fluorene[34] at C-8. The O^6 position of guanine as the main point of linkage of mitomycin C to nucleic acids has long been a subject of speculation, based on various indirect evidence.[1,8] It has now been shown that the O^6-substituted adduct is the major product with the dinucleoside phosphate d(GpC). Its method of isolation and characterization will facilitate the search for this and other mitomycin adducts in nucleic acids in vitro and in vivo. It is notable that **3** represents a product of monofunctional alkylation by activated mitomycin at its aziridine function. The nature of a second minor alkylating function, assumed because of the presence of cross-links in mitomycin-treated DNA,[4] remains unknown.

Acknowledgment. We thank Dr. W. T. Bradner, Bristol Laboratories, Syracuse, NY, for a gift of mitomycin C, Dr. Arthur I. Cederbaum, Mt. Sinai School of Medicine, for supply of rat liver microsomes, and Dr. D. Cozart for assistance in FT-IR difference measurements. This work was supported by a PSU–CUNY Faculty Research Award and grants from the National Cancer Institute, CA 28681 (to M.T.) and CA 11572 (to K.N.).

Registry No. 1, 50-07-7; **2**, 23405-83-6; **3**, 84731-28-2.

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A Catechol Receptor Model by Macrocyclic Polyamines

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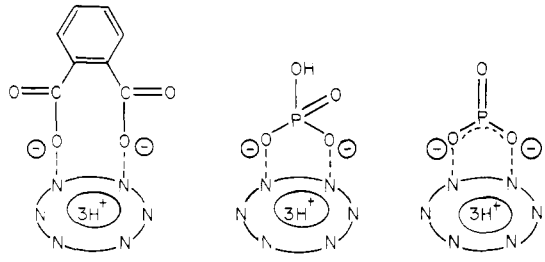
Abstract: 18-Azacrown-6 (L) (as triprotonated species) has been shown to form stable 1:1 complexes with catechol (**1**) and its biological derivatives **2–8** in neutral pH solutions. Their stability constants β_L were determined polarographically. The catechol receptor model L interacts with Dopa and dopamine with a similar order of β_L to indicate that the residual donor groups on the catecholamines do not significantly contribute to the complex formation. L has similar affinities to methyl ether derivatives of catechols. Further, L associates with an adrenergic blocking agent, dichloroisoproterenol (**10**). It also recognizes other drugs or drug functions such as resorcinol (**9**), tropolone (**11**), salicylic acid (**12**), *p*-aminosalicylic acid (**13**), and α-picolinic acid (**14**).

The catechol group is essential for biological activities in number of biogenic amines and their relevant drugs. The pharmacological studies have undeniably proved the presence of the catechol recognition and binding sites in biological systems. However, entities of the catechol receptors (like those of other receptors) remain almost unknown. So far few pictures have been proposed concerning the chemistry of the catechol recognition. Small molecular compounds having the efficient and selective catechol receptor functions would be very useful not only in the chemical elucidations but also in biological and medicinal applications. However, without precedent there had been no way of designing them.

We have shown that highly protonated macromonocyclic polyamines such as 18-azacrown-6 (as $3H^+$ species) make good



anion receptors (at neutral pH) for organic and inorganic oxygen anions, including polycarboxylates (e.g., citrate, succinate, *o*-phthalate, etc.),[2] phosphates (inorganic phosphate, AMP, ADP, and ATP),[3] and carbonate.[4] These polyoxyanions probably associate by ionic hydrogen bonds with the polyamine protons packed in the macrocyclic cavities, yielding highly stable and selective 1:1 anion complexes in aqueous solutions as postulated below.

Then, it occurred to us that the *o*-dihydroxy group of catecholamines might be a good donor to macrocyclic polyamine cations. The interaction has been examined with various polyamines by the anodic polarographic technique that we had previously used for the study of the macrocyclic polyamine complexes with polyoxyanions.[2-4] We have now found that 18-azacrown-6 (L) is indeed a strong receptor of catechol (**1**) and catecholamine derivatives **2–4** (see Figure 1). Our receptor model L moreover works on O-methylated catechols **5–8**. Interestingly, L further binds with drugs or drug functions **9–14**, some of which are recognized by biological catecholamine receptors.

