) 2023.
16 F.A. Cotton and L.W. Shive, Inorg. Chem., 14 (1975) 2027.
17 W.H. de Roode and K. Vrieze, J. Organometal. Chem., 145 (1978) 207 and ref. therein.
18 L. Toniolo, T. Boschi and G. Deganello, J. Organometal. Chem., 93 (1975) 405.
19 J.A. Potenza, R.J. Johnson and J. San Philippo Jr., Inorg. Chem., 15 (1976) 2216.
20 W.H. de Roode, J. Berke, A. Oskam and K. Vrieze, J. Organometal. Chem., 155 (1978) 307 and ref. therein.
21 T. Inglis and M. Kilner, J. Chem. Soc. Dalton, (1975) 930.
22 T. Inglis, M. Kilner, T. Reynoldson and E.E. Robertson, J. Chem. Soc. Dalton, (1975) 924.
23 T. Inglis and M. Kilner, J. Chem. Soc. Dalton, (1976) 562.
24 P.I. van Vliet, G. van Koten and K. Vrieze, J. Organometal. Chem., in press.
25 D.L. Tibbetts and T.L. Brown, J. Amer. Chem. Soc., 92 (1970) 2031.