

REACTIVITY OF ARENECHROMIUM CARBONYL COMPLEXES TOWARDS ISOTOPIC HYDROGEN EXCHANGE WITH ACIDS

A.A. TSOY, N.K. BARANETSKAYA, V.N. SETKINA and D.N. KURSANOV *

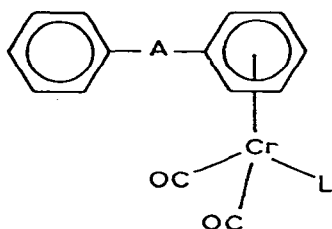
Institute of Organo-Element Compounds, Academy of Sciences of the USSR, Vasilova Street 28, Moscow B-312 (U.S.S.R.)

(Received December 16th, 1980)

Summary

The hydrogen isotopic exchange reaction (HIE) of the $\text{ArGr}(\text{CO})_2\text{L}$ complexes (I, $\text{L} = \text{CO}$; II, $\text{L} = \text{PPh}_3$, and Ar is biphenyl, diphenylmethane, dibenzyl, diphenyloxide and benzophenone, as well as the corresponding binuclear arenes) in CF_3COOD has been studied. The rate constants of HIE have been determined. It was shown that in the series of complexes II such ring substituents as Ph, PhCH_2 , PhCH_2CH_3 , PhO had no effect on the rate, in sharp contrast with the reaction of the corresponding free binuclear arenes. A quantitative estimation indicates that the *o*-, *m*- and *p*-positions in the π -coordinated ring of the complexes II have almost the same reactivity, i.e. the orientating effect of substituents in HIE is weak. The effect of the π -coordination with the transition metal atom on the uncoordinated ring of the binuclear aromatic π -ligand is discussed.

The reactivity of π -complexes is at present a major topic of investigation. The present paper deals with hydrogen isotopic exchange (HIE) of the π -arenechromium carbonyl complexes in CF_3COOD , i.e. with the reaction which may be regarded as the simplest model for electrophilic substitution. The chromium complexes studied contained the following aromatic binuclear π -ligands;



(I, $\text{L} = \text{CO}$; II, $\text{L} = \text{PPh}_3$)

a, $\text{A} = -$;

b, $\text{A} = -\text{CH}_2-$;

c, $\text{A} = -\text{CH}_2-\text{CH}_2-$;

d, $\text{A} = -\text{CO}-$;

e, $\text{A} = -\text{O}-$.

These compounds attract special interest because they simultaneously contain a π -coordinated and a non-coordinated benzene ring, either connected by a single bond or divided by different bridges —A—. On the basis of a study of the IR spectra of substituted biphenyltricarboxylchromium, Brown et al. [1] concluded that the substituent effect was transmitted to the carbonyl groups not only by the ring coordinated with the tricarboxylchromium group, but also by the uncoordinated ring. At the same time PMR spectral data show that the upfield shift of proton signals from the binuclear aromatic ligand occurs only for the ring coordinated with the tricarboxylchromium group [1].

It is of interest to estimate the reactivity of both rings in order to get an insight into the transfer of the effect of coordination with the transition metal atom to the uncoordinated ring. No less interesting is the estimation of the reactivity of different positions of the π -coordinated ring, which could supply valuable information on the orientating effect of the substituents. This problem has been previously studied only in the case of methylbenzoatechromium dicarbonyl triphenylphosphine [2]. Bearing this in mind, we have investigated the HIE reaction of the complexes Ia—Ie and IIa—IIe, and that of the corresponding uncoordinated binuclear arenes, using CF_3COOD both as reagent and medium (Table 1).

Comparison of HIE rate constants for the π -arenecarbonyl complexes and those for the initial binuclear arenes shows that the coordination with the tricarboxylchromium group leads to a decrease of HIE reaction rate, but to different extents. For instance, with biphenyl, diphenylmethane and dibenzyl the rate constants decrease by approximately an order of magnitude, while in the case of diphenyloxide the decrease is three orders of magnitude. This results for

TABLE 1

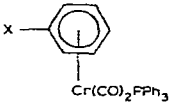
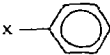
SUMMARY OF HIE REACTION RATE CONSTANTS FOR THE BINUCLEAR ARENES AND THEIR CARBOXYLCHROMIUM COMPLEXES IN CF_3COOD AT 50°C