Experimental Section

Materials. The catechol derivatives and other chemicals purchased were purified or were reagent grade. The macrocyclic hexaamine 18-azacrown-6 (L) was synthesized and purified as a 6HCl salt.[5] The purity was checked by TLC and gas chromatography techniques.[6]

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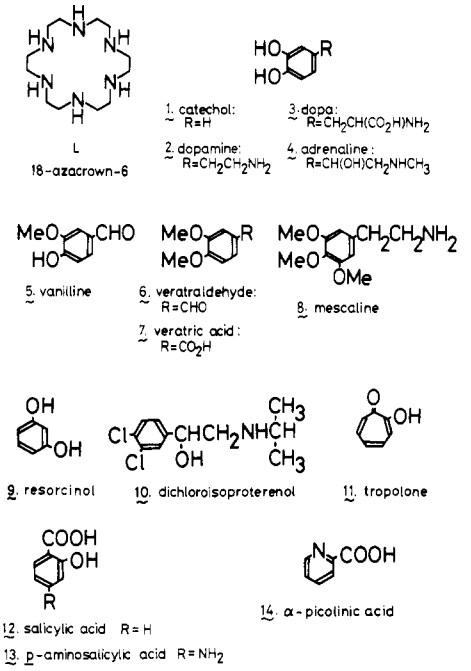

Figure 1. Catechol and its derivatives and other organic donor compounds studied for the complexation with 18-azacrown-6 (L).

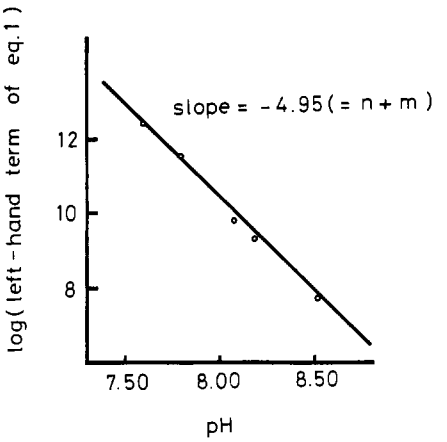

Figure 2. Plots of logarithmic (left-hand side of eq 1) against pH for 18-azacrown-6 (L) (0.4 mM)–catechol (**1**) (14.1 mM) in Tris buffer (0.1 M) at I = 0.2 M ($NaClO_4$) and 25 °C.

Since catechols are readily oxidized (to dark brown colors) in alkaline media, their solutions were carefully handled: a weighed catechol was first dissolved in acidified (to pH ~6) Tris or borate buffers (that had been thoroughly degassed by N_2), followed by immediate adjustments of the volumes and pH for the subsequent measurements.

Polarographic Method. The polarographic procedures and theories were the same as those applied to the previous macrocyclic polyamine–polycarboxylate[2] and -phosphate systems.[3] The half-wave potentials $E_{1/2}$ of the reversible polarograms of L in the presence of catechol, etc., shifted in an identical manner as in the presence of polycarboxylates[2] and phosphate.[3] Hence, an identical treatment of the data was applied.

Results and Discussion

As in the case for polycarboxylates and phosphates,[2,3] well-behaving anodic waves of macrocycle L (representing $Hg^0 + L \rightleftharpoons HgL^{2+}$) were recorded in the presence of catechol, etc., **1–14** (H_mA, where A denotes a completely proton-dissociated form) in Tris or borate buffers. Hence, we have measured the effects of the catechol concentration (at a given pH) and of pH (at a given catechol concentration) on the anodic half-wave potential $E_{1/2}$ for L (Table I) in order to calculate the complex stoichiometries, the number ($n + m$) of protons involved in the macrocyclic amine–catechol interaction, and complex stability constants β_L (= $[H_nL^{n+} - H_mA]/[H_nL^{n+}][H_mA]$). The results were all found to fit to a theoretical equation (1) previously derived for 1:1 macrocyclic polyamine–polyoxyanion complex formation.[2-4]

$$\left\{\text{antilog}\left(\frac{\Delta E_{1/2}}{0.0296}\right) - 1\right\}(\alpha_H)_L(\alpha_H)_A = \beta_L[A][H^+]^{(n+m)}K_1K_2...K_6K'_1K'_2 \quad (1)$$

Here $(\alpha_H)_L^{-1}$ is the ratio of [unprotonated L] to [total L], K_i is the ith protonation constant of macrocyclic polyamines and K'_i that of catechols. Accordingly, we have graphically determined the (n

