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PREPARATIVE CHEMISTRY WITH $[Ru(\eta^6\text{-ARENE})(H_2O)_3]^{2+}$: BIS-ARENE AND MONOBENZENE COMPLEXES WITH O, N AND S DONORS

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Abstract—The preparation, and electronic, ^1H and ^{13}C NMR spectra of the complex ions $[Ru(\eta^6\text{-}C_6H_6)L_3]^{2+}$ (L = acetonitrile, dimethylsulphoxide, dimethylsulphide or tetrahydrothiophene) from $[Ru(\eta^6\text{-}C_6H_6)(H_2O)_3]^{2+}$ are reported. The NMR data of coordinated benzene are discussed in terms of the π-backbonding capacity of the monodentate ligand.

Half-sandwich complexes of general stoichiometry $[Ru(\eta^6\text{-arene})L_1L_2L_3]^{2+}$ have been conventionally prepared using $[Ru(\eta^6\text{-arene})Cl_2]_2$ as the starting reagent, affording monomeric species still retaining one or two chloro ligands.[1] The chloro-bridged dimeric precursor itself is obtained by the reaction of "$RuCl_3 \cdot xH_2O$" with cyclohexadiene.[2] Hydrolysis of the dimer produces the ion $[Ru(\eta^6\text{-arene})(H_2O)_3]^{2+}$, which shows a very high tendency to dimerize and tetramerize.[3] We became interested in the monomeric ruthenium–arene–triaqua cation because it is a remarkable link between the classical hexaaqua ions and the organometallic $Ru(\eta^6\text{-arene})_2^{2+}$ sandwich compounds. A solution study of a variety of Os(benzene)$^{2+}$ complexes and some of their ruthenium analogs led to the conclusion that these Os(II)- and Ru(II)-arene moieties are perfectly stable in an aqueous environment, at least in the dark.[4] Our investigation of the $Ru(H_2O)_6^{2+/3+}$ couple[5] and of the formation, the molecular structure, and the substitution kinetics of $[Ru(\eta^6\text{-}C_6H_6)(H_2O)_3]^{2+}$[6] initiated a more general study of these "piano-stool" complexes, including the variation of the arene ligand and, more importantly, of the three monodentate ligands. Owing to its rather high substitution lability the ion $[Ru(\eta^6\text{-}C_6H_6)(H_2O)_3]^{2+}$ is a very convenient precursor in preparative ruthenium chemistry, as in a recent report dealing with the specific case of phosphine ligands.[7]

EXPERIMENTAL

Two different procedures have been used for the synthesis of the $[Ru(\eta^6\text{-arene})(H_2O)_3]^{2+}$ complex ion:

(A) An aqueous acidic (0.1 M) solution of the dimeric $[Ru(\eta^6\text{-arene})Cl_2]_2$[2] (2 mmol) is stirred for 3 h with the stoichiometric amount of an appropriate silver salt [SO_4^{2-}, tos$^-$ (*p*-toluenesulphonate) or tmms$^-$ (2,4,6-trimethylbenzenesulphonate)]. Solid AgCl is removed by filtration.

(B) $Ru(H_2O)_6^{2+}$ salts[5] smoothly react under argon in tetrahydrofuran or ethanol with cyclohexadiene to produce $[Ru(\eta^6\text{-}C_6H_6)(H_2O)_3]^{2+}$ in very good yield.[6] 1,3- as well as 1,4-cyclohexadiene may be used as the reagent. ^1H NMR monitoring of the reaction reveals the conversion of the 1,4- into the 1,3-isomer prior to substitution and further rearrangement. The complex disproportionation reaction produces the arene complex together with cyclohexene and cyclohexane.[6]

Subsequent concentration of the solutions obtained by procedures A or B under reduced pressure at 40°C and cooling to 5°C affords crystalline salts of the $[Ru(\eta^6\text{-arene})(H_2O)_3]^{2+}$ ion.