Ar	k_{HIE} (sec^{-1})		
	Arene	$\text{ArCr}(\text{CO})_3$	$\text{ArCr}(\text{CO})_2\text{PPh}_3$
	1.4×10^{-7}	1.0×10^{-8}	2.2×10^{-6}
	1.3×10^{-7}	2.1×10^{-8}	1.7×10^{-6}
	2.0×10^{-7}	1.2×10^{-8}	3.8×10^{-6}
	1.1×10^{-5}	4.1×10^{-8}	3.8×10^{-6}
	$2.2 \times 10^{-9} \text{ }^a$	$3.2 \times 10^{-9} \text{ }^a$	3.8×10^{-6}
	no exchange	no exchange	3.2×10^{-7}

^a See ref. 3.

TABLE 2

HIE REACTION RATE CONSTANTS FOR $\text{XC}_6\text{H}_5\text{Cr}(\text{CO})_2\text{PPh}_3$ AND XC_6H_5 (CF_3COOD , 50°C)

X			
	k_{HIE} (sec^{-1}) ^a	$k_{\text{rel.}}$	$k_{\text{rel.}}$
H	3.8×10^{-6}	1	1
PhO	3.8×10^{-6}	1	5×10^3
PhCH ₂ CH ₂	3.8×10^{-6}	1	91
PhCH ₂	4.3×10^{-6}	1.1	59
Ph	2.2×10^{-6}	0.6	64
PhCO	3.2×10^{-7}	0.08	no exchange

^a HIE reaction rate constants of the π -coordinated rings are given.

the reactivity of π -complexes of biphenyl, diphenylmethane, dibenzyl and diphenyloxide to be approximately the same. Replacement of one CO group in I by a donor PPh_3 ligand markedly increases the nucleophilicity of the benzene rings; the rate of HIE with acids increases by 2–3 orders of magnitude.

Consideration of the effect of PhO, PhCH₂, PhCH₂CH₂, Ph substituents on the π -benzene ring on the HIE reaction rate shows (Table 2) that these substituents have practically no effect on the HIE reaction rate of $\text{ArCr}(\text{CO})_2\text{PPh}_3$. At the same time, in the initial aromatic compounds the substituents increase the reaction rate by 1–3 orders of magnitude.

The PhCO substituent on the π -benzene ring of benzenechromium dicarbonyl triphenylphosphine (Table 2) decreases the rate of HIE by approximately an order of magnitude. Benzophenone and benzophenone-tricarbonylchromium undergo no exchange under the conditions used. This fact is somewhat unexpected, since electron-withdrawing substituents (CH_3OOC , CH_3CO) on the π -benzene ring of $\text{XC}_6\text{H}_5\text{Cr}(\text{CO})_2\text{PPh}_3$ were shown to accelerate the rate of HIE [4]. For example, methylbenzoatechromium dicarbonyl triphenylphosphine reacts about 10 times faster than benzenechromium dicarbonyl triphenylphosphine. Increase of the reaction rate is observed in the case where electron-withdrawing substituents are introduced into the π -benzene ring of $\text{ArCr}(\text{CO})_3$. For example, a protonated dimethylamino group accelerates the reaction by approximately two orders of magnitude [4], and a carbomethoxy group increases the rate constant by a factor of about 5 [3].

We have also studied the reactivity of different positions of the π -coordinated ring in arenecarbonyl chromium complexes. Using a combination of PMR and HIE methods the reactivity was estimated in terms of partial rate factors (Fig. 1).

It was found that the partial rate factor of the *p*-position, f_p , in benzophenonechromium dicarbonyl triphenylphosphine is 10 times lower than f_o and f_m , which means that the reactivity of the *para*-position is lower. This fact is in agreement with the orientating effect of PhCO as an acceptor substituent. In diphenyloxidechromium dicarbonyl triphenylphosphine, in line with the donor nature of PhO, the lowest reactivity is shown by the *meta*-position of the π -benzene ring.