Table I. Typical Data of the Effects of [Catechol (or Similar Compounds)] and pH on Anodic Wave Potentials $E_{1/2}$ of 18-Azacrown-6 (0.4 mM) in Tris (0.1 M) Buffer (I = 0.2 M and 25 °C)

$10^3 \times$ [catechol], M	pH	$\Delta E_{1/2}$, mV	$(\alpha_H)_L$	$(\alpha_H)_A$
		1		
10.6_7	8.18	10.0		
21.3_4	8.18	16.0		
14.1	7.60	16.5	$2.40_5 \times 10^5$	$4.05_9 \times 10^6$
14.1	7.80	17.6	$6.28_4 \times 10^4$	$1.63_4 \times 10^6$
14.1	8.08	11.2	$9.94_8 \times 10^3$	$4.62_2 \times 10^5$
14.1	8.51	10.1	$6.68_1 \times 10^2$	$6.98_0 \times 10^4$
		2		
5.48_3	7.44	25.1	$7.11_4 \times 10^5$	$3.17_5 \times 10^9$
10.9_7	7.44	33.2		
5.48_3	7.14	24.6	$5.50_8 \times 10^6$	$2.85_2 \times 10^{10}$
		3		
5.48_3	7.80	23.2	$6.30_9 \times 10^4$	$2.73_2 \times 10^8$
5.00	8.59	26.3	$4.53_5 \times 10^2$	$1.31_0 \times 10^5$
10.0	8.59	32.6		
5.00	7.83	33.4	$5.16_9 \times 10^4$	$1.87_0 \times 10^7$
5.00	8.20	33.7	$4.69_3 \times 10^3$	$1.58_9 \times 10^6$
		4		
5.0	7.34	22.4	$1.40_4 \times 10^6$	$6.14_1 \times 10^8$
10.0	7.34	30.1		
5.0	7.60	23.6	$2.40_5 \times 10^5$	$1.30_5 \times 10^8$
5.0	7.85	21.2	$4.52_8 \times 10^4$	$1.88_8 \times 10^7$

$10^3 \times$ [catechol], M	pH	$\Delta E_{1/2}$, mV
	5	
4.0	8.35	10.4
8.0	8.35	16.1
4.0	8.08	13.0
4.0	8.56	8.5
4.0	8.81	6.5
	6	
5.0	8.60	6.4
10.0	8.60	10.7
5.0	8.01	9.5
5.0	8.35	9.0
5.0	8.81	6.0
	7	
4.0	8.41	9.3
8.0	8.41	14.8
4.0	8.08	10.1
4.0	8.74	7.1
	8	
5.0	8.54	12.4
10.0	8.54	18.6
5.0	7.66	20.8
5.0	8.09	13.8
5.0	8.91	8.4
	9	
4.77	7.58	24.6
4.77	8.19	23.0
4.77	8.83	16.9

$10^3 \times$ [catechol], M	pH	$\Delta E_{1/2}$, mV
	10	
7.63	8.00	21.5
8.04	8.00	23.3
8.04	4.00	15.0
8.56	8.00	23.4
	11	
5.40	7.71	9.5
10.8	7.71	14.2
10.8	8.12	12.3
10.8	8.51	11.7
	12	
11.56	7.40	25.9
11.56	7.80	23.2
11.56	8.27	20.5
5.78	8.27	14.0
	13	
5.00	8.10	24.7
5.00	8.66	15.1
5.00	8.36	19.6
10.00	8.36	27.1
	14	
7.61	5.80	23.0
7.90	5.80	21.0
7.90	11.60	28.6
8.37	5.80	19.0
8.83	5.80	15.6

