

SYNTHESES AND REACTIONS OF $[\eta^5\text{-C}_3\text{H}_5\text{Cr}(\text{CO})_3]_2$

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Summary

The complexes $[\eta^5\text{-C}_3\text{H}_5\text{Cr}(\text{CO})_3]_2$ have been prepared, and their reactions with trivalent phosphorus ligands L (L = Ph_3P , $(\text{MeO})_3\text{P}$, $(\text{EtO})_3\text{P}$) shown to give $[\eta^5\text{-C}_3\text{H}_5\text{Cr}(\text{CO})_2\text{L}]_2$ complexes.

Introduction

The reactions of $[\eta^5\text{-C}_3\text{H}_5\text{Cr}(\text{CO})_3]_2$ (I) and its derivatives have been less extensively studied than those of their molybdenum analogues [1–5]. Hackett and co-workers described the reactions of I with Cd to give $[\eta^5\text{-C}_3\text{H}_5\text{Cr}(\text{CO})_3]_2\text{Cd}$ and with Hg or HgCl_2 to give $[\eta\text{-C}_3\text{H}_5\text{Cr}(\text{CO})_3]_2\text{Hg}$ [6]; Manning and Thornhill studied the reactions of the latter compound with halogens, HgX_2 (X = Cl, Br, or I) and various phosphorus ligands L (L = Ph_3P , $(\text{PhO})_3\text{P}$ and $(\text{MeO})_3\text{P}$) [7]. The reactions of I with thallium(I) acetate, HgCl_2 , Ph_3MCl , Ph_2MCl , R_6Pb_2 , Me_3PbOAc (M = Sn or Pb; R = Ph, *p*- MeC_6H_4 , *p*- MeOC_6H_9 or cyclohexyl), I_2 , phosphines, and phosphites have also been described [6].

The reactions of I with phosphines give compounds of the composition $[\eta^5\text{-C}_3\text{H}_5\text{Cr}(\text{CO})_2\text{L}]_2$ (II). With phosphites the reaction is more complex, and the phosphite may be incorporated as a $\text{P}(\text{OR})_3$, $\text{P}(\text{OR})_2$ or $\text{PO}(\text{OR})_2$ ligand. The dimer II was obtained in good yield only when a stoichiometric amount of trimethyl phosphite reagent was employed [8].

We extend the chemistry of I to a study of the influence of the methyl group substituted in the ring reactions of the mono- and penta-methyl derivatives [6,9] having not been examined previously. Thus we made $[\eta^5\text{-CH}_3\text{C}_3\text{H}_4\text{Cr}(\text{CO})_3]_2$ and examined its reactions with ligands L (L = Ph_3P , $(\text{MeO})_3\text{P}$ and $(\text{EtO})_3\text{P}$), which give complexes of the type $[\eta^5\text{-CH}_3\text{C}_3\text{H}_4\text{Cr}(\text{CO})_2\text{L}]_2$.

Discussion and results

The reaction of $[\eta^5\text{-CH}_3\text{C}_3\text{H}_4\text{Cr}(\text{CO})_3]_2$ with trivalent phosphorus ligands L (L = Ph_3P , $(\text{MeO})_3\text{P}$, $(\text{EtO})_3\text{P}$) under N_2 leads to release of CO and formation of

TABLE 1
 IR SPECTRAL DATA FOR THE COMPLEXES ^a

[RCr(CO) ₃] ₂	[RCr(CO) ₂ PPh ₃] ₂	[RCr(CO) ₂ P(OMe) ₃] ₂	[RCr(CO) ₂ P(OEt) ₃] ₂		
1945vs		1947m	1944s	ν(CO)	
1920vs		1924sh	1923sh		
1899vs					
1878vs					
	1803vs				
	1786vs				
	689s	ν(CP)	868vs	868vs	ν _s (PO ₃)
			682vs	675vs	ν _s (P-O-C) (aliphatic)
637vs	590m	δ(Cr-CO)			
615m	563w	ν(Cr-CO)	623w	623w	δ(Cr-CO), ν(Cr-CO)
593vs	554w				
	533w				
548vs	519s	γ(PC)			
528w	508m	ν(Cr-CO)	489s, br	497s, br	δ _s (PO ₃)
	496m	ν(PC)			δ(Cr-CO), ν(Cr-O)
452w	464w	ν(Cr-CO)			
420m					
			399vs	405vs	δ _{as} (PO ₃) deg.
397w	397m		387vs	386vs	ν(Cr-ring)
	287w		289w	281w	ν(Cr-P)

^a R = η⁵-CH₃C₅H₄.

