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Neutral Binuclear and Cationic Mononuclear η^6-Benzeneruthenium(II) Complexes Containing Neutral Bidentate Ligands

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Studies by Maitlis *et al.* [1] have shown that the substrates $[(\eta^5\text{-}C_5Me_5)MCl_2]_2$ (M = Rh, Ir) are suitable for the preparation of unusual pentamethylcyclopentadienyl-rhodium(III) and -iridium(III) complexes which act as very efficient catalysts. These results have stimulated further studies [2, 3] on the chemistry of $[(\eta^6\text{-arene})RuCl_2]_2$ complexes which are isoelectronic with $[(\eta^5\text{-}C_5Me_5)MCl_2]_2$. The reactions of $[(\eta^6\text{-arene})RuCl_2]_2$ (arene = benzene, mesitylene, hexamethylbenzene) with various monodentate nucleophiles to give $(\eta^6\text{-arene})RuLCl_2$ (L = tertiary phosphine, pyridine, tertiary arsine, isocyanide) complexes have been previously described [4–7]. A report on the reaction of $[(\eta^6\text{-benzene})RuCl_2]_2$ with the potentially bidentate nucleophiles $Ph_2PCH_2PPh_2$ and $Ph_2P(CH_2)_4PPh_2$ to give $(\eta^6\text{-}C_6H_6)RuCl_2(Ph_2PCH_2PPh_2)$ and $\{\mu\text{-}Ph_2P(CH_2)_4PPh_2\}[(\eta^6\text{-}C_6H_6)RuCl_2]_2$, with mono- and bidentate-bridging-coordination respectively of the phosphine ligand, prompted us to investigate more thoroughly such a type of reaction.

By refluxing a benzene solution of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with the bidentate ligand L–L (L–L = $Ph_2AsCH_2CH_2AsPh_2$, $Ph_2P(CH_2)_nPPh_2$; n = 2, 3, 4), in molar ratio 1:1, a red solid was formed. The solubility of the product depends on the ligand coordinated. Thus, while compounds with $Ph_2P(CH_2)_4PPh_2$ or $Ph_2As(CH_2)_2AsPh_2$ are almost insoluble in the common organic solvents, the complexes with $Ph_2P(CH_2)_nPPh_2$ (n = 2 or 3) are slightly soluble in chlorinated solvents; this allowed us to determine the molecular weight of the latter complexes. On the basis of analytical data and, where possible, molecular weight and conductivity measurements, the compounds could be formulated as neutral binuclear η^6-benzene complexes with bridging bidentate ligand of the type $(\mu\text{-L–L})[(\eta^6\text{-}C_6H_6)RuCl_2]_2$. The ^1H n.m.r. spectrum, in $CDCl_3$, of $\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ (n = 2, 3) complexes shows, besides broad multiplets in the 7.3–7.5 τ due to methylenic protons of the phosphine, a doublet at 4.63 (n = 2) or 4.78 τ (n = 3) (J_{H-P} = ~0.6 Hz) due to benzene π-bonded to ruthenium atom; this pattern indicates magnetic equivalence of the two phosphorus atoms to which the benzene protons are coupled.

$(\mu\text{-L–L})[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ were not converted into complexes with terminal hydride or μ-hydrido complexes by ethanol–base or H_2–base. In addition, attempts to obtain binuclear η^6-benzeneruthenium-(0) complexes containing bridged diphosphine and one neutral monodentate ligand L per ruthenium atom by reaction of $(\mu\text{-L–L})[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ complexes with L (L = PPh_3, pyridine) in the presence of ethanol and Na_2CO_3 or zinc dust failed. By this synthetic route arene–olefin–ruthenium(0) complexes have been obtained from $[(\eta^6\text{-arene})RuCl_2]_2$ [8]; recently [9] $(\eta^6\text{-}C_6H_6)RuLL'$ (L and L' are tertiary phosphines or phosphites) complexes have been also obtained by reduction of $(\eta^6\text{-}C_6H_6)RuLCl_2$.

The $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ reacted with the bidentate ligands $Ph_2P(CH_2)_nPPh_2$ (n = 2, 3, 4) and $Ph_2As(CH_2)_2AsPh_2$, in a molar ratio 1:2, in refluxed ethanol, to give a yellow solution from which the cationic complexes $[(\eta^6\text{-}C_6H_6)Ru\{Ph_2E(CH_2)_nEPh_2\}Cl]Cl$ (E = P, As, n = 2; E = P, n = 3, 4) could be isolated. The new complexes were characterized by elemental analyses, conductivity measurements and spectroscopic i.r. and ^1H n.m.r. data. The ionic nature of the complexes was confirmed by precipitation of the corresponding tetraphenylborate salts by adding to a solution of $[(\eta^6\text{-}C_6H_6)Ru\{Ph_2E(CH_2)_nEPh_2\}Cl]Cl$ in methanol a solution of $Na[BPh_4]$ in the same solvent.