Substitution of the three water molecules by other monodentate ligands (L) is carried out under quite mild conditions:

L	Solvent	*T* (°C)	Yield (%)	Color
Acetonitrile (AN)	AN	40	63	Yellow-white
Dimethylsulphoxide (DMSO)	H_2O	50	50	Orange
Dimethylsulphide (DMS)	MeOH	25	85	Yellow
Tetrahydrothiophene (THTP)	MeOH	50	90	Yellow

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Microcrystalline solids of the resulting $[Ru(\eta^6\text{-}C_6H_6)L_3]^{2+}$ ions are isolated as PF_6^- salts.

$[Ru(\eta^6\text{-}C_6H_6)(H_2O)_3]^{2+}$ is also a convenient precursor for simple and efficient syntheses of the known mixed bis-arene complexes $[Ru(\eta^6\text{-}C_6H_6)(\eta^6\text{-arene})]^{2+}$ (arene = benzene, mesitylene, hexamethylbenzene, *p*-cymene or anisole), originally prepared from $[Ru(\eta^6\text{-arene})Cl_2]_2$.[8] $Ru(\eta^6\text{-}C_6H_6)(H_2O)_3(tos)_2$ (0.87 mmol) dissolved in trifluoroacetic acid (20 cm^3) is heated for 1 h under reflux with 20 cm^3 of the appropriate arene. The resulting reaction mixture is evaporated to dryness under reduced pressure and the residue is dissolved in MeOH. Colorless solids are precipitated as tos^- or BF_4^- salts with yields in the 80–98% range.

Ruthenium was determined spectrophotochemically;[9] elemental analyses were carried out by Ciba-Geigy, Basel. Analytical results are collected in Table 1. ^1H NMR spectra were measured with a Bruker WP 80 or a Varian EM 360 instrument, and ^{13}C NMR spectra with a Varian XL 100. UV–VIS spectra were recorded on a Cary 17 DX.

RESULTS

Whereas complete removal of the chloro ligands is rather difficult for the conversion of $[Ru(\eta^6\text{-arene})Cl_2]_2$ into monomeric $[Ru(\eta^6\text{-arene})L_3]^{2+}$ species,[2,4] the precursor $[Ru(\eta^6\text{-arene})(H_2O)_3]^{2+}$ offers a very facile and efficient route for the synthesis of these half-sandwich complexes for a variety of monodentate ligands (L). As a byproduct of this study $[Ru(\eta^6\text{-arene})(H_2O)_3]^{2+}$ is also shown to be a very good starting reagent for high-yield preparations of mixed bis-arene compounds, $[Ru(\eta^6\text{-arene})(\eta^6\text{-arene})]^{2+}$.

The isolated solid salts of $[Ru(\eta^6\text{-arene})L_3]^{2+}$ are perfectly stable in air. Their solutions in aqueous and non-aqueous solvents do not show any feature in the cyclic voltammetry that could be assigned to a reversible redox process. In other words, the compounds described in this study are neither oxidized nor reduced in the potential interval −0.25 to +1 V (vs NHE). This considerably enhanced stability of the oxidation state II of ruthenium is generally attributed to the π-backbonding behavior of the arene ligands (cf. next section).

Solution spectra of the various half-sandwich complex ions exhibit absorption bands in the short visible and the UV region (Table 2). The lowest-energy band generally is observed around 400 nm. Considering the intensity of these absorptions we assign them to charge-transfer transitions which are significantly red-shifted with respect to the corresponding bis-arene compounds.[1,2] The very similar spectra for $[Ru(\eta^6\text{-}C_6H_6)(H_2O)_3]^{2+}$ and $[Ru(\eta^6\text{-}C_6H_6)(DMSO)_3]^{2+}$ are accepted as supporting evidence for oxygen-coordinated DMSO in line with the NMR data.