[η⁵-CH₃C₅H₄Cr(CO)₂L]₂. The IR spectra of the products, in the 4000–200 cm⁻¹ range show characteristic bands of the methylcyclopentadiene ligand with C_s symmetry [10]. Table 1 lists the IR spectral data for the complexes and the tentative assignments of the characteristic bands of CO, Ph₃P, (MeO)₃P and (EtO)₃P ligands, together with those for the metal–ligand bonds. The ν(CO) vibration frequencies are characteristic of terminal ligands [11]. All the disubstituted compounds give two terminal carbonyl stretching peaks, which is consistent with a structure belonging to the molecular point group C_{2h}. Some of the characteristic bands of Ph₃P, (MeO)₃P and (EtO)₃P ligands are masked by the methylcyclopentadienyl ligand.

In the triphenyl phosphine complex, the vibrations ν(CP) and γ(PC) are tentatively assigned to the bands at 689 and 519 cm⁻¹, respectively. These vibrations in free Ph₃P appear at 697 and 510 cm⁻¹ [12]. Thus a shift to lower and higher frequencies respectively, takes place as a result of the coordination to the metal.

In the [η⁵-CH₃C₅H₄Cr(CO)₂P(OR)₃]₂ (R = Me, Et) complexes, the ν_s(PO₃) vibration appears at 868 cm⁻¹ in both complexes. The vibration ν_s(P-O-C) (aliphatic) appears at 682 (R = Me), and at 675 cm⁻¹ (R = Et). In both cases there is a shift to lower frequencies from those of the free ligands [13,14]. The deformation vibration δ_s(PO₃) overlaps with δ(Cr-CO) and ν(Cr-CO) in the 497–489 cm⁻¹ range. The degenerate δ_{asym}(PO₃) is assigned to the strong band at 399 cm⁻¹ (R = Me), and at 405 cm⁻¹ (R = Et) [15].

In all the complexes the δ(Cr-CO) and ν(Cr-CO) band appear in the usual range [11,16]. The ν(Cr-ring) vibration appears in the 397–387 cm⁻¹ range, in agreement with data for similar compounds [17]. The metal–P vibration appears in

the 280–289 cm^{-1} range, in accord with literature data [11,18].

The ^1H NMR spectra of the $[\eta^5\text{-CH}_3\text{C}_5\text{H}_4\text{Cr(CO)}_3]_2$ and $[\eta^5\text{-CH}_3\text{C}_5\text{H}_4\text{Cr(CO)}_2\text{L}]_2$ complexes each display a multiplet due to the four ring hydrogens ($AA'BB'$) and a singlet arising from the methyl substituted, those features being in accord with those observed for other methylcyclopentadienyl metal complexes [19]. The trimethyl phosphite complex gives a singlet at δ 3.70 ppm assignable to the CH_3O groups of the $(\text{MeO})_3\text{P}$ ligand [20]. In the case of the triethylphosphite derivative, a broad singlet at δ 1.50 and a multiplet at 3.42 ppm can be attributed, respectively, to the CH_3 and CH_2 protons of the $(\text{EtO})_3\text{P}$ ligand.

The spectra of the triphenylphosphine complex could not be obtained because it is insoluble in the usual organic solvents.

Experimental

All reactions were carried out under oxygen-free N_2 . Trimethyl and triethyl phosphite were dried over sodium and then distilled and degassed before use. Ph_3P was recrystallized from absolute EtOH. Silica gel was activated at 120°C for 1 day, degassed in vacuum, and treated with N_2 before use for GLC. Solvents were dried and deoxygenated. A Osram "Ultra-Vitalux" 300 W lamp was used for photolyses. The chromium was determined by atomic absorption with a Perkin-Elmer 372 spectrophotometer. The phosphorus was determined with a Autoanalyzer Technicon A-II.

