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bilized by back-bonding with π-acid ligands and house the four metal-based electrons. This classification has the advantage of maintaining a simple electron counting procedure while still suggesting the importance of ligand-to-metal donation into vacant $d\pi$ orbitals.

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Registry No. $Mo(CO)(PhC_2Ph)(S_2CNMe_2)_2$, 81476-50-8; $Mo(CO)(PhC_2H)(S_2CNMe_2)_2$, 74456-79-4; $Mo(CO)(PhC_2Me)(S_2CNMe_2)_2$, 84943-89-5; $Mo(CO)(HC_2Bu\text{-}n)(S_2CNMe_2)_2$, 84943-90-8; $Mo(CO)(EtC_2Et)(S_2CNMe_2)_2$, 84943-91-9; PhC_2Ph, 501-65-5; PhC_2H, 536-74-3; PhC_2Me, 673-32-5; $HC_2Bu\text{-}n$, 693-02-7; EtC_2Et, 928-49-4; CO, 630-08-0; $P(OMe)_3$, 121-45-9; PEt_3, 554-70-1.

Homogeneous Catalysis of Arene Hydrogenation by Cationic Rhodium Arene Complexes

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Arenes react with $[Rh(DIPHOS)(MeOH)_2]^+$ to form 1:1 $[Rh(DIPHOS)(arene)]^+$ adducts. Equilibrium constants for the formation of such adducts in methanol were determined for benzene, naphthalene, and 9-methylanthracene, and the adducts were characterized by ^1H and ^{31}P NMR spectroscopy. The adducts of anthracene and of 9-substituted derivatives thereof catalyze the hydrogenation of the anthracenes to the corresponding 1,2,3,4-tetrahydroanthracenes under relatively mild conditions (50–75 °C (1 atm H_2)). The results of kinetic measurements on such catalytic hydrogenation reactions are reported.

Introduction

Cationic rhodium complexes containing phosphine ligands, notably $[Rh(DIPHOS)(MeOH)_2]^+$ (where DIPHOS = 1,2-bis(diphenylphosphino)ethane), have previously been reported to catalyze the hydrogenation of a variety of substrates including alkenes, alkynes, and ketones.[1] We now report that such complexes also are effective as catalysts for the hydrogenation of arenes, notably of anthracenes to the corresponding 1,2,3,4-tetrahydroanthracenes. The formation and characterization of $[Rh(DIPHOS)(arene)]^+$ complexes, which apparently are the effective catalysts in these hydrogenation reactions, are described, together with some kinetic measurements on the catalytic reactions.

Experimental Section

$[Rh(DIPHOS)(norbornadiene)]BF_4$ was prepared by adaptation of the procedure described for preparation of the corresponding perchlorate.[1b] $[Rh(DIPHOS)(MeOH)_2]^+$ was generated in situ by hydrogenation of $[Rh(DIPHOS)(norbornadiene)]^+$ as previously described.[2]

Equilibrium constants for the formation of $[Rh(DIPHOS)(arene)]^+$ complexes were determined in methanol by spectral titrations at ca 500 nm similar to those described previously for $[Rh(DIPHOS)(benzene)]^+$.[2]

^1H NMR spectra were determined with a Bruker HS-270 spectrometer and ^{31}P NMR spectra with a Bruker HFX-90 spectrometer.

Kinetic measurements were made on catalytic hydrogenation reactions performed in Fisher-Porter bottles. Initial reaction rates were determined by periodic sampling and analysis of the solution using a Varian 1400 gas chromatography equipped with a flame ionization detector and a $^1/_8$ in. × 10 ft 20% DEGS on Chrom W (60/80) column. The identification of the products was substantiated by ^1H NMR spectroscopy. The isotopic composition of the products of reaction with D_2 was determined mass spectrometrically. All equilibrium and kinetic measurements were made in methanol solution.

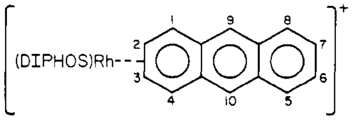
Results and Discussion

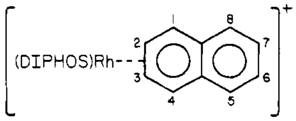
Formation and Characterization of $[Rh(DIPHOS)(arene)]^+$ Complexes. The formation of $[Rh(DIPHOS)(benzene)]^+$ according to reaction 1 and the characterization of this complex have previously been described.[2]

$$[Rh(DIPHOS)(MeOH)_2]^+ + \text{benzene} \overset{K_1}{\rightleftharpoons} [Rh(DIPHOS)(benzene)]^+ \quad (1)$$

These studies were extended to the corresponding naphthalene and anthracene complexes including (a) determination of the ^1H and ^{31}P NMR spectra of the complexes and (b) determination of the equlibrium constants (K_1) for the formation of the complexes according to eq 1. Because of the low solubility of anthracene in methanol, the equilibrium constant K_1 was determined for the adduct of 9-methylanthracene.