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Table II. 1:1 Association Constants β_L for 18-Azacrown-6 with Catechols at 25 °C and $I = 0.20$ M ($NaClO_4$)

catechol	experimental $(n+m)$ value	assigned complex formula[a]	β_L,[b] M^{-1}	buffers used
1	4.9_5	H_3L^{3+}-H_2A^0	$(1.6 \pm 0.2) \times 10^2$	pH 7.6-8.5 Tris (0.05-0.20 M)
2	6.0	H_3L^{3+}-H_3A^+	$(1.1 \pm 0.1) \times 10^3$	pH 7.1-7.8 Tris (0.05-0.20 M)
3	6.1	H_3L^{3+}-H_3A^0	$(3.7 \pm 0.4) \times 10^3$	pH 7.8-8.6 Tris (0.05-0.20 M)
4	5.9_0	H_3L^{3+}-H_3A^+	$(1.0 \pm 0.1) \times 10^3$	pH 7.1-7.9 Tris (0.05-0.20 M)
5	3.2_0	H_3L^{3+}-A^-	$(4.9 \pm 0.5) \times 10^2$	pH 8.1-8.4 borate (0.03-0.06 M)
6	2.9_8	H_3L^{3+}-A^0	$(2.5 \pm 0.3) \times 10^2$	pH 8.0-8.6 borate (0.03-0.06 M)
7	2.9_6	H_3L^{3+}-A^-	$(4.2 \pm 0.4) \times 10^2$	pH 8.1-8.4 borate (0.03-0.06 M)
8	4.0_6	H_3L^{3+}-HA^+	$(5.8 \pm 0.6) \times 10^2$	pH 7.7-8.9 Tris (0.05-0.20 M)
9	3.0_1	H_3L^{3+}-H_2A^0	$(1.3 \pm 0.2) \times 10^3$	pH 7.6-8.8 Tris (0.1 M)
10	2.9_6	H_3L^{3+}-A^0	$(8.5 \pm 0.8) \times 10^2$	pH 7.6-8.6 Tris (0.1 M)
11	2.9_5	H_3L^{3+}-A^-	$(2.3 \pm 0.2) \times 10^2$	pH 7.7-8.5 Tris (0.1 M)
12	4.0_5	H_3L^{2+}-HA^-	$(4.7 \pm 0.5) \times 10^2$	pH 7.4-8.3 Tris (0.1 M)
13	4.1_2	H_3L^{2+}-HA^-	$(4.5 \pm 0.5) \times 10^2$	pH 8.1-8.7 Tris (0.1 M)
14	2.9_3	H_3L^{3+}-A^-	$(8.3 \pm 0.8) \times 10^2$	pH 7.6-8.8 Tris (0.1 M)

[a] Log K_i values used for L are 10.19, 9.23, 8.73, 4.09, ~2, and ~1 (ref 5). Log K'_i values (all determined by us) are 12.49 and 9.31 (**1**); 12.20, 10.61, and 9.06 (**2**); 11.57, 10.21, and 8.95 (**3**); 11.74, 10.00, and 9.06 (**4**); 7.20 (**5**); 4.26 (**7**); 9.99 (**8**); 11.06 and 9.30 (**9**); 9.15 (**10**); 6.68 (**11**); 13.61 and 2.98 (**12**); 13.75 and 4.08 (**13**); and 5.40 and 1.60 (**14**). [b] Confidence limits (each for 3-5 experimental runs) are given.

$+ m$) and β_L values, respectively, from plots of log (left-hand side of eq 1) against pH (Figure 2) and against [catechol]. The final results are all summarized in Table II.

Just as earlier checked for the 1:1 polyamine–polycarboxylate complexation,[2] the 1:1 association constant β_L values can be assessed from the limiting current changes by using eq 2,[7] where β_L' is the conditional association constant expressed in terms of β_L by eq 3. For the typical case of catechol (**1**) complexation,

$$\beta_L'[A]_{\text{uncomplexed}} = \frac{(i_d)_L^2 - (i_d)_{obsd}^2}{(i_d)_{obsd}^2 - (i_d)_{LA}^2} \quad (2)$$

$$\beta_L' = \frac{\beta_L}{(\alpha_H)_L(\alpha_H)_A}([H^+]^3K_1K_2K_3)([H^+]^2K'_1K'_2) \quad (3)$$

the observed limiting current heights $[i_d]_{obsd}$ were 9.45 cm (at $[A]_{\text{uncomplexed}} \approx [A]_{\text{total}} = 7.05$ mM) and 9.10 cm (at $[A]_{tot} = 14.10$ cm) when $[L]_{tot} = 0.40$ mM, pH 7.80, [Tris buffer] = 0.1 M, $T = 25$ °C, $[i_d]_L = 10.30$ cm, and $[i_d]_{LA} = 8.40$ cm (extrapolated from the concentration dependence). Substitution of these two observed values into the right-hand side of eq 2, respectively, gives 0.896 and 1.900. These experimental values are in good agreement with 0.948 and 1.896 obtained with the β_L value and eq 3. The agreement of the two independent measurements is a good support for the postulated 1:1 catechol–H_3L^{3+} complexation. We have ivariably seen good agreement for all the rest of the donor compounds **2**–**14**.