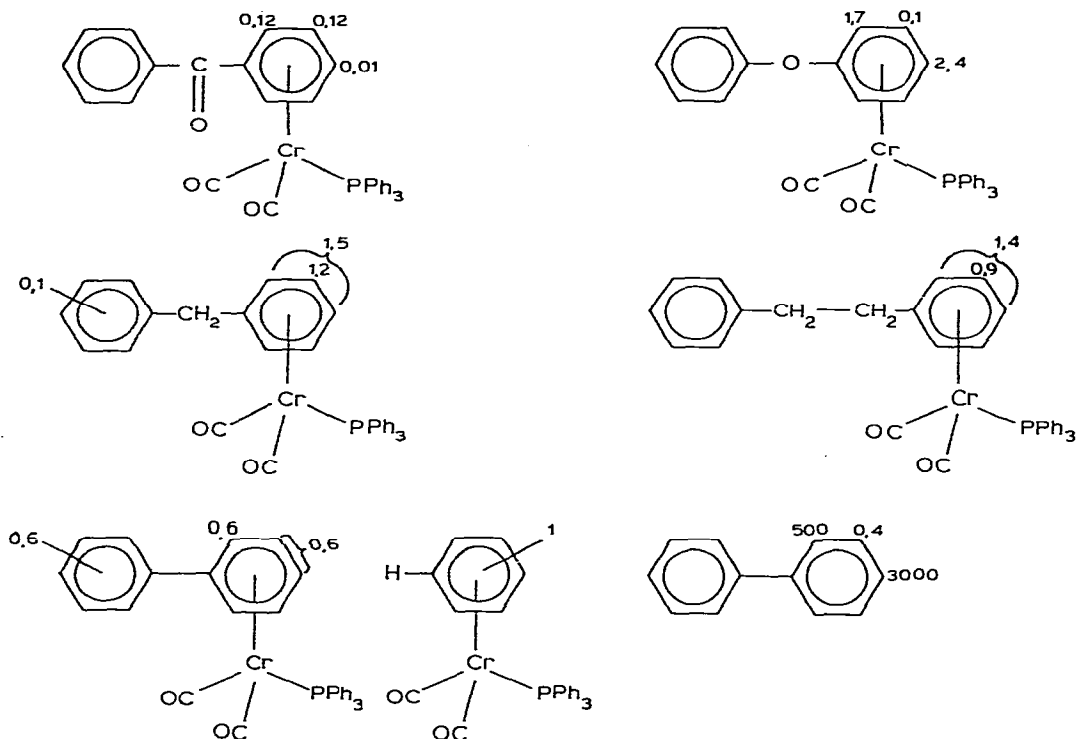


Fig. 1. Partial rate factors towards isotopic hydrogen exchange.

Meta- and *para*-protons in the PMR spectrum of biphenylchromium dicarbonyl triphenylphosphine (spectrometer working frequency 250 MHz), as well as *ortho*- and *para*-protons in the spectra of diphenylmethanechromium dicarbonyl triphenylphosphine (90 MHz) and dibenzylchromium dicarbonyl triphenylphosphine (360 MHz), gave overlapping signals, which made it impossible to estimate the partial rate factors for all the unequal positions in these systems. In chromium dicarbonyl triphenylphosphine complexes of diphenylmethane and dibenzyl the reactivity of the *meta*-position is close to that of (*ortho* + *para*)-positions, despite the fact that, according to the donor nature of PhCH_2 and PhCH_2CH_2 , this position should have shown the lowest reactivity. Figure 1 gives, for the sake of comparison, the partial rate factors for biphenyl [5] which range over almost 4 orders of magnitude. At the same time, the partial rate factors for different positions in the π -coordinated ring of biphenylchromium dicarbonyl-triphenylphosphine are close to each other. Accordingly, π -coordination with the transition metal weakens the orientating effect of substituents on the π -benzene ring.

Using the data on HIE rate constants for I and II under identical conditions, we could consider the question of whether coordination with the transition metal atom affects the uncoordinated ring of the binuclear aromatic π -ligand. In the case of compounds Ia–Ie an unambiguous answer could be obtained by estimating the amount of deuterium incorporated into the uncoordinated and coordinated phenyl rings of the complex and the phenyl rings of the initial

TABLE 3

HIE OF BINUCLEAR AROMATIC COMPOUNDS AND THEIR TRICARBONYL CHROMIUM COMPLEXES (CF₃COOD, 50°C)

