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THE EFFECT OF REPLACING CARBONYL GROUPS BY OTHER LIGANDS ON THE CATALYTIC PROPERTIES OF ARENECHROMIUM CARBONYL COMPLEXES

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Summary

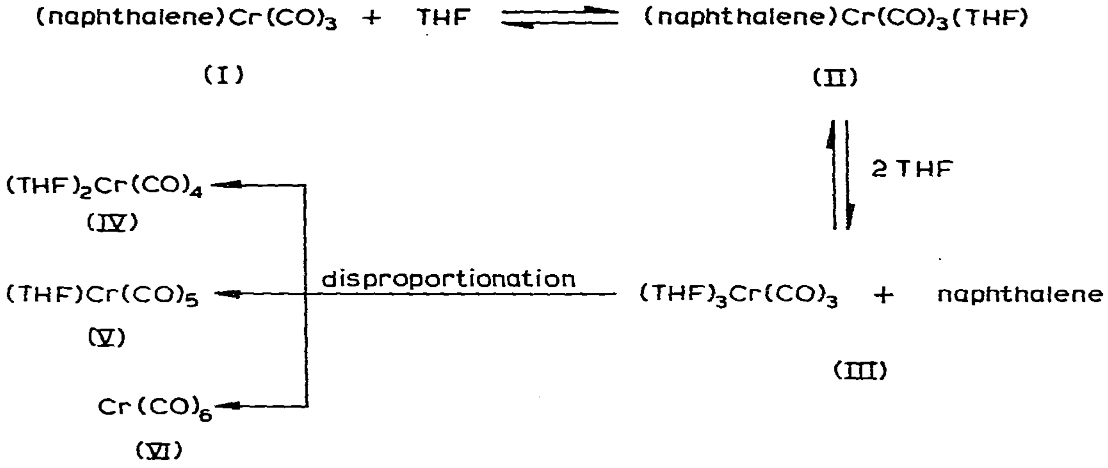
The activities of a series of arene$Cr(CO)_2L$ complexes in catalytic hydrogenation has been studied and found to be poorer than those of the $Cr(CO)_3$ analogs. The IR ν(CO) changes of these complexes in THF have been shown to have value in predicting catalytic properties.

Introduction

The effectivenes of arenechromium tricarbonyl complexes as homogeneous catalysts in the hydrogenation of dienes has been demonstrated with open-chain conjugated dienes [1], bicyclo[2.2.1]hepta-2,5-dienes [2], tricyclic-*propella*-tetraenes [3] and tricyclo[4.2.2.$0^{2,5}$]deca-3,9-dienes [4]. The major advantages as catalysts of this type of complex is total stereospecificity in the hydrogen addition to the diene and a high degree of regioselectivity. Kinetic and mechanistic studies [1,2,5,6] have shown that the efficiency of the chromium complex catalyst is largely dependent on the nature of the arene moiety, and by suitable choice of the arene (e.g. naphthalene) it is possible to effect hydrogenations at ambient temperatures and pressures. These features led us to consider the possible extension of arenechromium carbonyl catalysis to some aspects of asymmetric synthesis. In particular, the availability of chiral complexes prepared by the successive exchange of carbonyl groups in arenechromium tricarbonyl derivatives [7—10] prompted us to undertake this study. We describe below some properties, including catalytic behaviour, of complexes of chromium in which carbonyl groups have been replaced by other ligands.

Results and discussion

In a previous communication [5] we reported that solutions of naphthalenechromium tricarbonyl or anthracenechromium tricarbonyl in tetrahydrofuran (THF), acetone and other coordinating solvents, upon standing at room temperature under nitrogen, exhibited extensive changes in the carbonyl stretching band region of the infrared spectrum. Subsequently [6] we showed that these changes were intimately connected with the catalysis of hydrogenation, and thus could serve as an aid in predicting catalytic properties of arenechromium tricarbonyl complexes. The relevant chemical species formed in the reaction between naphthalenechromium tricarbonyl and THF are shown in Scheme 1 [2,6].



SCHEME 1. Reaction of (naphthalene) $Cr(CO)_3$ with THF.