The only successful receptor of catechols among the polyamines (N_4, N_5, and N_6) tested was 18-membered hexaamine L. All the others, including 12–16-membered macromonocyclic tetraamines (e.g., 1,4,8,11-tetraazacyclotetradecane, "cyclam") or 15–17-membered pentaamines (e.g., 1,4,7,10,13-pentaazacyclohexadecane) failed to form complexes with catechols. Recall that the macrocyclic pentaamine ligands (as triprotonated species) are as good as or in some cases even better than the hexaamine L for polyoxyanions.[2-4] The narrower selection of the receptor molecules indicates a stricter geometric requirement for the catechol recognition. The involvement of $(n + m) = 5$ protons in the polyamine L–catechol **1** association permits us to formulate the complex as H_3L^{3+} (triprotonated form of L)–H_2A (proton-undissociated, neutral form of A), taking into account the protonation constants of L and A (see Table II). The value of $\beta_L \approx 10^2$ M^{-1} is greater than those of $\beta_L \approx 10$ M^{-1} for the H_3L^{3+}–dicarboxylate^{2-} interactions,[2] which suggests firmer hydrogen bondings between the rigid chelating oxygens of neutral catechol and the protons on H_3L^{3+}.

Interstingly, the monomethyl ether **5** and dimethyl ether **6** of catechol derivatives form also 1:1 complexes having the same order (ca. 10^2 M^{-1}) of β_L values, leading to an conclusion that the methylated catechols are as good donors as the free catechol group.

(7) Kodama, M.; Kimura, E. *Inorg. Chem.* **1978**, *17*, 2446.

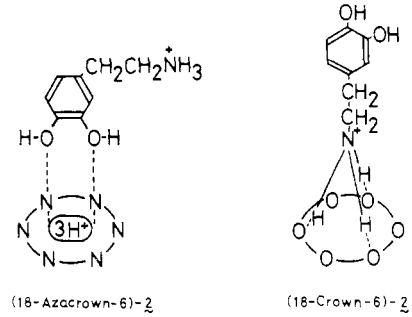

Figure 3. Proposed binding mode of dopamine (**2**) vs. 18-azacrown-6 (L) vs. 18-crown-6.

Further, the similar stabilities for **6** and **7** suggest minor roles of the oxygen groups (CHO, CO_2^-) of the other side of benzene for the association. 1,2,3-Trimethoxybenzene derivative **8** shows a similar β_L value, which may imply little contribution to the complexation from the third methoxy group.

Biologically most interesting with the present catechol receptor model L are the facts that it strongly binds with catecholamines such as dopamine (**2**), Dopa (**3**), and adrenaline (**4**) and that its binding constants are almost the same $\beta_L \sim 10^3$ M^{-1} regardless of the residual groups. The latter fact supports the notion that the interaction occurs with the *o*-dihydroxy benzene part in these catecholamine molecules and is not significantly perturbed by the residual NH_3^+, $N^+H_2CH_3$, CO_2^-, and OH groups on the other side of the donor molecules. On the basis of this knowledge we propose the dopamine–(18-azacrown-6) complex structure as depicted in Figure 3.

Biological receptors of catecholamines in general are supposed to interact with catecholamines at the three binding sites; the ammonium cation, β-hydroxy, and catechol groups.[8] The protonated macrocyclic hexaamine L·3H$^+$ recognizing catecholamines only with the catechol part may be called a partial model of the catecholamine receptor. Whether the biological receptors actually carry the highly protonated active sites for the catechol binding remains to be seen. In this context, it is of interest to note that polyoxygen ligands such as ionophore X 537 A[9-11] and macrocyclic polyethers (crown ethers)[12] are prone to interact with ammonium cations and may be another partial mimic of the catecholamine

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receptor, as often illustrated by the formation of stable 1:1 complexes with catecholamines.[9-11] Thus the oxygen counterpart of L (i.e., 18-crown-6) would recognize dopamine as postulated in Figure 3, wherein the reversed roles of donor-acceptor by the macrocyclic receptor models are compared.