The NMR parameters of the $[Rh(DIPHOS)(arene)]^+$ complexes are listed in Table I using the numbering systems shown below. Where appropriate, the assignments were confirmed by using selective decoupling to identify adjacent protons. Some NMR data for $[Rh(DIPHOS)(diene)]^+$ complexes also are listed in Table I for comparison.





The structure of the $[Rh(DIPHOS)(benzene)]^+$ adduct has previously been inferred to involve symmetrical η^6

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Table I. Formation Constants (K_1) and NMR Parameters of $[Rh(DIPHOS)(arene)]^+$ Complexes in Methanol at 25 °C

arene	K_1, M^{-1}	arene ^1H NMR (δ)			^{31}P NMR	
		protons	coordinated	free	δ	J_{Rh-P}, Hz
benzene[a]	20	1-6	6.36[b]	7.4[b]	75.3[b]	204[b]
naphthalene	2.6×10^2	2, 3	6.24	7.45	77.2	205
		1, 4	6.78	7.80		
		5, 8	7.33	7.80		
		6, 7	7.16	7.45		
anthracene	. . .	2, 3	6.32	7.49	75.6	202
		1, 4	6.80	8.00		
		5, 8	7.85	8.00		
		6, 7	7.70	7.49		
		9, 10	c	8.44		
9-Me-anthracene	1.6×10^3	. . .	. . .	. . .	71.3	202
1,3-cyclohexadiene	5.7×10^3	. . .	. . .	. . .	60	171
norbornadiene	$>10^5$	. . .	. . .	. . .	9.8	156

[a] From ref 2. [b] In CD_2Cl_2. [c] Obscured by phenyl protons ($7.7 > \delta > 7.2$).

Table II. Kinetic Data

arene	[arene], M	10^3[Rh], M	$10^2[H_2]$,[a] M	temp, °C	10^6 × initial rate, M s^{-1}	10^2k_2, M^{-1} s^{-1}
9-CF_3CO-anthracene	0.183	9.0	1.85	59.7	12.4	7.4
9-CF_3CO-anthracene	0.183	5.0	1.85	59.7	7.4	8.0
9-CF_3CO-anthracene	0.183	2.3	1.85	59.7	3.4	8.1
9-CF_3CO-anthracene	0.183	9.0	2.38	59.7	16.1	7.8
9-CF_3CO-anthracene	0.183	9.0	1.05	59.7	8.5	9.0
9-CF_3CO-anthracene	0.183	9.0	0.40	59.7	4.2	10.7
9-CF_3CO-anthracene	0.146	9.0	1.85	59.7	12.4	9.5
9-CF_3CO-anthracene	0.109	9.0	1.85	59.7	11.9	9.1
9-CF_3CO-anthracene	0.074	9.0	1.85	59.7	12.4	9.5
9-CF_3CO-anthracene	0.037	9.0	1.85	59.7	11.2	8.6
9-CF_3CO-anthracene	0.118	9.0	1.85	53.2	9.6	7.4
9-CF_3CO-anthracene	0.103	9.0	1.85	66.2	30.6	23.7
9-CF_3CO-anthracene	0.107	9.0	1.85	75.9	48.4	37.1
9-CH_3-anthracene	0.151	9.0	1.85	60.8	13.6	10.4
anthracene	slurry	9.3	1.85	60.0	9.1	5.3
naphthalene	0.63	9.0	2.38	60.7	1.5[b]	0.6[b]

[a] Based on H_2 solubility in methanol of 3.9×10^{-3} M atm^{-1}. [b] Based on initial rate; catalyst decomposes after 2-3 turnovers.