Compound	Exchange time (h)	Deuterium atom content in molecule ^a	k _{HIE} (sec ⁻¹)
C ₆ H ₅ C ₆ H ₅ Cr(CO) ₃	600	0.19	1.0 × 10 ⁻⁸
C ₆ H ₅ C ₆ H ₅	600	2.31 ^b	1.4 × 10 ⁻⁷
C ₆ H ₆ Cr(CO) ₃	600	~0.02 ^b	2.2 × 10 ⁻⁹
C ₆ H ₅ CH ₂ C ₆ H ₅ Cr(CO) ₃	462	0.35	2.1 × 10 ⁻⁸
C ₆ H ₅ CH ₂ C ₆ H ₅	462	1.70 ^b	1.3 × 10 ⁻⁷
C ₆ H ₆ Cr(CO) ₃	462	~0.02 ^b	2.2 × 10 ⁻⁹
C ₆ H ₅ CH ₂ CH ₂ C ₆ H ₅ Cr(CO) ₃	482	0.36	1.2 × 10 ⁻⁸
C ₆ H ₅ CH ₂ CH ₂ C ₆ H ₅	482	2.58 ^b	2.0 × 10 ⁻⁷
C ₆ H ₆ Cr(CO) ₃	482	~0.02 ^b	2.2 × 10 ⁻⁹
C ₆ H ₅ OC ₆ H ₅ Cr(CO) ₃	459	0.59	4.1 × 10 ⁻⁸
C ₆ H ₅ OC ₆ H ₅	459	8.00 ^b	1.1 × 10 ⁻⁵
C ₆ H ₆ Cr(CO) ₃	459	~0.02 ^b	2.2 × 10 ⁻⁹

^a Deuterium atom content determined by mass spectrometry. ^b Calculated from the established HIE rate constants.

binuclear arene during the same reaction time (Table 3).

For example, after 600 hours of HIE the deuterium content in biphenylchromium tricarbonyl is equal to 0.19 D, in biphenyl to 2,31 D and in benzenechromium tricarbonyl ~0.02 D, i.e. the reactivity of biphenylchromium tricarbonyl is lower than that of biphenyl, but higher than the reactivity of benzenechromium tricarbonyl. This correlation between deuterium content in biphenyl, biphenylchromium tricarbonyl and benzenechromium tricarbonyl points to the transfer of tricarbonylchromium group effect to the uncoordinated ring of biphenylchromium tricarbonyl.

The same pattern is observed with compounds Ib, Ic and Ie. Therefore, the transfer of the tricarbonylchromium group effect to the uncoordinated ring of the binuclear π -ligand occurs whatever the nature of the bridge —A— (A = —, CH₂, CH₂CH₂, O).

The amount of deuterium in the coordinated and the uncoordinated phenyl rings of deuterated triphenylphosphinechromium dicarbonyl complexes was determined from PMR spectra. These data were compared with similar data for the amount of deuterium accumulated during the same time interval by the corresponding tricarbonyl complexes, the starting binuclear arenes and benzenechromium dicarbonyl triphenylphosphine, in order to consider the transfer of the effect of the triphenylphosphinechromium dicarbonyl group to the uncoordinated ring of the binuclear aromatic ligand. The coordinated and the uncoordinated phenyl rings of biphenylchromium dicarbonyl triphenylphosphine contained virtually the same amount of deuterium (Table 4) and therefore possess close reactivity in HIE. Significantly, in the course of the same reaction time the uncoordinated ring of biphenylchromium dicarbonyl triphenylphosphine acquires far more deuterium (up to 0.78 D) than the whole molecule of biphenylchromium tricarbonyl (0.01 D) and even the starting biphenyl (0.12 D). (Table 5). This means that the substitution of a CO group in biphenylchromium tricarbonyl

TABLE 4

DISTRIBUTION OF DEUTERIUM BETWEEN THE COORDINATED AND THE UNCOORDINATED PHENYL RINGS OF BIPHENYLCHROMIUM DICARBONYL TRIPHENYLPHOSPHINE

No.	Exchange time (h)	Deuterium content (atoms)		k_{HIE} (sec ⁻¹)	
		coord. ring	uncoord. ring	coord. ring	uncoord. ring
1	25	0.78	0.78	2.1×10^{-6}	2.1×10^{-6}
2	27	0.82	0.82		