^1H and ^{13}C NMR spectroscopic results of the various complex ions are collected in Tables 3 and 4. We observe an overall upfield shift for the signals

Table 1. Analytical data[a]

	Ru	C	H	S	H_2O	N	F
$[Ru(\eta^6\text{-}C_6H_6)(H_2O)_3](tos)_2$	17.6	41.7	4.6	11.1	9.4		
	17.3	41.6	4.6	11.0	9.7		
$[Ru(\eta^6\text{-}C_{10}H_{14})(H_2O)_3](tos)_2$[b]	16.0	45.6	5.4	10.2	8.6		
	15.3	45.3	5.4	10.9	9.4		
$[Ru(\eta^6\text{-}C_6(CH_3)_6)(H_2O)_3]SO_4 \cdot 2H_2O$	21.6	30.8	6.0	6.9	19.3		
	22.6	32.5	6.2	7.1	19.4		
$[Ru(\eta^6\text{-mes})(H_2O)_3]SO_4 \cdot H_2O$[c]	26.0	27.8	5.2	8.2	18.5		
	25.0	27.1	5.3	8.0	20.8		
$[Ru(\eta^6\text{-}C_6H_6)(AN)_3](PF_6)_2$	17.1	24.3	2.5			7.1	38.5
	16.9	24.3	2.7			7.1	38.3
$[Ru(\eta^6\text{-}C_6H_6)(DMSO)_3](PF_6)_2$	14.4	20.5	3.4	13.7			32.4
	14.0	21.0	3.4	13.7			31.3
$[Ru(\eta^6\text{-}C_6H_6)(THTP)_3](PF_6)_2$	13.8	29.5	4.1	13.1			31.1
	13.5	29.7	4.2	13.1			31.2
$[Ru(\eta^6\text{-}C_6H_6)(DMS)_3](PF_6)_2$	15.4	22.0	3.7	14.7			34.8
	15.2	22.2	3.7	14.8			34.3

[a] Upper line: calculated; lower line: found.

[b] $C_{10}H_{14}$ = *p*-cymene.

[c] mes = mesitylene.

Table 2. UV–VIS spectra of $[Ru(arene)L_3]^{2+}$ ions

	λ (nm)	ε $(M^{-1}\,cm^{-1})$
$[Ru(\eta^6\text{-}C_6H_6)(H_2O)_3]^{2+}$ [a]	400	550
	314	750
	248 sh	
$[Ru(\eta^6\text{-}C_6(CH_3)_3H_3)(H_2O)_3]^{2+}$ [a]	402	610
	315	660
	250 sh	
$[Ru(\eta^6\text{-}C_6(CH_3)_6)(H_2O)_3]^{2+}$ [a]	415	700
	326	680
	240 sh	
$[Ru(\eta^6\text{-cymene})(H_2O)_3]^{2+}$ [a]	404	670
	316	750
	268	820
$[Ru(\eta^6\text{-}H_6C_6)(AN)_3]^{2+}$ [b]	368	570
$[Ru(\eta^6\text{-}C_6H_6)(DMSO)_3]^{2+}$ [b]	400	1500
$[Ru(\eta^6\text{-}C_6H_6)(DMS)_3]^{2+}$ [b]	387	2290
$[Ru(\eta^6\text{-}C_6H_6)(THTP)_3]^{2+}$ [b]	390	1410

[a] 0.5 M H_2SO_4.

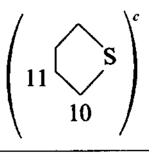
[b] Acetone, PF_6^- salts.