coordination of the benzene ligand to Rh,[2] in agreement with the X-ray structures of several closely related arene adducts.[2-4] Coordination of the arene through one of the end rings in the corresponding $[Rh(DIPHOS)(naphthalene)]^+$ and $[Rh(DIPHOS)(anthracene)]^+$ adducts also can be inferred from the large upfield shifts of the 1,2,3,4-protons in each case (Table I). The pattern of chemical shifts for $[Rh(DIPHOS)(anthracene)]^+$ resembles that for $[Cr(CO)_3(anthracene)]^+$ (η^6)[5] rather than for $[Fe(CO)_3(anthracene)]$ (η^4)[5] or $[RuH(PPh_3)_2(anthracene)]^-$ (η^4),[6] particularly in respect of the displacements of the chemical shifts of the 2,3-protons to higher fields than those of the 1,4-protons. This suggests that the mode of bonding of the arene is η^6 (as in $[Rh(DIPHOS)(benzene)]^+$) rather than η^4. This conclusion also is consistent with (a) the fact that Rh achieves an 18-valence-electron configuration in these complexes through η^6 bonding of the arene and (b) the finding (Table I) that the Rh–P coupling constants of $[Rh(DIPHOS)(naphthalene)]^+$ and $[Rh(DIPHOS)(anthracene)]^+$ are close to that of $[Rh(DIPHOS)(benzene)]^+$ rather than to those of the diene adducts $[Rh(DIPHOS)(1,3\text{-cyclohexadiene})]^+$ and $[Rh(DIPHOS)(\text{norbornadiene})]^+$.

The equilibrium constants, K_1, for the formation of the $[Rh(DIPHOS)(arene)]^+$ complexes also are listed in Table I.[7] These increase markedly along the sequence: benzene (20 M^{-1}) < naphthalene (2.6×10^2 M^{-1}) < 9-methylanthracene (1.6×10^3 M^{-1}).

Catalytic Hydrogenation

Under relatively mild conditions (≲60 °C (1 atm H_2)), the rate of hydrogenation of benzene in the presence of the corresponding $[Rh(DIPHOS)(arene)]^+$ complex was negligible. However hydrogenation of anthracene, 9-methylanthracene and 9-CF_3CO-anthracene was found to be catalyzed by the corresponding $[Rh(DIPHOS)(arene)]^+$ adducts at conveniently measurable rates. The product in each case was the 1,2,3,4-tetrahydroanthracene, together with a small amount (~1%) of the corresponding 1,2,3,4,5,6,7,8-octahydroanthracene. The catalyst system was stable, and no diminution of rate could be detected after ca. 20 turnovers. Under the same conditions, the hydrogenation of naphthalene (to 1,2,3,4-tetrahydronaphthalene) was considerably slower but still measurable.

Table II summarizes the results of kinetic measurements on the $[Rh(DIPHOS)(9\text{-}CF_3CO\text{-anthracene})]^+$-catalyzed hydrogenation of 9-CF_3CO-anthracene as well as on the corresponding hydrogenations of several other arenes.[7]

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The data are consistent with the second-order rate law corresponding to eq 2 with k (59.7 °C) = $(9.0 \pm 1.0) \times 10^{-2}$ $M^{-1}\ s^{-1}$, $\Delta H^{\ddagger} = 16.6 \pm 2$ kcal/mol, and $\Delta S^{\ddagger} = -14 \pm 5$ cal/mol K (all for 9-CF_3CO-anthracene).

$$-d[\text{arene}]/dt = k[\text{Rh(DIPHOS)(arene)}^+][H_2] \quad (2)$$

The rate law is similar to that found earlier for the [Rh(DIPHOS)(olefin)]$^+$-catalyzed hydrogenation of olefins[2,8] and may be interpreted in terms of a similar mechanism, depicted by eq 3–5.

$$[\text{Rh(DIPHOS)(anthracene)}]^+ + H_2 \xrightarrow[\text{rate determining}]{k_2} \text{1,2-dihydroanthracene} + [\text{Rh(DIPHOS)(MeOH)}_2]^+ \quad (3)$$

$$\text{1,2-dihydroanthracene} + H_2 \xrightarrow{[\text{Rh(DIPHOS)(MeOH)}_2]^+} \text{1,2,3,4-tetrahydroanthracene} \quad (4)$$

$$[\text{Rh(DIPHOS)(MeOH)}_2]^+ + \text{anthracene} \overset{\text{fast}}{\rightleftharpoons} [\text{Rh(DIPHOS)(anthracene)}]^+ \quad (5)$$

The following features of this interpretation warrant comment. 1. The stepwise hydrogenation, i.e., via 1,2-dihydroanthracene, is consistent with earlier demonstrations that other dienes (norbornadiene, 1,3-cyclohexadiene, etc.)[1c] are hydrogenated in two stages via the intermediate monoenes. Since olefins typically are hydrogenated more rapidly than anthracene, the failure of the 1,2-dihydroanthracene to accumulate is expected. In line with this, the rate constant for the hydrogenation of 1,2-dihydronaphthalene to 1,2,3,4-tetrahydronaphthalene was found to be 2.2 $M^{-1}\ s^{-1}$ at 60 °C (vs. $5 \times 10^{-2}\ M^{-1}\ s^{-1}$ for anthracene and $6 \times 10^{-3}\ M^{-1}\ s^{-1}$ for naphthalene).

