Journal of Organometallic Chemistry, 125 (1977) C1–C4

Preliminary Communication

Π-ARENE COMPLEXES OF CADMIUM(II) AND ZINC(II)

LESLIE C. DAMUDE and PHILIP A.W. DEAN

Department of Chemistry, University of Western Ontario

London, Ontario N6A 5B7 (Canada)

(Received September 7th, 1976)

SUMMARY

^{13}C n.m.r. complexation shifts of arenes are observed in the systems $Cd(AsF_6)_2$-arene-SO_2 and $Zn(SbF_6)_2$-arene-SO_2 and provide evidence for arene complexes of cadmium(II) and zinc(II) resembling those of Ag(I). Representative complexes of cadmium(II) and zinc(II) have 1:1 stoichiometry.

Though π-arene complexes of Cu(I) and Ag(I) are well known, such complexes of Zn(II) and Cd(II) are not. We are unaware of any evidence for arene complexes of zinc, and only for benzene and the xylenes is there evidence for Cd(II)-arene complexes: the aromatics are selectively retarded when CdF_2-Al_2O_3 is used as the stationary phase in a gas-solid chromatographic column [1]. We now report that the ^{13}C nmr spectra of the systems $Cd(AsF_6)_2$-arene-SO_2 provide good evidence for the occurrence of π-arene complexes of Cd(II) in liquid SO_2. The method of continuous variations shows the hexamethylbenzene complex to have 1:1 stoichiometry in dilute SO_2 solution. Analogous Zn(II) complexes are readily prepared in the system $Zn(SbF_6)_2$-arene-SO_2. They are less soluble than the cadmium complexes and therefore more difficult to study in solution but easier to isolate. Typical zinc-arene complexes have 1:1 stoichiometry.

For the group IIB-containing systems at ambient probe temperature (32°), separate ^{13}C nmr spectra for free and coordinated arene are not observed, only an exchange-averaged spectrum. However, significant complexation shifts, $\Delta\delta_C$ ($=\delta_C^{obsd}$ - δ_C^{arene}), are found for the more electron-rich arenes, showing that complexation [illegible] in the Table, which also includes comparable data for the similar silver(I) systems where available. For a given arene the pattern of complexation shifts is the same for the zinc(II), cadmium(II) and silve systems, eg. for durene $\Delta\delta_c^{C1} > \Delta\delta_c^{C3}$ in all cases. On the basis of previous arguments [2] this can be taken as evidence that, like Ag^+, Zn^{2+} and Cd^{2+} coordina to arenes via a localized π-interaction and that all three cations have the same preferred binding sites. Interestingly, the average complexation shifts, $\Delta\delta_c^{ave}$ $(=\frac{1}{6}\sum_{i=1-6}\Delta\delta_c^{Ci})$, of the various methyl-substituted benzenes are positive for the zinc and cadmium systems, in contrast to the negative values for the silver system: eg. $\Delta\delta_c^{ave}$ is -1.3, +0.8 and -+0.3 for Ag^+, Cd^{2+} and Zn^{2+}, respectively, when the substrate is durene (Table). In terms of a model proposed earlier [2] for this typ

TABLE

^{13}C Chemical Shifts, $\Delta\delta_c$, Induced in Some Aromatic Substrates by $Cd(AsF_6)_2$, $Zn(SbF_6)_2$ and Ag AsF_6 [a,b]

Substrate	Metal Cation	Arene:Salt Ratio	$\Delta\delta_c$(p.p.m.)[c]			
			C_1	C_2	C_3	C
Hexamethylbenzene	Cd^{2+}	2.2	[1.33]	[1.33]	[1.33]	0.
	Ag^+	2.0	[-0.83]	[-0.83]	[-0.83]	0.
1,2,4,5-Tetramethylbenzene	Cd^{2+}	2.5	[1.55]	[1.55]	-0.61	0.
	Zn^{2+}	2.5[d]	[0.37]	[0.37]	0.19	0.
	Ag^+	2.0	[1.19]	[1.19]	-6.26	0.
1,4-Dimethylbenzene	Cd^{2+}	2.5	[1.69]	0.23	0.23	0.
	Ag^+	2.0	[2.46]	-3.13	-3.13	0.
Benzene	Cd^{2+}	2.5	0.29	0.29	0.29	
Naphthalene	Cd^{2+}	2.7	0.43[e]	0.23[e]	0.43[e]	

[a] SO_2 solutions with [arene] ≃ 0.75 M; proton-decoupled spectra were measured at using a Varian XL-100-15 Spectrometer, shifts of free and complexed arenes initi being determined relative to external dioxane-D_2O (10/90% v/v) as previously rep [2].

[b] Data for Ag AsF_6 from Ref. 2; similar data have been reported using different solvents [3,4].

[c] Square brackets denote substituted carbons; estimated error due to spectral measurement ±0.06 p.p.m.

[d] This solution was saturated with $Zn(SbF_6)_2$·durene.

of complex, the differing values of $\Delta\delta_c$ are consistent with the expected higher acidity of the divalent cations compared with Ag^+, but could also mean that smaller upfield shifts are induced in olefins by coordination with Zn^{2+} or Cd^{2+} than by coordination with Ag^+. We are presently investigating the latter possibility.

For the cadmium system at constant arene/Cd^{2+} and arene concentration, $\Delta\delta_c^{ave}$ tends to decrease with decreasing methyl substitution of the various methylbenzenes. This contrasts with the approximately constant value of $\Delta\delta_c^{ave}$ found in the analogous silver systems. It seems the stabilities of the cadmium complexes must fall off more rapidly with decrease in methylation than do those of the silver complexes. Stability constants for a range of complexes are currently being determined, but it should be noted that even the hexamethylbenzene complex has quite limited stability (see below).

Representative zinc(II)-arene complexes have 1:1 stoichiometries. Thus the red 1:1 durene complex is isolable quantitatively on removal of all volatiles from a durene-rich reaction mixture in liquid SO_2, and the red 1:1 hexamethylbenzene complex precipitates on mixing SO_2 solutions of the reactants (Found: C, 20.47; H, 2.70. $C_{12}H_{18}F_{12}Sb_2Zn$ calcd: C, 20.61; H, 2.59%). To date we have been unable to isolate pure cadmium-arene complexes. However, a Job's plot based on the visible spectrum* of the system $Cd(AsF_6)_2$-C_6Me_6 at low concentration (0.074m) in SO_2 demonstrates the occurrence of a Cd(II)-C_6Me_6 complex with 1:1 stoichiometry and a formation constant of ca. 50 m^{-1}. (At higher concentrations there is evidence for some simultaneous n:1 complex formation where n is probably 2; eg., at a concentration of 0.33m, the Job's plot maximum occurs at a mole fraction of $C_6Me_6 \simeq 0.55$). An impure red product can be obtained from the system $Cd(AsF_6)_2$-C_6Me_6-SO_2. Both it and the zinc complexes are decomposed by many of the more common solvents, eg. water, alcohols, acetone, ether. Such ready solvolysis is probably one reason these complexes have not been observed earlier.

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* The colour of the Cd(II)-C_6Me_6 complex is due to the visible tail of an intense (presumably) charge-transfer band in the UV region. All of the cadmium-containing

ACKNOWLEDGEMENT

This work was carried out with the support of the National Research Council of Canada.

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