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THE SYNTHESIS AND DECARBONYLATION OF $(\eta^5\text{-}C_5H_5)Mo(CO)_2(COCH_3)E(C_6H_5)_3$, WHERE E IS ARSENIC OR ANTIMONY

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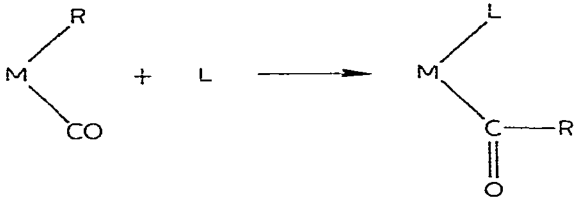
Summary

The synthesis of the title compounds by reaction of $(\eta^5\text{-}C_5H_5)Mo(CO)_3CH_3$ with excess $As(C_6H_5)_3$ or $Sb(C_6H_5)_3$ in CH_3CN is described. Thermal decarbonylation results in the preferential ejection of $As(C_6H_5)_3$ or $Sb(C_6H_5)_3$ from the new acetyl complexes, which accounts for the failure of previous attempts to synthesise the acetyl complexes. Photolytic decarbonylations lead to new alkyl complexes $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CH_3)E(C_6H_5)_3$. IR and NMR data for the new complexes are tabulated.

Introduction

Carbon monoxide insertion reactions of the type shown in eq. 1 have been



(1)

reported for a large number of σ-bonded ligands (R), metals (represented by M to include ancillary ligands) and incoming nucleophiles (L) [1]. Some transition metal systems react with a wide range of L, e.g. phosphites, phosphines, arsines, stibines, organic sulphides, organic amines, iodide and CO, to yield the acyl complexes according to the above reaction. Other systems, notably $(\eta^5\text{-}C_5H_5)Mo(CO)_3R$ [2] and $(\eta^5\text{-}C_5H_5)Fe(CO)_2(R)$ [3], display a marked selectivity towards L and phosphines are the only generally successful type of ligand promoting reaction 1.

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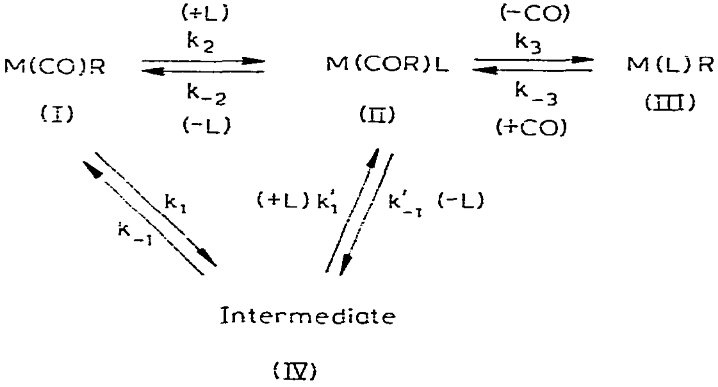
We demonstrated recently that $As(C_6H_5)_3$ could react with $(\eta^5\text{-}C_5H_5)Mo(CO)_3CH_3$ under carefully controlled temperature conditions [4] and with $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ under mild photolysis [5] to yield $M(COCH_3)As(C_6H_5)_3$ complexes, contrary to previous reports [2,3]. We report here the conditions under which $As(C_6H_5)_3$ and $Sb(C_6H_5)_3$ react with $(\eta^5\text{-}C_5H_5)Mo(CO)_3CH_3$ and on the decarbonylation of the new acetyl complexes $(\eta^5\text{-}C_5H_5)Mo(CO)_2(COCH_3)E(C_6H_5)_3$ (E = As, Sb). We relate the findings of the decarbonylation studies to the kinetic investigations [2,6–8] of the reaction of $(\eta^5\text{-}C_5H_5)Mo(CO)_3R$ with phosphorus ligands and studies of the decarbonylation of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(COR)PR'_3$ complexes [9,10].