The initial carbonyl stretching bands at 1960 and 1880 cm^{-1} of naphthalene-$Cr(CO)_3$ (I) decreased in intensity with time. The first new band, which appeared within a few minutes of reaction time, at 1940 cm^{-1}, was assigned to the intermediate II. This was followed by the appearance of bands at 1920 and 1780 cm^{-1}, assigned to III, subsequently shown to be the active catalytic species in the hydrogenation reaction [6]. Decrease in catalytic activity was found to be connected with appearance of new bands identified as belonging to species IV—VI, arising by disproportionation reactions of III. The structure of the arene, including the type of substituents on the ring bearing the $Cr(CO)_3$ moiety, has been shown to affect the behaviour of the complexes in coordinating solvents as well as the catalytic efficiency in the hydrogenation of dienes [1,2,5,6]. The effect of replacing carbonyl groups by other ligands was studied first by monitoring the changes in the carbonyl stretching band region of the infrared spectrum in THF solutions at various temperatures.

The IR $\nu(CO)$ changes caused by replacing one CO group with a CS ligand in arene $Cr(CO)_3$ complexes are relatively small ($\Delta\nu(CO) \leqslant 10$ cm^{-1}; for symmetry reasons, only the νCO (A_1) bands are considered). According to this criterion, it would seem that the σ-donor, π-acceptor properties of the thiocarbonyl and

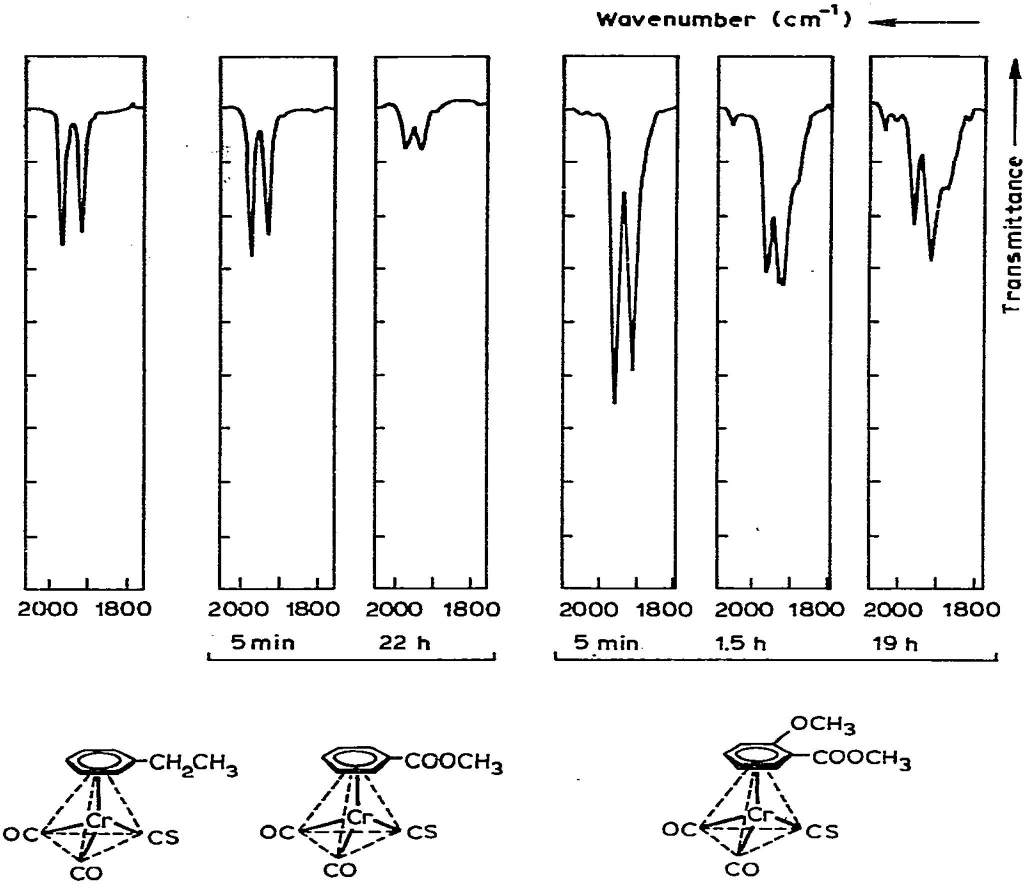
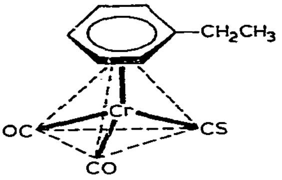
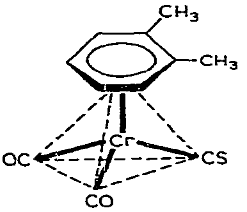
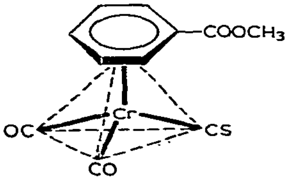
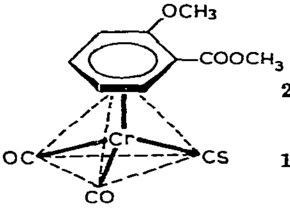
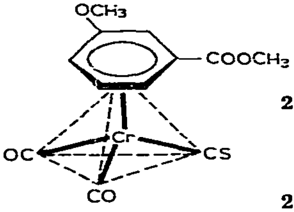