TABLE 5

DEUTERIUM CONTENT IN BIPHENYLCHROMIUM DICARBONYL TRIPHENYLPHOSPHINE, BIPHENYLCHROMIUM TRICARBONYL, BIPHENYL AND BENZENECHROMIUM DICARBONYL TRIPHENYLPHOSPHINE

Compound	Exchange time (h)	Deuterium content (atoms)	k_{HIE} (sec ⁻¹)
$\text{C}_6\text{H}_5\text{C}_6\text{H}_5\text{Cr}(\text{CO})_2\text{PPh}_3$	25	0.78 + 0.78 ^a	2.2×10^{-6}
$\text{C}_6\text{H}_5\text{C}_6\text{H}_5\text{Cr}(\text{CO})_3$	25	0.01 ^b	1.0×10^{-8}
$\text{C}_6\text{H}_5\text{C}_6\text{H}_5$	25	0.12 ^b	1.4×10^{-7}
$\text{C}_6\text{H}_6\text{Cr}(\text{CO})_2\text{PPh}_3$	25	1.38 ^b	3.8×10^{-6}
$\text{C}_6\text{H}_5\text{C}_6\text{H}_5\text{Cr}(\text{CO})_2\text{PPh}_3$	27	0.82 + 0.82	
$\text{C}_6\text{H}_5\text{C}_6\text{H}_5\text{Cr}(\text{CO})_3$	27	0.01	
$\text{C}_6\text{H}_5\text{C}_6\text{H}_5$	27	0.13	
$\text{C}_6\text{H}_6\text{Cr}(\text{CO})_2\text{PPh}_3$	27	1.46	

^a The addends are the amounts of deuterium in the coordinated and the uncoordinated ring respectively. ^b Calculated from the rate constants of HIE (for all the reaction times considered).

bonyl by a donor PPh_3 ligand affects the reactivity of the coordinated as well as the uncoordinated ring in one and the same manner.

PMR evidence (Table 6) indicates that the coordinated phenyl ring of diphenylmethanechromium dicarbonyl triphenylphosphine is more susceptible to HIE than the uncoordinated ring.

The data on the deuterium content were checked by the ^2H NMR method.

TABLE 6

DISTRIBUTION OF DEUTERIUM BETWEEN THE COORDINATED AND THE UNCOORDINATED PHENYL RINGS OF DIPHENYLMETHANECHROMIUM DICARBONYL TRIPHENYLPHOSPHINE

No.	Exchange time (h)	Deuterium content (atoms)		k_{HIE} (sec ⁻¹)	
		coord. ring	uncoord. ring	coord. ring	uncoord. ring
1	24	1.22	0.13	4.3×10^{-6}	4.0×10^{-7}
2	48	2.16	0.25		
3	56	2.23	0.34		
4	284	3.82	1.16		

TABLE 7
 DEUTERIUM CONTENT OF DIPHENYLMETHANECHROMIUM DICARBONYL TRIPHENYLPHOSPHINE, BENZENECHROMIUM DICARBONYL TRI-
 PHENYLPHOSPHINE, DIPHENYLMETHANECHROMIUM TRICARBONYL AND DIPHENYLMETHANE

Exchange time (h)	Deuterium content (atoms)			
	$C_6H_5CH_2C_6H_5Cr(CO)_2PPh_3$	$C_6H_6Cr(CO)_2PPh_3$ ^b	$C_6H_5CH_2C_6H_5Cr(CO)_3$ ^b	$C_6H_5CH_2C_6H_5$ ^b
24	1.22 + 0.13 ^a	1.12	0.02	0.09
48	2.16 + 0.25	1.98	0.03	0.18
56	2.23 + 0.34	2.14	0.03	0.21
284	3.82 + 1.16	3.92	0.18	1.08
k_{HIE} , mid. (sec^{-1})	1.7×10^{-6}	3.8×10^{-6}	2.1×10^{-8}	1.3×10^{-7}

^a The first addend is the content of deuterium in the coordinated ring, the second in the uncoordinated ring. ^b Calculated from the rate constants of HIE determined for all the reaction times considered.

The spectrum of sample 4 (Table 6) contained two ^2H nuclei signals, one with a chemical shift $\delta = 2.53$ ppm, corresponding to the ^2H nuclei of the coordinated ring, and one with $\delta = 5.03$ ppm, corresponding to the ^2H nuclei of the uncoordinated ring. Integration of the relevant signals showed that the coordinated ring contains 3.79 D and the uncoordinated 1.15 D, in fair agreement with the PMR data.