Surprisingly, we have found that the 1,2-dioxychelate is not essential for the interaction with L, as shown by the strong association of resorcinol (1,3-dihydroxybenzene, **9**) (see Table II). However, this is in line with a property of biological catechol receptors that can often recognize resorcinols, as illustrated by some commercial adrenergic drugs bearing the resorcinol function (e.g., metaproterenol). Our catechol receptor model L (as $3H^+$ species) further recognizes an adrenergic blocking drug, dichloroisoproterenol (**10**), most likely for its 1,2-dichlorobenzene part.

Still further, the catechol receptor model L was discovered to be a useful complexing agent with drugs and some functions of drugs or biochemical reagents: tropolone (**11**) (e.g., 4-isopropyltropolone is an inhibitor of tyrosine hydroxylase),[13,14] salicylic acid (**12**) (e.g., aspirin), *p*-aminosalicylic acid (**13**), and α-picolinic acid (**14**) (e.g., fusaric acid, i.e., 5-butylpicolinic acid, is an inhibitor of dopamine β-hydroxylase).[13] Biological activities (e.g., as catecholamine-related enzyme inhibitors), medicinal applications (e.g., drug carriers)[15] or analytical applications (e.g., biochemical analysis of catecholamines and their methoxy metabolites) of L and its various derivatives are now underway in our laboratory.

Registry No. 1, 120-80-9; **1**·L, 84775-03-1; **2**, 51-61-6; **2**·L, 84775-04-2; **3**, 59-92-7; **3**·L, 84775-05-3; **4**, 51-43-4; **4**·L, 84775-06-4; **5**, 121-33-5; **5**·L, 84775-07-5; **6**, 120-14-9; **6**·L, 84775-08-6; **7**, 93-07-2; **7**·L, 84775-09-7; **8**, 54-04-6; **8**·L, 84775-10-0; **9**, 108-46-3; **9**·L, 84775-11-1; **10**, 59-61-0; **10**·L, 84775-12-2; **11**, 533-75-5; **11**·L, 84775-13-3; **12**, 69-72-7; **12**·L, 84775-14-4; **13**, 65-49-6; **13**·L, 84775-15-5; **14**, 98-98-6; **14**·L, 84775-16-6; L, 296-35-5.

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(14) We have tested with colchicine, which has both the 1,2,3-trimethoxybenzene and tropolone parts. Because of the poor reversibility of the polarogram, we could not estimate the β_L value, although the interaction was certain.

(15) We have also found that L is a good carrier of penicillins at neutral pH, which will be reported elsewhere.

Communications to the Editor

Coordination Chemistry and Catalytic Properties of Hydrido(phosphine)ruthenate Complexes

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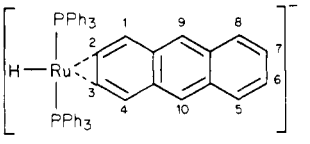
The recently synthesized anionic hydride complex $[RuH_2(PPh_3)_2(PPh_2C_6H_4)]^-$ (**1**)[1] has been reported to exhibit distinctive catalytic properties, including the ability to catalyze the selective hydrogenation of arenes, for example, of anthracene to 1,2,3,4-tetrahydroanthracene.[2] While the role of $[RuH_2(PPh_3)_2(PPh_2C_6H_4)]^-$ as the catalyst precursor was clearly demonstrated, neither the chemistry of the complex under the conditions of the catalytic reactions nor the mechanistic features of the reactions were elucidated. We report here the results of our preliminary studies directed at these themes. These studies encompass the synthesis and characterization of several new anionic ruthenium hydride complexes and the elucidation of their chemistry.