Fig. 1. IR spectra of solutions of arenechromiumdicarbonylthiocarbonyl complexes in tetrahydrofuran at room temperature.

carbonyl groups are very similar in arene $Cr(CO)_2L$ (L = CO, CS) complexes. On the other hand, on the basis of mass spectrometric studies [9] it has been suggested that CS is both a better σ-donor and π-acceptor than CO in these complexes. If the latter were the case, it would be expected that THF attack on a complex arene$Cr(CO)_2CS$, by the route given in Scheme 1, would lead to a relatively long-lived catalytic species $(THF)_3Cr(CO)_2(CS)$, analogous to III, which should be detectable by infrared spectroscopy. The typical IR ν(CO) changes illustrated in Fig. 1 and the results summarized in Table 1 indicate that this is not the case. Both ethylbenzene$Cr(CO)_2CS$ and *o*-xylene$Cr(CO)_2CS$ remained unchanged in THF over a period of 23 h, behaviour similar to that observed for alkylbenzene$Cr(CO)_3$ complexes. There was no observable change in the intensity of the IR ν(CO) bands of these complexes and no new carbonyl stretching bands were exhibited. Methyl benzoate$Cr(CO)_2CS$, as expected from the electron-withdrawing nature of the ring substituent and the consequent weakening of the ring—Cr bond, was less stable in THF. At room temperature about 20% of the complex decomposed after 2.5 h, and 75% after 22 h. At a higher temperature (90°C), 75% of the complex was destroyed after only 30

TABLE 1

CHANGES IN INFRARED SPECTRUM OF (ARENE)$Cr(CO)_2(CS)$ COMPLEXES IN THF

Complex	Conc. (mmol/l)	Temp. (°C)	Time (h)	Intensity change of initial ν(CO) (%)	ν(CO) cm^{-1}	
					Initial	New
	7.9	25	23	0	1970, 1920	
	7.8	25	23	0	1965, 1915	
	7.3	25	0.7	0	1980, 1935	
			2.5	20		
			22	75		
	6.9	90	0.5	75	1980, 1935	
	20	25	0.5	30	1970, 1925	2065, 1985 1940, 1900
			1.5	50		
			19	~100		
	10.6	50	1.25	~100	1970, 1925	1985, 1945 1900
	20	25	2	0	1970, 1925	
			25	50		2065, 1945 1910
	20.5	50	0.2	0	1970, 1925	2065, 1980 1940, 1900
			0.7	20		
			1.5	~100		

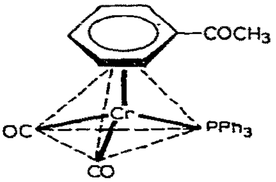
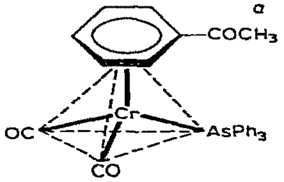
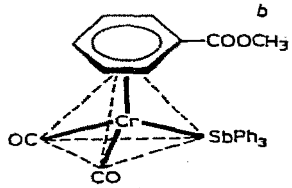
min. The decomposition was accompanied by formation of a brown precipitate in the solution. On the other hand, both 1-carbomethoxy-2-methoxybenzene-$Cr(CO)_2CS$ and 1-carbomethoxy-3-methoxybenzene$Cr(CO)_2CS$ underwent extensive decomposition both at room temperature and at 50° C, whilst at the same time new carbonyl bands made their appearance in the IR spectrum. Simultaneous with the appearance of these new CO bands, there was a gradual disappearance of the CS stretching band at 1220 cm^{-1}. It should be noted that the new CO stretching bands were at a significantly higher frequency than those observed for the catalytic species $(THF)_3Cr(CO)_3$ described above. The bands at 2065, 1945 and 1900 cm^{-1} indicate the presence of $(THF)Cr(CO)_5$ and the absorption at 1985 cm^{-1} could be due to $Cr(CO)_6$. The immediate conclusion drawn from these results was that replacement of a carbonyl ligand in arene $Cr(CO)_3$ complexes by a thiocarbonyl ligand would not be expected to improve their catalytic hydrogenation properties. As described below, this conclusion proved to be correct.