To consider the transfer of the effect of the chromium dicarbonyl triphosphine group to the uncoordinated ring of diphenylmethanechromium dicarbonyl triphenylphosphine, the data on the deuterium content of the coordinated and the uncoordinated ring of this complex were compared to those for diphenylmethanechromium tricarbonyl, diphenylmethane and benzenechromium dicarbonyl triphenylphosphine (Table 7). The coordinated ring was found to contain almost as much deuterium (1.22 D) as the π -benzene ring of benzenechromium dicarbonyl triphenylphosphine (1.12 D). The deuterium content in the uncoordinated ring is higher (0.13 D) than that in one phenyl ring of diphenylmethanechromium dicarbonyl (0.01 D), and even that in the starting diphenylmethane (0.04 D).

Therefore, the separation of the phenyl rings by a CH_2 group in diphenylmethanechromium dicarbonyl triphenylphosphine does not prevent, but only decreases the transfer of the PPh_3 group effect: the coordinated ring of diphenylmethanechromium dicarbonyl triphenylphosphine contains more deuterium (1.22 D) than the uncoordinated ring (0.13 D).

With dibenzylchromium dicarbonyl triphenylphosphine, the mass spectrometry data on the overall content of deuterium in the molecule are in fair agreement with the PMR evidence concerning the deuterium content of the coordinated ring (Table 8). This means the uncoordinated ring contains no deuterium, as is also demonstrated by the ^2H NMR spectrum of sample 4 (82% conversion, Table 8): the only signal with the chemical shift $\delta = 2.59$ ppm is that of the ^2H nuclei of the coordinated ring. The absence of deuterium in the uncoordinated ring indicates that the HIE with this ring is essentially slower than that with the coordinated ring, so that during the reaction times investigated the uncoordinated ring merely fails to accumulate enough deuterium to be detected by the PMR method (the accuracy of deuterium content measurements was $\epsilon = \pm 0.04$ D).

Table 9 gives the results on the deuterium content of dibenzylchromium dicarbonyl triphenylphosphine, benzenechromium dicarbonyl triphenylphosphine,

TABLE 8

DEUTERIUM CONTENT OF DIBENZYLCHROMIUM DICARBONYL TRIPHENYLPHOSPHINE AS DETERMINED BY PMR AND MASS SPECTROSCOPY

No.	Exchange time (h)	Deuterium content (D)		Exchange (%)
		PMR data (in the coord. ring)	Mass spectr. data (in the molecule)	
1	20	1.11	0.96	24
2	30	1.37	1.36	33
3	40	1.69	1.66	41
4	143	2.84	2.84	82

TABLE 9

DEUTERIUM CONTENT OF DIBENZYLCHROMIUM DICARBONYL TRIPHENYLPHOSPHINE, BENZENECHROMIUM DICARBONYL TRIPHENYLPHOSPHINE, DIBENZYLCHROMIUM TRICARBONYL AND DIBENZYL

Exchange time (h)	Deuterium content (D)			
	$C_6H_5CH_2CH_2C_6H_5Cr(CO)_2PPh_3^a$	$C_6H_6Cr(CO)_2PPh_3^b$	$C_6H_5CH_2CH_2C_6H_5Cr(CO)_3^b$	$C_6H_5CH_2CH_2C_6H_5^b$
20	1.11	0.93	0.01	0.11
30	1.36	1.32	0.01	0.17
40	1.65	1.65	0.01	0.23
143	2.84	2.95	0.07	0.69
k_{HIE} , mid. (sec^{-1})	3.8×10^{-6}	3.8×10^{-6}	1.2×10^{-8}	2.0×10^{-7}

^a Deuterium content in the coordinated ring. ^b Calculated from the rate constants of HIE determined for all the reaction times considered.

dibenzylchromium tricarbonyl and dibenzyl. The reactivity of the π -coordinated ring of dibenzylchromium dicarbonyl triphenylphosphine is evidently similar to that of the π -benzene ring in benzenechromium dicarbonyl triphenylphosphine. The reactivity of the uncoordinated ring of complex IIc is lower than that of the starting dibenzyl and is comparable to the reactivity of dibenzylchromium tricarbonyl. In fact, after 40 hours of HIE each phenyl ring of dibenzyl contains about 0.12 D. Dibenzylchromium tricarbonyl contains so little deuterium (~ 0.01 D in the whole molecule) that it seems likely this complex has a reactivity comparative to that of the uncoordinated ring in dibenzylchromium dicarbonyl triphenylphosphine. This, in turn, suggests that the PPh_3 group has no donor effect on the uncoordinated ring.