2. In one set of comparisons (Table II), anthracene, 9-methylanthracene, and 9-CF_3CO-anthracene exhibited very similar rates of catalytic hydrogenation. From the relative rates of formation of 1,2,3,4-tetrahydroanthracene and 1,2,3,4,5,6,7,8-octahydroanthracene, the rate of hydrogenation of 1,2,3,4-tetrahydroanthracene can be estimated to be about 10^{-1}–10^{-2} that of anthracene. In accord with this the corresponding rate constant for hydrogenation of the closely related substrate, naphthalene, was found to be $6 \times 10^{-3}\ M^{-1}\ s^{-1}$ at 60 °C (vs. $5 \times 10^{-2}\ M^{-1}\ s^{-1}$ for anthracene).

3. The hydrogenation of the [Rh(DIPHOS)(arene)]$^+$ adduct (reaction 3) presumably proceeds through the following sequence, previously demonstrated[5] for olefinic substrates, in which step a is rate determining: (a) oxidative addition of H_2 to form [RhH_2(DIPHOS)(arene)]$^+$, (b) migratory insertion to form a hydridoalkyl complex [RhH(>C–C(H)<(DIPHOS)S_n]$^+$, and (c) C–H bond-forming reductive elimination to yield the hydrogenated product and regenerate [Rh(DIPHOS)S_2]$^+$. For oxidative addition of H_2 to occur, the [Rh(DIPHOS)(arene)]$^+$ adduct presumably must adopt the 16-electron η^4 configuration. Such a configuration is expected to be readily accessible for anthracene in view of the fairly low localization energy (1.16 β, Hückel approximation) involved in going from the "anthracene" to the "diene + naphthalene" configuration. The corresponding localization energies for naphthalene and, especially, for benzene are considerably higher (1.21 and 1.53 β, respectively) presumably contributing to the lower reactivities of these arenes. Indeed, slight displacement from a symmetrical η^6 configuration toward such a η^4 configuration can be discerned in the structurally characterized [$Cr(CO)_3$(anthracene)] complex.[9] The readier accessibilty of the η^4 configuration also has been invoked to explain the more facile displacement of anthracene and naphthalene (relative to benzene) from [$Cr(CO)_3$(arene)] and [Cr(arene)$_2$] complexes.[10]

4. Hydrogenation of anthracene with D_2 in CH_3OH yielded a mixture (identified mass spectrometrically and by ^2H NMR spectroscopy) comprising tetrahydroanthracene-d_1, d_2, d_3, and d_4 with D incorporation in the 1-, 2-, 3-, and 4-positions only. Hydrogenation with H_2 in CH_3OD yielded a similar product mixture, whereas reaction with D_2 in CH_3OH yielded predominantly the d_4 product. This demonstrates the occurrence of exchange between some intermediate rhodium hydride species (i.e., [RhH_2(DIPHOS)(arene)]$^+$ or [RhH(CCH)(DIPHOS)S_n]$^+$ and the –OH(D) protons of the solvent. Such exchange also has been observed[11] in certain olefin hydrogenation reactions and is not unexpected in view of the acidic properties of cationic rhodium hydrides.[1c]

The selectivity exhibited by this catalyst system for anthracene hydrogenation (reflected in the formation of 1,2,3,4-tetrahydroanthracene) differs from that previously found for the $HCo(CO)_4$-catalyzed hydrogenation which yields 9,10-dihydroanthracene and which has been interpreted in terms of a free radical mechanism.[12,13] In this connection it is noteworthy that the same selectivity (i.e., to 1,2,3,4-tetrahydroanthracene) now has been observed also for neutral [$Rh(\eta^5\text{-}C_5Me_5)Cl_2]_2$[14] and anionic [$RuH_2(PPh_3)_2(PPh_2C_6H_4)]^-$[6,15] catalysts and probably reflects the ability of the catalyst, in each case, to hydrogenate anthracene while coordinated in a "diene" (i.e., 1,2,3,4-η^4) mode.

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Registry No. [Rh(DiPHOS)(naphthalene)]$^+$, 85004-99-5; [Rh(DiPHOS)(anthracene)]$^+$, 85005-00-1; [Rh(DiPHOS)(9-Me-anthracene)]$^+$, 85005-01-2; [Rh(CiPHOS)(1,3-cyclohexadiene)]$^+$, 85005-02-3; [Rh(DiPHOS)(norbornadiene)]BF_4, 60430-43-5; [Rh(DiPHOS)(9-CF_3CO-anthracene)]$^+$, 85005-03-4; 9-CF_3CO-anthracene, 53531-31-0; 9-CH_3-anthracene, 779-02-2; anthracene, 120-12-7; naphthalene, 91-20-3.

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