The complexes $[(\eta^6\text{-}C_6H_6)Ru\{Ph_2E(CH_2)_nEPh_2\}Cl]Cl$ (E = As, P, n = 2; E = P, n = 3, 4) could be obtained also by reacting $\{\mu\text{-}Ph_2E(CH_2)_nEPh_2\}[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with the appropriate bidentate ligand in refluxed ethanol. Using an excess of ligand, the reactions resulted in loss of the benzene ring from $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ or $\{\mu\text{-}Ph_2E(CH_2)_2EPh_2\}[(\eta^6\text{-}C_6H_6)RuCl_2]_2$.

In the ^1H n.m.r. spectrum, in $CDCl_3$, the benzene proton resonance of $[(\eta^6\text{-}C_6H_6)Ru\{Ph_2E(CH_2)_nEPh_2\}Cl]Cl$ complexes was found at lower field than the corresponding neutral bridged compounds as a triplet (J_{H-P} = ~0.6 Hz); in some cases the limited solubility of the compound and the J_{H-P} value beyond the resolution of the spectrophotometer used, prevented the observation of the benzene proton resonance as a triplet.

Of the prepared cationic complexes, particularly interesting is $[(\eta^6\text{-}C_6H_6)Ru\{Ph_2P(CH_2)_4PPh_2\}Cl]Cl$ in which a seven-membered chelate ring is present. Examples of complexes containing a bidentate ligand coordinated to a metal atom in such a way as to form a seven-membered chelate ring are uncommon and in many cases their formation has been established only by spectroscopic evidence [10]; recently a platinum-

TABLE I. Analytical and Physical Data.

Compound	Colour	Analysis, %[a]			Conductivity[b]	I.R. ν(Ru–Cl)	^{1}H NMR $\tau(C_6H_6)$[c]
		C	H	Cl			
$\{\mu\text{-}Ph_2P(CH_2)_2PPh_2\}[(\eta^6\text{-}C_6H_6)RuCl_2]_2$[d]	red	50.76 (50.79)	4.09 (4.04)	15.86 (15.78)		295 s 272 m	4.63[d]
$\{\mu\text{-}Ph_2P(CH_2)_3PPh_2\}[(\eta^6\text{-}C_6H_6)RuCl_2]_2$[e]	red	51.37 (51.33)	4.22 (4.19)	15.48 (15.54)		290 s 275 m	4.78[d]
$\{\mu\text{-}Ph_2P(CH_2)_4PPh_2\}[(\eta^6\text{-}C_6H_6)RuCl_2]_2$	red-brown	51.92 (51.84)	4.38 (4.35)	15.26 (15.30)		292 s 275 m	[f]
$\{\mu\text{-}Ph_2As(CH_2)_2AsPh_2\}[(\eta^6\text{-}C_6H_6)RuCl_2]_2$	red-brown	46.29 (46.26)	3.69 (3.67)	14.32 (14.37)		295 s 277 m	[f]
$[(\eta^6\text{-}C_6H_6)Ru\{Ph_2P(CH_2)_2PPh_2\}Cl]Cl$	yellow	59.30 (59.26)	4.68 (4.66)	10.87 (10.93)	93	292 m	4.03 t
$[(\eta^6\text{-}C_6H_6Ru\{Ph_2P(CH_2)_3PPh_2\}Cl]Cl$	yellow	59.80 (59.82)	4.91 (4.86)	10.64 (10.70)	98	292 m	4.09 t
$[(\eta^6\text{-}C_6H_6)Ru\{Ph_2P(CH_2)_4PPh_2\}Cl]Cl$	yellow	59.96 (60.35)	5.12 (5.06)	10.58 (10.48)	92	290 m	4.29 t
$[(\eta^6\text{-}C_6H_6)Ru\{Ph_2As(CH_2)_2AsPh_2\}Cl]Cl$	yellow	52.04 (52.22)	3.95 (3.90)	9.88 (9.63)	103	295 m	4.03 s

[a]Calculated values in parentheses. [b]For 5×10^{-4} *M* solutions in CH_3OH, ohm^{-1} mol^{-1} cm^2. [c]In $CDCl_3$ using TMS as internal standard; J(H–P) = ~0.6 Hz. [d]Molecular weight, osmometrically in $CHCl_3$ solution 900 (898). [e]Molecular weight, osmometrically in $CHCl_3$ solution 920 (912). [f]Insoluble to obtain a satisfactory n.m.r. spectrum.

