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SUBSTITUTION AND INSERTION REACTIONS OF $(\eta^5\text{-}C_5H_5)Cr(CO)_3C_2H_5$

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Summary

The complex $(\eta^5\text{-}C_5H_5)Cr(CO)_3C_2H_5$ has been made and its reactions with σ donor ligands L ($L = (MeO)_3P$ and $(EtO)_3P$) and with SO_2 studied. The alkyl phosphites give compounds of the composition $(\eta^5\text{-}C_5H_5)Cr(CO)_2LC_2H_5$, and sulfur dioxide gives the corresponding S-sulfinato $(\eta^5\text{-}C_5H_5)Cr(CO)_3SO_2C_2H_5$.

Introduction

Among complexes with stoichiometry $(\eta^5\text{-}C_5H_5)M(CO)_3R$ (M = Cr, Mo or W; R = alkyl or aryl) (I), chromium derivatives have received far less attention than those of molybdenum and tungsten, perhaps because they are less stable to air and consequently more difficult to handle. Only the methyl derivative has been obtained [1,2], and the photo-induced replacement of CO by other ligands L ($L = Ph_3P$, $(MeO)_3P$) in solution has been studied.

The photo-induced replacement of carbonyl ligands in a complex of the general formula I has been suggested to proceed dissociatively via 16-electron $(\eta^5\text{-}C_5H_5)M(CO)_2R$ species [3–6]. It has been recognised that $(\eta^5\text{-}C_5H_5)M(CO)_3Me$ (M = Cr, Mo or W) complexes can be dealkylated in solution [4,7] if the solvent cannot stabilise the 16-electron species $(\eta^5\text{-}C_5H_5)M(CO)_2Me$ formed initially or when there is no other potential ligand is present.

One of the most important reactions of transition metal-alkyl complexes is the so-called insertion of unsaturated molecules, usually electrophilic species, into metal–carbon σ bonds. One such species is sulfur dioxide. Hanna and Wojcicki [8] have investigated its reactions with the nitrosyl derivative $(\eta^5\text{-}C_5H_5)Cr(NO)_2R$ ($R = CH_3$ and $CH_2C_6H_5$), but its behaviour towards alkyl cyclopentadienyltricarbonylchromium complexes has not previously been investigated.

We present below the results of experiments on the synthesis of $(\eta^5\text{-}C_5H_5)Cr(CO)_3C_2H_5$, its photoinduced reactions with the σ donor ligands $(MeO)_3P$ and $(EtO)_3P$ and its reaction with SO_2.

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Results and discussion

The reaction under UV irradiation of $(\eta^5\text{-}C_5H_5)Cr(CO)_3C_2H_5$ with an excess of the trivalent phosphorus ligands L (L = $(MeO)_3P$ and $(EtO)_3P$) under N_2 results in loss of CO and formation of $(\eta^5\text{-}C_5H_5)Cr(CO)_2LC_2H_5$. The final product is the monosubstituted derivative, in contrast with the reaction of $(\eta^5\text{-}C_5H_5)Cr(CO)_3CH_3$ with an excess of $(MeO)_3P$ which yields the disubstituted derivative $(\eta^5\text{-}C_5H_5)$-$Cr(CO)(P(OMe)_3)_2CH_3$ [2].

Table 1 lists the infrared and ^1H NMR spectra of the new complexes. The $\nu(CO)$ frequencies are characteristic of terminal ligands [9]. In the phosphite derivatives the frequencies are lower than those of $(\eta^5\text{-}C_5H_5)Cr(CO)_3C_2H_5$ owing to the electronic donor effect of the phosphite ligands. The shift is slightly larger in the triethyl phosphite derivative, in agreement with its greater basicity [10].

The ^1H NMR spectra of the $(\eta^5\text{-}C_5H_5)Cr(CO)_3C_2H_5$ and $(\eta^5\text{-}C_5H_5)Cr(CO)_2$-$LC_2H_5$ complexes display the signal due to the five ring protons in the range usual for cyclopentadienylchromiun complexes [2,8]: it appears as a multiplet in the parent complex and a triplet in the phosphite derivatives.

The trimethyl phosphite derivative gives a doublet at δ 3.65 ppm assignable to the CH_3O groups of the $(MeO)_3P$ ligand [2]. A multiplet at δ 3.50 and a triplet at δ 1.10 ppm can be attributed to the CH_2 and CH_3, respectively, of the C_2H_5 ligand [11].