The results on HIE have shown, therefore, that in the π -biphenyl ligand of biphenylchromium dicarbonyl triphenylphosphine (IIa) both ligands undergo the same effect of the PPh_3 group, and thus the coordinated ring has approximately the same reactivity as the uncoordinated one. The separation of the phenyl rings by a CH_2 group (in diphenylmethanechromium dicarbonyl triphenylphosphine) partially impedes the transfer of the PPh_3 group effect, and the coordinated ring becomes more reactive than the uncoordinated ring. A second methylene bridge (in the dibenzyl system) stops the transfer altogether.

Experimental

The arenecarbonyl complexes were obtained as described elsewhere [6,7]. CF_3COOD was obtained from $(\text{CF}_3\text{CO})_2\text{O}$ and D_2O . All the experiments on the kinetics of HIE were performed under purified argon in sealed ampoules at 50°C under the conditions of a monomolecular reaction. The reaction was stopped by pouring a portion of the solution into cold water; the mixture was neutralised by NaHCO_3 and the product extracted by benzene. The ampoules were opened and the solution neutralised in the argon atmosphere. The purity of the samples was controlled by melting point measurements and IR spectra. The total content of deuterium was determined by mass spectrometry [8], the content in the coordinated and the uncoordinated rings of complexes II was inferred from the variation of the integral intensity of the corresponding proton signals as compared to the integral intensity of the proton signals of a reference substance. The reference used with the complex IIa was ferrocene (Fc) in the molar ratio IIa: Fc = 1 : 0.5, with IIb,c the CH_2 group signals and with IId,e the signals of the protons on the uncoordinated ring. The partial rates of HIE were calculated by means of the formula

$$f_i = \frac{n_i k_i \alpha_i}{k}$$

where n_i is the ratio between the number of equivalent positions in the coordinated ring of complex II and the number of equivalent positions in benzenechromium dicarbonyl triphenylphosphine; k_i the rate constant of HIE (II), k the rate constant for $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_2\text{PPh}_3$, α_i the proportion of D substitution for H in a given position i .

The PMR spectrometers used were as follows: Perkin-Elmer R-32 (90 MHz), Comeca RMN-250 (250 MHz) and Brooker WH-360 (360 MHz). The solvent

was carbon disulfide, and the internal standard was hexamethylsiloxane.

The ^2H NMR spectra were recorded on a Brooker HX-90 (13.82 MHz) Fourier spectrometer with acetone as solvent. The chemical shifts to the weak field were calculated with respect to the signal of deuterioacetone.

References

- 1 D.A. Brown and J.R. Raju, *J. Chem. Soc. (A)*, (1966) 1617.
- 2 D.N. Kursanov, V.N. Setkina, N.K. Baranetskaya, E.I. Fedin, E.I. Mysov and K.N. Anisimov. *Dokl. Akad. Nauk. SSSR*, 202 (1972) 601.
- 3 D.N. Kursanov, V.N. Setkina, N.K. Baranetskaya, V.I. Zdanovich, A.I. Yurtanov and K.N. Anisimov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1973) 1359.
- 4 N.K. Baranetskaya, V.I. Zdanovich, E.I. Mysov, N.E. Kolobova, K N. Anisimov, V.N. Setkina and D.N. Kursanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1974) 758.
- 5 E.N. Yurygina, P.P. Alikhanov, E.A. Izrailevich, P.N. Manochkina and A.I. Shatenstein, *Zh. Fiz. Khim.*, 34 (1960) 591.
- 6 B. Nicholls and M.C. Whiting, *J. Chem. Soc.*, (1959) 551.
- 7 W. Strohmeier and N. Hellmann, *Chem. Ber.*, 96 (1963) 2859.
- 8 Yu.N. Sukharev and Yu.S. Nekrasov, *Org. Mass Spectrom.*, 11 (1976) 1239.