Results and discussion

Kinetic studies of the insertion reactions (Scheme 1: I → II) of molybdenum complexes have shown that in polar solvents, e.g. CH_3CN, the rate is first order in [Mo] and independent of the nature and concentration of the phosphorus ligand, i.e. k_1 pathway. Only in non-polar solvents with strongly basic phosphines does a second order term appear in the rate law [2,7,8]. Decarbonylation reactions (II → III) to yield molybdenum alkyl complexes (Mo(L)R), however, proceed at rates which are markedly dependent on the steric size of the phosphine and are virtually independent of the solvent [9,10]. A complicating feature of decarbonylation studies is the formation of I by ejection of L rather than CO and this reaction also shows a marked dependence on the bulk of the phosphine [10].



The lack of success obtained in extending studies of insertion reactions of $(\eta^5\text{-}C_5H_5)Mo(CO)_3CH_3$ with various phosphines to arsenic, sulphur and nitrogen ligands was ascribed [2] to the failure of the intermediate IV to react with these ligands. This was correlated with the lower nucleophilicity of arsenic, sulphur and nitrogen compared to phosphorus. In terms of reaction rates this would correspond [2] to:

P: $k'_1 > k_{-1} >> k_1$

As: $k_{-1} > k'_1 \geqslant k_1$

The facile thermal ejection of $As(C_6H_5)_3$ and $Sb(C_6H_5)_3$ from the new acetyl complexes, i.e. II → I, in CH_3CN or THF at 40° C confirms the rates relationship:

$$\text{As, Sb: } k'_{-1}, k_{-1} > k'_1 >> k_1$$

The isolation of the new acetyl complexes probably resulted from the low reaction temperature together with the 3-fold excess of $As(C_6H_5)_3$ and $Sb(C_6H_5)_3$ ligands.

The photolytic decarbonylation (II → III) can be attributed to the excited state species M(COR) (CO)L * (V) being produced by excitation via a charge transfer band (metal to terminal CO) which leads to ejection of the terminal CO ligand [11]. The photolytically ejected CO in the decarbonylation reaction (II → III) has been shown to arise from a terminal CO group rather than from the acetyl ligand in the solution photolysis of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(^{13}COCH_3)$ where all the ^{13}C label was retained in the complex (conversion of acetyl-^{13}CO to terminal ^{13}CO) [12]. Low temperature matrix isolation studies [13] have shown that a coordinatively unsaturated species $(CH_3CO)Mn(CO)_4$ is produced on photolysis of $(CH_3CO)Mn(CO)_5$, in accordance with ejection of a terminal CO group. Nevertheless, the photolytic decarbonylation of the new molybdenum acetyl complexes did not give exclusive ejection of L and this is probably because there is some thermal reversal (II → I) even at the lower temperature at which the photolysis was carried out (~25° C)

For a series of phosphorus ligands, the decarbonylation (II → III) and dissociation reactions (II → I) of molybdenum acetyl complexes have been correlated [10] with the bulkiness of the phosphorus ligand rather than with σ/π effects as assessed by positions of terminal CO stretching vibrations [14]. Bulkiness was assessed by calculating or measuring the steric cone angle (ϕ_L) subtended at the metal atom by the freely rotating ligand [15]. The larger value of ϕ_L for $P(o\text{-}C_6H_4CH_3)_3$ than for $P(C_6H_5)_3$ was used to account for the failure to prepare a substituted acetyl complex (M(COR)L) for the former ligand, i.e. 100% dissociation (II → I), whereas the $P(C_6H_5)_3$ acetyl complex undergoes 25% dissociation and 75% decarbonylation [10]. Calculation of ϕ_L for $E(C_6H_5)_3$ ligands using data from the X-ray crystal structure of a series of isostructural complexes $(Co(CO)_2(NO)E(C_6H_5)_3$ (E = P [16,17], As [18], Sb [19]) gives $\phi_{Sb} < \phi_{As} < \phi_P$ [132°, 138°, 145°]. This is because increases in M—E and E—C_6H_5 bond lengths result in the phenyl rings being further from the metal for the heavier elements. On steric grounds, therefore, the ejection (II → I) of $As(C_6H_5)_3$ and $Sb(C_6H_5)_3$ from the acetyl complexes should have been less likely than for $P(C_6H_5)_3$. The IR data (Table 1) similarly gives no indication of significant σ/π differences [14] between the ligands when bound to the metal. The nature of the dissociation/decarbonylation balance can be expressed in terms of rates as:

$$\text{P: } k_3 \sim k'_{-1}$$

$$\text{As, Sb: } k_3 << k'_{-1}$$

with the overall dominance of k'_{-1} for arsenic accounting for the failure of previous workers to isolate acetyl complexes from the insertion reactions of $(\eta^5\text{-}C_5H_5)Mo(CO)_3CH_3$ with arsenic ligands.

TABLE 1

IR (2200—1500 CM^{-1}) AND NMR DATA FOR (η^5-C_5H_5)Mo(CO)$_2$(R)L COMPLEXES

R	L	IR ^{a}		NMR ^{b}	
$COCH_3$	$P(C_6H_5)_3$	1943s	terminal CO	7.40	acetyl protons
		1858vs		4.99	η^5-C_5H_5 protons
		1603m	acetyl CO	2.5—2.8	phenyl protons
$COCH_3$	$As(C_6H_5)_3$	1946s	terminal CO	7.36	acetyl protons
		1860vs		4.96	η^5-C_5H_5 protons
		1605m	acetyl CO	2.4—2.7	phenyl protons
$COCH_3$	$Sb(C_6H_5)_3$	1940s	terminal CO	7.34	acetyl protons
		1860vs		4.83	η^5-C_5H_5 protons
		1602m	acetyl CO	2.4—2.8	phenyl protons
CH_3	$P(C_6H_5)_3$	1940s (——)	terminal CO	9.61	methyl protons (doublet)
		1850vs		5.25	η^5-C_5H_5 protons
				2.5—2.8	phenyl protons
CH_3	$As(C_6H_5)_3$	1938s	terminal CO	9.59	methyl protons
		1848vs		5.21	η^5-C_5H_5 protons
				2.6—2.8	phenyl protons

^{a} In $CHCl_3$ solution. ^{b} In $CDCl_3$ solution with TMS an internal standard.

Experimental

All operations were carried out under nitrogen, including admission of nitrogen to evacuated flasks and collection of samples under nitrogen during chromatography. THF was distilled under nitrogen from phosphorus pentoxide and then lithium aluminium hydride before immediate use. All other solvents were used without further purification. (η^5-C_5H_5)Mo(CO)$_3$CH$_3$ was prepared by the standard method [20]. Triphenylphosphine, triphenylarsine and triphenylstibine were purchased from the Aldrich Chemical Company Limited and used without further purification. Photolysis reaction used a Philips HPK-125W medium pressure Hg arc lamp placed close to the pyrex reaction vessel. Reactions were monitored by observing changes in the infrared spectra (terminal carbonyl stretching region) of samples obtained by syringing aliquots from the reaction vessel through a subaseal cap. Chromatographic separation used alumina (type H).

Elemental analyses were conducted by The Microanalytical Laboratory, Department of Chemistry, University College, 20 Gordon Street, London WClH OAJ. Infrared spectra were recorded on a Perkin—Elmer Model 337 spectrometer and were calibrated with a polystyrene reference. NMR spectra were obtained on a Varian Associates XL-100 spectrometer. Melting points (uncorrected) were taken on an Electrothermal Melting Point Apparatus. Examples of procedures utilized are given below.

Synthesis of ($\eta^5$$C_5H_5$)Mo(CO)$_2$(COCH$_3$)As($C_6H_5$)$_3$

(η^5-C_5H_5)Mo(CO)$_3$CH$_3$ (2.5 mmol) and triphenylarsine (7.5 mmol) were stirred overnight in acetonitrile (25 ml) at 28° C. The solvent was removed on a rotary evaporator. The resultant solid was dissolved in the minimum amount of chloroform and chromatographed on alumina. Elution with a 1 : 1 mixture of chloroform and petroleum ether (40—60° C) gave a yellow band which was shown to contain (η^5-C_5H_5)Mo$(CO)_2CH_3$ by infrared spectroscopy. Further, elution with chloroform gave a second yellow band from which a yellow solid was obtained by evaporating off the solvent. The yield of bright yellow crystals (recrystallization from chloroform-petroleum ether mixtures, melting point 118° C) of (η^5-C_5H_5)Mo$(CO)_2(COCH_3)As(C_6H_5)_3$ (Found: C, 57.35; H, 4.17. $C_{27}H_{23}AsMoO_3$ calcd: C, 57.27; H, 4.10%) was 39%.