In the triethyl phosphite complex quartets at δ 4.00 and δ 3.78 ppm are assigned to the CH_2 protons of the C_2H_5 and $(EtO)_3P$ ligands, respectively. A triplet at δ 1.18 ppm is attributed to the CH_3 protons of both ligands.

The reaction of $(\eta^5\text{-}C_5H_5)Cr(CO)_3C_2H_5$ with sulfur dioxide in pentane solution yields a 1/1 adduct formulated as the S-sulfinato, $(\eta^5\text{-}C_5H_5)Cr(CO)_3SO_2C_2H_5$. It is a green powder stable to air for at least a short period.

TABLE 1

IR AND ^1H NMR SPECTRA OF THE COMPLEXES

Compound	IR (cm^{-1})		^1H NMR	
	$\nu(CO)$	$\nu(SO)$	δ [a] (ppm)	Assignment
$C_5H_5Cr(CO)_3C_2H_5$	2012vs [b]		4.81–4.38 m	5H, C_5H_5
	1933vs		3.61 q	2H, CH_2
			1.11 t	3H, CH_3
$C_5H_5Cr(CO)_2P(OMe)_3C_2H_5$	1945vs [b]		4.42 t	5H, C_5H_5
	1871vs		3.65 d	9H, OCH_3
			3.50 m	2H, CH_2
			1.10 t	3H, CH_3
$C_5H_5Cr(CO)_2P(OEt)_3C_2H_5$	1943vs [b]		4.44 t	5H, C_5H_5
	1868vs		4.00 q	2H, CH_2
			3.78 q	6H, OCH_2
			1.18 t	12H, CH_3
$C_5H_5Cr(CO)_3SO_2C_2H_5$	2028vs [c]	1168s [d]	5.05qt	5H, C_5H_5
	1971vs	1036vs	4.58 q	2H, CH_2
			1.18 t	3H, CH_3

[a] In $CDCl_3$ solution. Abbreviations: d, doublet; t, triplet; q, quartet; qt, quintuplet; m, multiplet. [b] In pentane solution. [c] In $CHCl_3$ solution. [d] Nujol mull. Abbreviations: vs, very strong; s, strong.

Infrared and ^{1}H NMR spectral data for the complex are listed in Table 1. The SO_2-containing product shows $\nu(SO)$ absorptions at 1168 and 1036 cm^{-1} in the range expected for metal S-sulfinato complexes [12]; they thus provide good evidence for the proposed mode of metal-SO_2 attachement. As expected for the assigned structure, the CH_2 protons in $(\eta^5\text{-}C_5H_5)Cr(CO)_3SO_2C_2H_5$ resonate at lower field (δ 4.58 ppm) than those in the parent complex (δ 3.61 ppm). A comparable shift was observed on insertion of SO_2 into $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2H_5$ [13].

The signal from the cyclopentadienyl ring protons in the sulfinato complex appears at δ value which is 0.46 unit larger than the corresponding signal for the alkyl precursor. King [14] reports that electronegative groups (Y) attached to iron in $C_5H_5Fe(CO)_2Y$ cause shifts of the proton resonance to lower fields, probably owing to the inductive effects of Y. We suggest that the observed position of the C_5H_5 proton resonance signal in the sulfinato is also the result of a strong electron-withdrawing effect of the $C_2H_5SO_2$ group.

The values of $\nu(CO)$ for the S-sulfinato complex are higher than those for the parent alkyl. A comparable change in $\nu(CO)$ occurs on going from $(\eta^5\text{-}C_5H_5)\text{-}Fe(CO)_2R$ to $(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_2R$ (R = alkyl and aryl) [13], and in $\nu(NO)$ on going from $(\eta^5\text{-}C_5H_5)Cr(NO)_2R$ to $(\eta^5\text{-}C_5H_5)Cr(NO)_2SO_2R$ ($R = CH_3$ and $CH_2C_6H_5$) [8].

Experimental

All reactions were carried out under oxygen-free N_2. Ethyl iodide was dried over sodium and distilled. Trimethyl and triethyl phosphite were dried over sodium and then distilled and degassed before use. Solvents were dried and deoxygenated. The SO_2 was passed through concentrated H_2SO_4 and a $P_4O_{10}/CaCl_2$ column. Silica gel (activated at 120°C for 1 d, degassed in vacuum and treated with N_2) or Fluka alumina (neutral, type 507 C) deactivated with H_2O (6%) was used for chromatographic separations. An Osram "Ultra-Vitalux" 300 W lamp was used for photolysis. Chromium was determinated by atomic absorption with a Perkin–Elmer 372 spectrophotometer. The phosphorus was determined with a Autoanalyzer Technicon A-II.