The IR spectra were recorded in the range 4000–200 cm^{-1} with a Nicolet 5DX spectrometer using Nujol and hexachlorobutadiene mulls between CsI windows. ^1H NMR spectra were recorded with a Bruker WM-200-SY spectrometer.

Preparation of $[\eta^5\text{-CH}_3\text{C}_5\text{H}_4\text{Cr(CO)}_3]_2$

This was prepared as described by Birdwhistell et al. [21]. Anal.: Found: C, 49.99; H, 3.05; Cr, 23.96. $\text{C}_{18}\text{H}_{14}\text{O}_6\text{Cr}_2$ calcd.: C, 50.26, H, 3.25; Cr, 24.17%. ^1H NMR (CDCl_3): δ 6.32 (m, 4H, C_5H_4), 2.20 (s, 3H, CH_3) ppm.

Preparation of $[\eta^5\text{-CH}_3\text{C}_5\text{H}_4\text{Cr(CO)}_2\text{PPh}_3]_2$

A mixture of equimolar amounts of PPh_3 and $[\eta^5\text{-CH}_3\text{C}_5\text{H}_4\text{Cr(CO)}_3]_2$ (0.48 g, 1.1 mmol) in ethanol (25 ml) contained in a 100 ml two-neck flask fitted with N_2 inlet and magnetic stirrer was irradiated with UV light for 2 h. The colour of solution changed from a brown-yellow to a indigo-blue and a yellow-green precipitate formed; this was filtered off, washed several times with ethanol, and dried in vacuum. It was essentially insoluble in the usual organic solvents. The yield was 0.12 g (12%).

Anal.: Found: C, 69.44; H, 5.01; P, 6.79; Cr, 11.49. $\text{C}_{52}\text{H}_{44}\text{O}_4\text{P}_2\text{Cr}_2$ calcd.: C, 69.51; H, 4.89; P, 6.89; Cr, 11.57%.

Preparation of $\{\eta^5\text{-CH}_3\text{C}_5\text{H}_4\text{Cr(CO)}_2\text{P(OCH}_3)_3\}_2$

Trimethyl phosphite (0.42 ml, 3.4 mmol) was added with stirring to a solution of $[\eta^5\text{-CH}_3\text{C}_5\text{H}_4\text{Cr(CO)}_3]_2$ (0.77 g, 1.7 mmol) in 250 ml of tetrahydrofuran contained in a 500 ml two-neck flask fitted with N_2 inlet and magnetic stirrer. Stirring was continued until reaction was complete (ca. 17 min), and during this time the solution changed from a green-yellow to a brownish-yellow as CO was evolved. The THF was

removed under vacuum at room temperature and the brown-green residue was extracted with benzene. The solution was chromatographed under N_2 on a silica gel column (13×3 cm) which had been deactivated with ether and then washed with hexane. This complex was eluted with hexane, hexane/benzene, then benzene. The solvent was removed to leave a green-yellow oil, which was dried thoroughly; it could not be obtained in crystalline form.

Anal.: Found: C, 42.29; H, 4.99; P, 9.89; Cr, 16.43. $C_{22}H_{32}O_5P_2Cr_2$ calcd.: C, 42.47; H, 5.14; P, 9.95; Cr, 16.71%. 1H NMR ($CDCl_3$, $-45^\circ C$) δ 5.99 (m, 4H, C_5H_4), 3.70 (s, 9H, OCH_3), 1.80 (s, 3H, CH_3) ppm.

Preparation of $[\eta^5-C_5H_4Cr(CO)_2P(OCH_2CH_3)_3]_2$

The procedure described above was used, but with triethyl phosphite (1 ml, 5.6 mmol) and $[\eta^5-C_5H_4Cr(CO)_3]_2$ (1.24 g, 2.8 mmol) as reactants. A green-yellow oil was obtained.

Anal.: Found: C, 47.48; H, 6.10; P, 8.56; Cr, 14.48. $C_{28}H_{44}O_{10}P_2Cr_2$ calcd.: C, 47.62; H, 6.23; P, 8.77; Cr, 14.72%. 1H NMR ($CDCl_3$): δ 6.02 (m, 4H, C_5H_4), 3.42 (m, 6H, CH_2), 2.10 (s, 3H, CH_3), 1.50 (s, br, 9H, CH_3) ppm.

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