The same screening procedure was used to study the effect of replacing a CO group by ligands other than the thiocarbonyl group. Table 2 summarizes the infrared changes observed with THF solutions of arene$Cr(CO)_2L$ (L = $P(C_6H_5)_3$, $As(C_6H_5)_3$ and $Sb(C_6H_5)_3$) and Table 3 presents the results for arene-$Cr(CO)_2L$ (L = $CNC(O)C_6H_5$, $CNCH_2C_6H_5$ and $CNC(O)N(CH_3)_2$). For the purpose of this discussion we also include in Table 4 the data for three complexes with centrometallochirality, arene$Cr(CO)L^1L^2$ (L^1 = CS, L^2 = $P(C_6H_5)_3$; L^1 = CS, L^2 = $P(OC_6H_5)_3$; L^1 = $CNC(O)C_6H_5$, L^2 = $P(OC_6H_5)_3$).

Replacement of a CO group in arene $Cr(CO)_3$ by a $—P(C_6H_5)_3$ ligand (as well as by $—As(C_6H_5)_3$ and $—Sb(C_6H_5)_3$) causes a relatively large shift to lower IR

TABLE 2

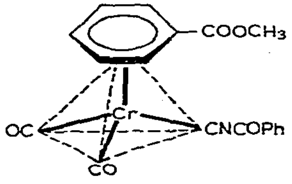
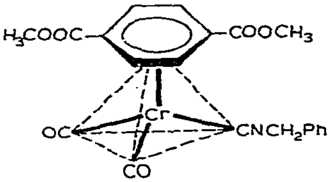
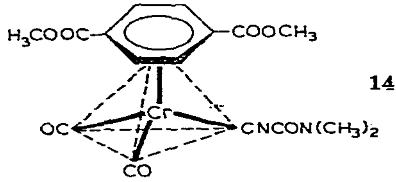
CHANGES IN INFRARED SPECTRUM OF $ArCr(CO)_2L$ COMPLEXES IN THF

Complex	Conc. (mmol/l)	Temp. (°C)	Time (h)	Intensity change of initial ν(CO)	ν(CO) (cm^{-1})	
					Initial	New
	6.8	25	1.75	0	1920, 1865	
		90	21	15		
	6.1	90	1.25	0		
 [a]	7.2	25	1.5	0	1920, 1870	
 [b]	7.0	25	1.75	0	1920, 1870	
			22	30		1990, 1965
	6.3	85	0.3	0		
		100	1.75	30		1965
		150	2.75	85		1965

[a] Anal. Calc. for $C_{28}H_{23}CrAsO_3$: C, 62.92; H, 4.30%; Found: C, 62.80; H, 4.34%. [b] Anal. calc. for $C_{28}H_{23}CrSbO_4$: C, 56.31; H, 3.88%; Found: C, 56.40; H, 3.63%.

TABLE 3

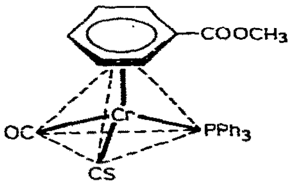
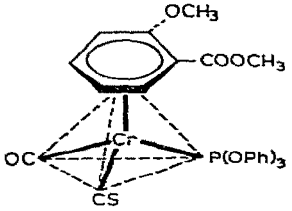
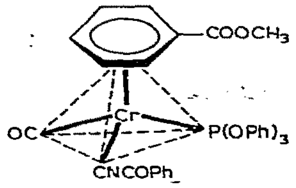
CHANGES IN INFRARED SPECTRUM OF ARENECHROMIUMDICARBONYLISOCYANIDE COMPLEXES IN THF