The IR spectra were recorded with a Nicolet 5 DX spectrometer using Nujol mulls between CsI windows. For spectra in solution NaCl windows were used. ^{1}H NMR spectra were recorded with a Bruker WM-200-SY spectrometer.

Preparation of $(\eta^5\text{-}C_5H_5)Cr(CO)_3C_2H_5$

A solution of sodium cyclopentadienide in diglyme (100 ml) was prepared from sodium hydride (0.60 g, 25 mmol) and freshly-cracked cyclopentadiene (6 ml, 72.8 mmol) in a 500 ml three-necked flask equipped with nitrogen inlet, stirrer, reflux condenser, and pressure-equalizing dropping funnel. When all the metal hydride had dissolved, hexacarbonylchromium (6.60 g, 29.9 mmol) was added, and the mixture was heated under reflux for 3 h. The colour changed from a pink-violet to a green-brown. The solvent was removed by distillation under reduced pressure and the residue sublimed in vacuum. (No $Cr(CO)_6$ was recovered.) The $(\eta^5\text{-}C_5H_5)Cr\text{-}(CO)_3Na$ was taken up in THF and ethyl iodide was added in sufficient excess to react with the total amount of sodium (NaH) used in the preparation. The mixture was stirred and heated to reflux during 4 h. The colour was green-yellow. The solvent was removed under vacuum and the residue extracted with pentane. A green-yellow solution was obtained and cooled to −78°C to yield (50%) of yellow crystals.

Anal. Found: C, 51.80; H, 4.25; Cr, 22.46. $C_{10}H_{10}O_3Cr$ calcd.: C, 52.17; H, 4.37; Cr, 22.59%.

Preparation of $(\eta^5\text{-}C_5H_5)Cr(CO)_2P(OCH_3)_3C_2H_5$

Trimethyl phosphite (4.00 ml, 33.9 mmol) was added with stirring to a solution of 1.50 g (4.5 mmol) of $(\eta^5\text{-}C_5H_5)Cr(CO)_3C_2H_5$ in pentane (60 ml) in a 100 ml two-neck flask fitted with N_2 inlet and magnetic stirrer and the mixture was irradiated with UV light for 20 min with stirring. The colour of the solution changed from a green-yellow to darkgreen. The pentane was removed under vacuum at room temperature and the green oily residue was dissolved in benzene. The solution was chromatographed under N_2 on a silica gel column (13 × 3 cm); the product being eluted with benzene. The solvent was removed to leave a green-yellow oil, which was dried thoroughly. It could not be crystallized.

Anal. Found: C, 43.90; H, 5.76; P, 9.40; Cr, 15.80. $C_{12}H_{19}O_5PCr$ calcd.: C, 44.17; H, 5.86; P, 9.49; Cr, 15.94%.

Preparation of $(\eta^5\text{-}C_5H_5)Cr(CO)_2P(OC_2H_5)_3C_2H_5$

The procedure described above was used, but with triethyl phosphite (3.80 ml, 22.1 mmol) and $(\eta^5\text{-}C_5H_5)Cr(CO)_3C_2H_5$ (1.00 g, 2.7 mmol) as reactants. A green-yellow oil was obtained.

Anal. Found: C, 48.70; H, 6.70; P, 8.29; Cr, 13.86. $C_{15}H_{25}O_6PCr$ calcd.: C, 48.91; H, 6.84; P, 8.40; Cr, 14.11%.

Reaction of $(\eta^5\text{-}C_5H_5)Cr(CO)_3C_2H_5$ *with* SO_2

Sulphur dioxide was bubbled for 6.5 h at room temperature through a solution of $(\eta^5\text{-}C_5H_5)Cr(CO)_3C_2H_5$ (0.30 g, 1.30 mmol) in pentane (50 ml). The progress of the reaction was monitored by infrared spectroscopy in the 1800–2300 cm^{-1} region. The solvent was removed under reduced pressure and the residue dissolved in chloroform. The resulting solution was chromatographed on alumina (6% H_2O), with $CHCl_3$ as eluent. The sole band gave a reddish-yellow solution, which was concentrated and diluted with pentane to give a green powder (60%).

Anal. Found: C, 40.77; H, 3.40; S, 10.78; Cr, 17.60. $C_{10}H_{10}O_5SCr$ calcd.: C, 40.81; H, 3.42; S, 10.89; Cr, 17.67%.

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