Table 3. ^1H and ^{13}C NMR spectra of $[Ru(\eta^6\text{-arene})(H_2O)_3]^{2+}$ complex ions[a]

Arene	Atom	^1H	^{13}C
Benzene	1	6.1, s (6)	81.9
p-Cymene (1-isopropyl-4-methylbenzene)	1	—	93.3
	2, 6	5.7, d (2)	94.1
	3, 5	5.5, d (2)	93.0
	4	—	93.3
	7	2.1, s (3)	23.5
	8	2.6, s (1)	32.2
	9, 9′	1.2, d (6)	22.6
Mesitylene (1,3,5-trimethylbenzene)	1	—	74.2
	2	5.1, s (3)	102.5
	7	2.2, s (9)	24.6
Hexamethylbenzene	1	—	90.8
	7	2.1, s (18)	17.3

[a] Chemical shifts (δ) in ppm; numbering scheme: ring atoms, 1–6; methyl, 7; isopropyl, 8, 9, 9′: s, singlet; d, doublet; number of protons in parantheses: ^1H: WP-80, D_2O, TMSP; ^{13}C: XL-100, D_2O, TMSP.

Table 4. ^1H and ^{13}C NMR spectra of $[Ru(\eta^6\text{-}C_6H_6)L_3]^{2+}$ complex ions[a]

L	Atom	^1H	^{13}C
H_2O[b]	1	6.1, s (6)	81.9
DMSO $[(C_{(10)}H_3)_2SO]$[c]	1	6.2, s (6)	81.0
	10	3.0, m (18)	38.5
AN $[C_{(10)}H_3\text{-}C_{(11)}N]$[c]	1	6.5, s (6)	89.0
	10	2.6, s (9)	3.6
	11	—	86.2
DMS $[(C_{(10)}H_3)_2S]$[d]	1	6.6, s (6)	92.9
	10	2.7, s (18)	26.5
THTP 	1	6.7, s (6)	93.6
	10	3.5, m (12)	43.7
	11	2.3, m (12)	31.1

[a] Cf. footnote of Table 3.
[b] ^1H: WP-80, D_2O, TMSP; ^{13}C: XL-100, D_2O, TMSP.
[c] ^1H: EM-360, $(CD_3)_2CO$, TMS; ^{13}C: XL-100, $(CD_3)_2CO$, TMS.
[d] ^1H: EM-360, $(CD_3)_2SO$, TMSP; ^{13}C: XL-100, $(CD_3)_2SO$, TMSP.

of the carbon and hydrogen atoms within the ring of the arene ligands compared to the free aromatic molecule. The uncoordinated hydrocarbons show ^1H signals for the ring protons between 6.73 ppm (mesithylene) and 7.27 ppm (benzene) and ^{13}C resonances between 126 and 136 ppm. Significantly smaller shifts, upfield as well as downfield, are recorded for the C and H atoms of the ring substituents.

DISCUSSION

The most important general feature of the NMR data for the arene ligands, the high-field shift of the ring carbon and hydrogen signals (Table 3), is attributed to π-backbonding within the ruthenium–arene moiety.[10] Accordingly, electron density is removed from the metal atom to the arene molecule, thus leading to an enhanced shielding of the ring atoms. This effect is opposed by the positive charge of the metal center. We do not attempt, however, to assess a closer or quantitative relation between these or other effects on the chemical shifts.

A somewhat more informative picture is presented by the NMR data for $[Ru(\eta^6\text{-}C_6H_6)L_3]^{2+}$ (Table 4). ^1H and ^{13}C NMR signals of coordinated benzene show a strong dependence on the bonding properties of the ligand L, in particular, whether L itself is a π-acceptor or not. Spectroscopic data of η^6-benzene can thus be used to probe selected properties of the remaining monodentate ligands. The ordering of ligands according to measured ^1H and ^{13}C shift differences (Table 5) matches a ligand series of π-acidity observed for ruthenium(II) pentaammine complexes.[11] The selection of ligands employed in our study ranges from virtually pure σ-donors, such as H_2O, to the typical π-acceptors AN and dialkyl sulfide. The observed NMR behavior is thus qualitatively attributed to the influence of the monodentate ligand competing in the bonding scheme of the $[Ru(\eta^6\text{-arene})L_3]^{2+}$ ions with the aromatic molecule. π-Acidity is also strongly reflected in thermodynamic and kinetic properties of related hexacoordinated complex ions such as $[Ru(H_2O)_6]^{2+}$ and $Ru(AN)_6^{2+}$. The reduction potential of the $[Ru(H_2O)_6]^{3+/2+}$ couple is 0.21 V, whereas $Ru(AN)_6^{2+}$ cannot be oxidized up to 1.9 V.[12] Similarly, the rates for ligand exchange are $2 \times 10^{-2}\ s^{-1}$ for water[13] and $10^{-9}\ s^{-1}$ for AN.[14] Current studies in our laboratory dealing with a variety of ligands within the series $[Ru(\eta^6\text{-arene})_2]^{2+} \rightarrow [Ru(\eta^6\text{-arene})L_3]^{2+} \rightarrow RuL_6^{2+}$ are expected to provide further insight into this relationship between electronic structure and chemical reactivity.