Complex	Conc. (mmol/l)	Temp. (°C)	Time (h)	Intensity change of initial ν(CO) (%)	ν(CO) (cm^{-1})	
					Initial	New
	6.6	25	1.5	0	1985, 1920	
			19	30		
	7.6	90	1.5	0		
	15.9	50	23	0	1940, 1895	
	14.5	50	3	0	2010, 1940 1925	
			21	25		

stretching frequency ($\Delta\nu \simeq$ 50—70 cm^{-1}) for the remaining CO ligands (Table 2). The pertinent question in the context of this work is whether the increased electron density on the Cr atom due to the good σ-donor, poor π-acceptor properties of $P(C_6H_5)_3$, relative to CO, is π-back-donated solely, or nearly so, to the remaining two CO groups or is there also significantly increased π-back-donation to the arene ligand, as compared to the bonding in areneCr$(CO)_3$ complexes [5]. The increased bond order, and hence increased bond strength in the arene—Cr bond, which would ensue from higher metal—arene back-donation, should make arene displacement by the coordinating solvent (see Scheme 1) more difficult. Therefore catalysis of the hydrogenation by the intermediacy of an active species analogous to III (Scheme 1), might be reduced or even suppressed altogether. Results of the hydrogenation (vide infra) could be considered as supporting evidence for this latter hypothesis. However, other factors could have a bearing on the decreased catalytic properties of areneCr$(CO)_2P(C_6H_5)_3$ complexes, and in an accompanying communication [11] steric hindrance effects are discussed in this context. It should be noted at this point that in view of the similarity of PF_3 and CO in their electronic character and small size [12] it was expected that areneCr$(CO)_2PF_3$ com-

TABLE 4

CHANGES IN INFRARED SPECTRUM OF ASYMMETRIC CHROMIUM COMPLEXES IN TETRAHYDROFURAN

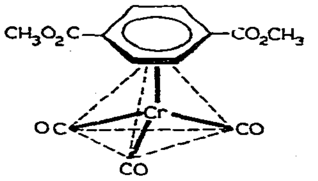
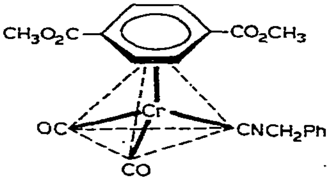
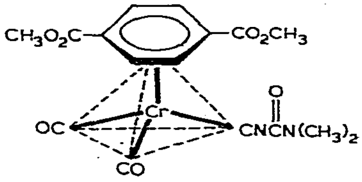
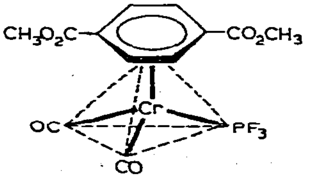
Complex	Conc. (mmol/l)	Temp. (°C)	Carbonyl bands (cm^{-1})	Time (h) (% unchanged)
	6.5	25	1920	1.5 (100%); 19 (90%)
	9.25	50	1935	20 (100%)
	8.3	50	1935	1.5 (100%); 17 (60%)

plexes would have catalytic properties very similarly to those of their arene-$Cr(CO)_3$ analogs. The behaviour of (dimethylterephthalate)$Cr(CO)_2PF_3$ in THF is predictive of such behaviour. A solution of this complex kept at 50°C for 17 h, exhibited in the IR spectrum two new bands at 1915 and 1885 cm^{-1}, in addition to the original absorptions at 1970 and 1930 cm^{-1}. The ν(CO) at 1915 cm^{-1}, probably the A_1 band, is reminiscent of that observed at 1920 cm^{-1} for the $(THF)_3Cr(CO)_3$ species (see Scheme 1). The results of hydrogenation experiments (vide infra) were in accord with these expectations.

Recently [10] *N*-acyl isocyanide ligands (CNC(O)R) have been used to replace CO groups in arene$Cr(CO)_3$ complexes. The overall electronic effects resulting from this ligand replacement, as demonstrated by high stability in THF solution at both room and higher temperatures (Table 3), appear to be rather similar to those observed in the analogous arene$Cr(CO)_3$ complexes. It can be predicted that with judicious choice of the arene (e.g. phenanthrene or naphthalene) a complex of this type, arene$Cr(CO)_2$(CNC(O)R), may have satisfactory catalytic properties. This would be of interest in connection with the synthesis of centrochiral chromium complexes as potential catalysts in asymmetric synthesis. The high stability of such complexes in THF solution (see Table 4) and the other results obtained in the potential catalyst screening experi-