Reaction of $[RuH_2(PPh_3)_2(PPh_2C_6H_4)]^-$ with H_2. Formation of *fac*-$[RuH_3(PPh_3)_3]^-$ (2). $K[RuH_2(PPh_3)_2(PPh_2C_6H_4)]$, prepared as previously described,[1] reacted with H_2 (1 atm) in THF at 25 °C (eq 1) to form, after 24 h in ca. 85% yield, *fac*-$[RuH_3(PPh_3)_3]^-$, which was isolated as the yellow K^+ salt.[3,4] The ^1H NMR signal[3] at δ −9.53 due to the three Ru-bonded protons corresponded to a six-peak multiplet resembling that previously reported for *fac*-$[IrH_3(PPhEt_2)_3]$ and analyzed by computer simulation as an AA′A″XX′X″ pattern.[5]

$$[RuH_2(PPh_3)_2(PPh_2C_6H_4)]^- + H_2 \rightarrow \underset{\mathbf{2}}{fac\text{-}[RuH_3(PPh_3)_3]^-} \quad (1)$$

Reaction of *fac*-$[RuH_3(PPh_3)_3]^-$ with Anthracene. Formation of $[RuH(PPh_3)_2(anthracene)]^-$ (3). *fac*-$[RuH_3(PPh_3)_3]^-$ reacted with an excess of anthracene in THF to form, in quantitative yield (NMR), a new red complex, $[RuH(PPh_3)_2(anthracene)]^-$ (**3**), which was isolated as the K^+ salt.[6] The reaction (eq 2) went to completion in ca. 24 h at 65 °C. The ^1H NMR spectrum[6] of **3** resembles that previously reported for $[Fe(CO)_3(anthracene)]$[7] and is interpreted in terms of an analogous structure (**3**). A structurally related compound, $[IrH(P\text{-}i\text{-}Pr_3)_2(butadiene)]$,[8] has been characterized crystallographically.[9]

$$\underset{\mathbf{2}}{fac\text{-}[RuH_3(PPh_3)_3]^-} + 1.5\text{anthracene} \rightarrow \underset{\mathbf{3}}{[RuH(PPh_3)_2(anthracene)]^-} + 0.5(1,2,3,4\text{-tetrahydroanthracene}) + PPh_3 \quad (2)$$



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Reaction 2 exhibited the same rate law as the isotopic exchange of **2** with D_2 (eq 3), i.e., $-d[\mathbf{2}]/dt = k_4[\mathbf{2}]$, where $k_4 = 7.6 \times 10^{-4}$ s^{-1} at 65 °C, independent of the H_2 (or anthracene) concentration. This implies that both reactions proceed through a common

(1) Pez, G. P.; Grey, R. A.; Corsi, J. *J. Am. Chem. Soc.* **1981**, *103*, 7528-7535.

(2) Grey, R. A.; Pez, G. P.; Wallo, A. *J. Am. Chem. Soc.* **1980**, *102*, 5948-5949.

(3) **2**: ^1H NMR (THF-d_8) δ −9.53 (m, 3 H), 6.70 (m, 18 H), 6.79 (m, 9 H), 7.15 (m, 18 H); $^{31}P\{^1H\}$ NMR (THF-d_8) δ 65.9 (relative to external 85% H_3PO_4; m, 3 P); IR (Nujol) 1857, and 1815 cm^{-1} (RuH); IR (THF) 1835 cm^{-1} (RuH).

(4) All the new complexes described in this communication are extremely air and water sensitive in both the solid state and solution. Compounds **5** and **6** thermally decompose in THF solution over a period of several hours.

(5) Mann, B. E.; Masters, C.; Shaw, B. L. *J. Inorg. Nucl. Chem.* **1971**, *33*, 2195-2204.

(6) **3**: ^1H NMR (THF-d_8) δ −14.1 (t, 1 H, RuH, J_{P-H} = 24 Hz), 2.43 (d, 2 H, $H_{1,4}$), 4.65 (br s, 2 H, $H_{2,3}$), 5.38 (s, 2 H, $H_{9,10}$), 6.52 (m, 4 H, $H_{5,6,7,8}$), 6.87-7.60 (m, 30 H, PPh_3 H); $^{31}P\{^1H\}$ NMR (THF-d_8) δ 69.8 (s, 2 P; splits into expected doublet upon selective decoupling from aromatic protons); IR (Nujol) 1850 cm^{-1} (m, br, RuH).

(7) Manuel, T. A. *Inorg. Chem.* **1964**, *3*, 1794-1796.

(8) Clerici, M. G.; Di Gioacchino, S.; Maspero, F.; Perrotti, M.; Zanobi, A. *J. Organomet. Chem.*, **1975**, *84*, 379-388.

(9) Del Piero, G.; Perego, G.; Cesari, M. *Gazz. Chim. Ital.* **1975**, *105*, 529-537.

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