Table 5. Chemical-shift differences for $[Ru(\eta^6\text{-}C_6H_6)L_3]^{2+}$[a]

L	$\Delta\ [^1H(C_6H_6)]$	$\Delta\ [^{13}C(C_6H_6)]$
N_2H_4[b]	1.7	—
H_2O	1.2	46.5
DMSO	1.0	47.4
AN	0.8	39.4
DMS	0.7	35.5
THTP	0.6	34.8

[a] Free benzene: 7.27 and 128.4 ppm for ^1H and ^{13}C NMR, respectively; $\Delta = \delta(\text{complex ion}) - \delta(\text{free } C_6H_6)$.
[b] R. H. Crabtree and A. L. Pearman, *J. Organomet. Chem.* 1977, **141**, 325.

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REFERENCES

1. M. A. Bennett, M. I. Bruce and T. W. Matheson, In *Comprehensive Organometallic Chemistry* (Edited by G. Wilkinson, F. G. A. Stone and E. W. Abel), Vol. 4, p. 691. Pergamon Press, Oxford (1982). E. A. Seddon and K. R. Seddon, *The Chemistry of Ruthenium*. Elsevier, Amsterdam (1984).

2. M. A. Bennett and A. K. Smith, *J. Chem. Soc., Dalton Trans.* 1974, 233.
3. R. O. Gould, C. L. Jones, D. F. Robertson and T. A. Stephenson, *J. Chem. Soc., Chem. Commun.* 1977, 222.
4. Y. Hung, W. J. Kung and H. Taube, *Inorg. Chem.* 1981, **20**, 457.
5. P. Bernhard, H. B. Bürgi, J. Hauser, H. Lehmann and A. Ludi, *Inorg. Chem.* 1982, **21**, 3936.
6. M. Stebler, H. B. Bürgi and A. Ludi, *Proceedings of the XIIth International Conference on Organometallic Chemistry, Vienna* (1985). M. Stebler, W. Hummel, P. A. Pittet, H. B. Bürgi, A. E. Merbach and A. Ludi, to be published.
7. O. H. Bailey and A. Ludi, *Inorg. Chem.* 1985, **24**, 2582.
8. M. A. Bennett and T. W. Matheson, *J. Organomet. Chem.* 1979, **175**, 87.
9. E. D. Marshall and R. R. Rickard, *Anal. Chem.* 1950, **22**, 795; J. L. Woodhead and J. M. Fletcher, *J. Chem. Soc.* 1961, 5039.
10. D. M. P. Mingos, In *Comprehensive Organometallic Chemistry* (Edited by G. Wilkinson, F. G. A. Stone and E. W. Abel), Vol. 3, p. 1. Pergamon Press, Oxford (1982).
11. H. Lehmann, K. J. Schenk, G. Chapuis and A. Ludi, *J. Am. Chem. Soc.* 1979, **101**, 6197.
12. P. Bernhard, Ph.D. Thesis, University of Bern (1984).
13. P. Bernhard, L. Helm, I. Rapaport, A. Ludi and A. E. Merbach, *J. Chem. Soc., Chem. Commun.* 1984, 302.
14. A. E. Merbach, personal communication.