TABLE 5

HYDROGENATION OF NORBORNADIENE BY DIMETHYLTEREPHTHALATE $Cr(CO)_2L$ CATALYSTS [a]

Catalyst	Initial conc. (mol/l)	Reaction time (h)	Composition of reaction mixture (%)			
			Norbornadiene	Nortricyclene	Norbornene	Norbornane
	5×10^{-3}	6	5	35	45	15
	5×10^{-3}	15	100		traces	
		30	80	8	10	2
	5×10^{-3}	4	90	4	6	traces
		27	35	30	32	3
	5×10^{-3}	6	15	25	40	20
		8	0	32	37	31

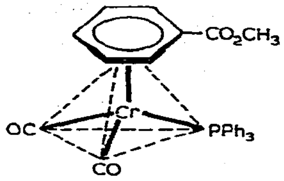
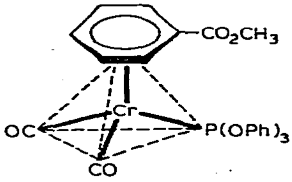
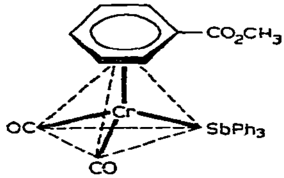
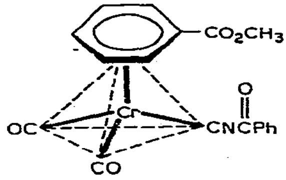
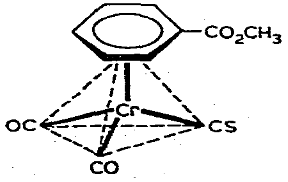
[a] Reaction conditions: 0.1 *M* norbornadiene, 700 psi H_2, 170°C, cyclohexane solution.

ments described above, indicated that the catalytic properties in the hydrogenation of dienes might be drastically affected upon replacement of a CO group by other ligands.

With norbornadiene as substrate, naphthalenechromium tricarbonyl and phenanthrenechromium tricarbonyl catalyze the hydrogenation reaction in THF solution very effectively [2] leading under mild reaction conditions (even at ambient temperature and pressure) to quantitative conversion of the diene to the 1,4- and 1,2-hydrogenation products, nortricyclene and norborene respectively, in a 4 : 1 ratio. None of the complexes arene$Cr(CO)_2L$ described in Tables 1—4 showed any catalytic properties under similar mild hydrogenation

TABLE 6

HYDROGENATION OF NORBORNADIENE BY METHYLBENZOATE $Cr(CO)_2L$ CATALYSTS [a]

Complex	Initial conc. (mol/l)	Reaction time (h)	Composition reaction mixture (%)			
			Norbornadiene	Nortricyclene	Norbornene	Norbornane
	5×10^{-3}	5	100	no reaction		
		30	85	5	8	2
	5×10^{-3}	5	98	<1	<1	<1
		30	85	3	10	2
	5×10^{-3}	8	85	2.5	10	2.5
		20	68	10	16	6
	5×10^{-3}	7	47	15	30	7
	5×10^{-3}	20	98	<1	<1	<1

[a] Reaction conditions: 0.1 *M* norbornadiene, 700 psi H_2, 170°C, cyclohexane solution.

conditions. Partial hydrogenation of norbornadiene was achieved with some of these complexes as catalysts only under much more drastic conditions of temperature (170°C), pressure (50 atm) and longer reaction times. Some of the results of hydrogenation experiments are summarized in Tables 5 and 6. With dimethyl terephthalate as the arene, the $Cr(CO)_3$ complex led to 95% hydrogenation after 6 h reaction time and about 90% of the catalyst concentration remained at the end of the reaction. However, the product distribution was different from that obtained with the naphthalene and phenanthrene complexes, indicating that the drastic conditions may affect the regioselectivity previously attained with these complexes [2]. With the same arene, the —$Cr(CO)_2CNCH_2C_6H_5$ complex gave only traces of hydrogenation products after 15 h, and about 20% hydrogenation after 30 h. Extensive catalyst decomposition was found to have occurred in this time. The *N*-functionalized isocyanide ligand, in the complex dimethyl terephthalate$Cr(CO)_2(CNC(O)N(CH_3)_2)$, proved to be a relatively better ligand for a hydrogenation catalyst than the *N*-substituted benzylisocyanide ligand. With the former about 65% hydrogenation had occurred after 27 h. However, as predicted by the IR screening experiments, the best ligand in this series and nearest to CO was PF_3. Dimethyl terephthalate$Cr(CO)_2PF_3$ showed practically the same catalytic hydrogenation properties as the —$Cr(CO)_3$ analog, with 100% conversion having taken place after 8 h.