Synthesis of (η^5-C_5H_5)Mo$(CO)_2(COCH_3)Sb(C_6H_5)_3$

(η^5-C_5H_5)Mo$(CO)_3CH_3$ (2.5 mmol) and triphenylstibine (7.5 mmol) were stirred for 27 h in acetonitrile (30 ml) at 27° C. The solution had become a paler yellow. The solvent was removed on a rotary evaporator. The resultant solid was dissolved in the minimum amount of chloroform and chromatographed on alumina. Elution with a 1 : 1 mixture of chloroform and petroleum ether (40—60° C) gave a yellow band which was shown (see above) to contain (η^5-C_5H_5)Mo$(CO)_3CH_3$. Further elution with chloroform gave a second yellow band from which a yellow solid was obtained by evaporating off the solvent. The yield of bright yellow crystals (recrystallization from chloroform/petroleum ether mixtures, melting point 114° C) of (η^5-C_5H_5)Mo$(CO)_2(COCH_3)Sb(C_6H_5)_3$ (Found: C, 52.71; H, 4.04. $C_{27}H_{23}SbMoO_3$ calcd.: C, 52.88; H, 3.78%) was 37%.

Thermal decarbonylation of (η^5-C_5H_5)Mo$(CO)_2(COCH_3)As(C_6H_5)_3$

(η^5-C_5H_5)Mo$(CO)_2(COCH_3)As(C_6H_5)_3$ (150 mg) was dissolved in acetonitrile (15 ml) and the solution was stirred at 40° C. Aliquots, taken for analysis by infrared spectroscopy, showed that the reaction was complete after 1 h. The reaction was terminated and the solvent removed on a rotary evaporator. The resultant solid was chromatographed on alumina and elution with a 1 : 1 mixture of chloroform and petroleum ether (40—60° C) gave a yellow band which was shown (see above) to contain only (η^5-C_5H_5)Mo$(CO)_3CH_3$. Elution with chloroform gave no further products. A similar reaction procedure using dry THF (15 ml) as solvent also gave only (η^5-C_5H_5)Mo$(CO)_3CH_3$.

Photolytic decarbonylation of (η^5-C_5H_5)Mo$(CO)_2(COCH_3)As(C_6H_5)_3$

(η^5-C_5H_5)Mo$(CO)_2(COCH_3)As(C_6H_5)_3$ (200 mg) was dissolved in dry THF (20 ml) and irradiated, with stirring, using the medium pressure Hg lamp. Aliquots, taken for analysis by infrared spectroscopy, showed that the acetyl band had disappeared after 1 h and the initially yellow solution had turned yellow-brown. The reaction was terminated and the solvent removed on a rotary evaporator. The resultant solid was chromatographed on alumina. Elution with a 1 : 1 mixture of chloroform and petroleum ether (40—60° C) gave a yellow band which was shown by infrared spectroscopy to contain more than one complex. Further chromatography (using different ratios of chloroform:petroleum ether) failed to produce separated bands, however, crystallization from chloroform/petroleum ether mixtures gave yellow crystals (60 mg) while the mother liquor was shown by infrared spectroscopy, to contain (η^5-C_5H_5)Mo-$(CO)_3CH_3$. Further recrystallization yielded bright yellow crystals (24 mg; melting point 143° C) of (η^5-C_5H_5)Mo$(CO)_2(CH_3)As(C_6H_5)_3$ (Found: C, 58.64; H, 4.32. $C_{26}H_{23}AsMoO_2$ calcd: C, 58.01; H, 4.31%).

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