(II) complex containing a seven membered chelate ring with the coordinated 1,4-diaminobutane was characterized also by single-crystal structure analysis [11, 12].

Even using mild conditions, we had no evidence for formation of neutral mononuclear complexes with monocoordination of the bidentate ligand, as obtained by Zelonka and Baird for the $Ph_2PCH_2PPh_2$ phosphine [4]. This result seems surprising also because 1,2-bis(diphenylphosphino)methane is known to have suitable geometry for bridging two metal atoms [13, 14].

Experimental

The complex $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ and the phosphines 1,3-bis(diphenylphosphino)propane and 1,4-bis(diphenylphosphino)butane were prepared according to literature methods [4, 10, 15]. Other chemicals were reagent grade and were used without purification. I.r. and ^1H n.m.r. spectra are recorded on Perkin-Elmer mod. 457 and Perkin-Elmer R 24B spectrophotometers respectively. A conductivity meter WTW LBR was used for conductivity measurements. Molecular weights were determined with a Knauer vapour pressure osmometer. All reactions were carried out under oxygen-free nitrogen. Elemental analyses were by Bernhardt Mikroanalytisches Laboratorium, Germany.

Some characteristic data for the prepared complexes are listed in Table I.

$\{\mu$-1,2-Bis(diphenylphosphino)ethane$\}$bis(η^6-benzene)tetrachlorodiruthenium(II), $\{\mu\text{-}Ph_2P(CH_2)_2PPh_2\}[(\eta^6\text{-}C_6H_6)RuCl_2]_2$

To a suspension of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ (0.580 g, 1.16 mmol) in benzene (60 ml), a solution of 1,2-bis(diphenylphosphino)ethane (0.462 g, 1.16 mmol) in the same solvent was added and the mixture was refluxed for about 2 h. A red solid was formed. This was collected on a buckner, washed with benzene and crystallized from dichloromethane–hexane (yield 86%).

Working-up as above and using the appropriate ligand, the complexes $\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ (n = 3, 4) and $\{\mu\text{-}Ph_2As(CH_2)_2AsPh_2\}[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ were obtained.

(η^6-Benzene)chloro$\{$1,2-bis(diphenylphosphino)ethane$\}$ruthenium(II) Chloride, $[(\eta^6\text{-}C_6H_6)Ru(Ph_2PCH_2CH_2PPh_2)Cl]Cl$

Method A

To a suspension of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ (0.52 g, 1.04 mmol) in ethanol (70 ml), 1,2-bis(diphenylphosphino)ethane (0.836 g, 2.1 mmol) was added and the mixture was refluxed until a yellow solution was obtained (about 50 min). The solution was filtered and the solvent evaporated to reduce the volume to 2 ml; by adding diethylether a yellow solid was obtained. This was collected on a buckner, washed with diethylether and dried.

By this procedure, using the appropriate ligand, the complexes $[(\eta^6\text{-}C_6H_6)Ru\{Ph_2P(CH_2)_nPPh_2\}Cl]Cl$ (n = 3, 4) and $[(\eta^6\text{-}C_6H_6)Ru(Ph_2AsCH_2CH_2AsPh_2)Cl]Cl$ were also obtained.

Method B

To a suspension of $\{\mu\text{-}Ph_2P(CH_2)_2PPh_2\}[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ (0.16 g, 0.144 mmol) in ethanol (60 ml), 1,2-bis(diphenylphosphino)ethane (0.057 g, 0.144 mmol) was added and the mixture was refluxed for about 1 h. Working-up as above, the product $[(\eta^6\text{-}C_6H_6)Ru(Ph_2PCH_2CH_2PPh_2)Cl]Cl$ was obtained as yellow solid.

The complexes $[(\eta^6\text{-}C_6H_6)Ru\{Ph_2P(CH_2)_nPPh_2\}Cl]Cl$ (n = 3, 4) and $[(\eta^6\text{-}C_6H_6)Ru\{Ph_2As(CH_2)_2AsPh_2\}Cl]Cl$ were also obtained using a similar procedure.

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