The results in Table 6 show that with methyl benzoate as the arene, the triphenylphosphine and triphenylphosphite ligands upon replacing a CO group in $Cr(CO)_3$ did not impart good catalytic hydrogenation properties to the complex, as had already been foreseen from the IR screening experiments. Similarly, as predicted, the arene$Cr(CO)_2CS$ complex had no catalytic hydrogenation properties at all and it decomposed during the hydrogenation reaction. On the other hand, the *N*-benzoyl isocyanide ligand in the complex methyl benzoate $Cr(CO)_2CNC(O)C_6H_5$ produced better than 50% hydrogenation after 7 h.

In a preliminary experiment under somewhat similar reaction conditions, (150°C; pH_2 60 atm; 5 h) the centrochiral complex (methyl 3-methoxybenzoate)$Cr(CO)(P(OC_6H_5)_3)$ $(CNC(O)C_6H_5)$ gave 15% 1,4-hydrogenation of methyl sorbate.

From all the results presented it may be inferred that a centrochiral complex Arene$Cr(CO)(L^1)(L^2)$ with an arene such as naphthalene or phenanthrene and a combination L^1, L^2 from the ligands PF_3, CNC(O)R, could lead to a hydrogenation catalyst of potential use in asymmetric synthesis. Work is currently in progress to study this possibility.

Experimental

Apparatus

IR-spectra were recorded on a Perkin—Elmer 257 (ν(CO) values given in Tables are ±3 cm^{-1}). GLC analyses were performed on a Packard 805/7300 with flame ionization detector and disc integrator using glass columns packed with 15% DEGS on Chromosorb W. The high pressure hydrogenations (50 atm) were carried out in an ABP-300 MC "Magne Drive" autoclave by procedures already described [1]. The medium pressure ($\simeq$ 4 atm) hydrogenations were performed with a modified Paar-hydrogenator as previously reported [5].

Materials

The sources and purification of solvents, hydrogen and diene substrates have been described previously [2,4,5]. The syntheses of arenechromium$(CO)_3$ [1—6], arenechromium$(CO)_2L$ and arenechromium $(CO)(L^1)(L^2)$ [7—10] have been published, except for that of (dimethylterephthalate)$Cr(CO)_2PF_3$, which is given below.

Preparation of dimethylterephthalate$Cr(CO)_2PF_3$

A solution of 1,4-dicarbomethoxybenzenechromium tricarbonyl (0.66 g, 5 mmol) in THF was irradiated, under nitrogen, with a UV lamp (Hanau T 150) for 1 h. The yellow-orange solution turned progressively red, following the replacement of a CO group by a THF molecule. At the end of the irradiation period, the gas PF_3 was bubbled through the solution for 10 min, during which time the colour changed back to yellow-orange. After removal of the solvent in vacuum, the residue was purified by preparative TLC on silica gel plates with hexane as eluent to yield 0.55 g (70% yield) of dimethylterephthalate$Cr(CO)_2$-PF_3, m.p. 88°C. Molecular weight calcd. for $C_{12}H_{10}CrF_3O_6P$, 389.9572; found 389.9585. Major ions observed in the mass spectrum: m/e 390 (M^+); 359 $(M - OCH_3)^+$; 274 $(M - CO - PF_3)^+$; 246 (parent peak) $(M - 2\ CO - PF_3)$.

Procedure for monitoring IR ν(CO) changes in arenechromium carbonyl complexes

A sample of the complex (2—10 mg) was dissolved under nitrogen in THF (0.7—2 ml), previously dried over CaH_2 or K wire and thoroughly degassed in a capped glass vial. Immediately following the preparation of the solution, a sample was withdrawn with a syringe and transferred to the IR cell for recording of the spectrum. The vials were either kept at room temperature or heated in a bath between 50—100°C, with samples being withdrawn for IR measurements at predetermined time intervals. In some instances, the same concentration of a complex was placed in several vials, which were then heated in the same bath. Single vials were removed for each IR measurement at consecutive time intervals, thus avoiding the process of repeatedly cooling and reheating the same sample.

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