

SHORT COMMUNICATION

PREPARATION AND DECOMPOSITION OF BROMOACETYL METAL DERIVATIVES OF MOLYBDENUM, TUNGSTEN AND PLATINUM

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INTRODUCTION

Several carbene complexes have been described which lack heteroatom stabilization (1-4). Such complexes have generated considerable interest due to their potentially high chemical reactivity for cyclopropanation of olefins.

Most of the preparations of cationic alkylidene complexes reported to date have involved the electrophilic cleavage of alkoxy methyl complexes (5-11), although a few have employed alternative routes such as hydride abstraction (8,12), thermal loss of SMe_2 from a dimethylsulfonium alkyl complex (13), or protonation of a vinyl complex (14,15). Yet another approach is the thermal or photochemical decarbonylation of bromoacetyl transition metal derivatives.

Brookhart et al have shown that the low temperature protonation of alkylmetal derivatives produced from bromoacetylmetal species leads to the formation of cationic methylene complexes as intermediates which are capable of methylene transfer (17). We have now examined the reaction of bromoacetyl bromide with $\text{NaMC}_5\text{H}_5(\text{CO})_3$, ($\text{M} = \text{Mo}, \text{W}$), $\text{NaFeC}_5\text{H}_5(\text{CO})_2$ and $\text{Pt}(\text{Ph}_3\text{P})_4$ and investigated the thermal and photochemical decomposition of the resulting metal acyl complexes.

EXPERIMENTAL

All metal carbonyl compounds were operated under an atmosphere of dry, oxygen-free nitrogen. Solvents were deaerated with nitrogen and dried over molecular sieves. Freshly distilled and dry THF was used. Solutions of the complexes, in pyrex round bottomed flasks, were exposed to direct sunlight for one hour to study their decomposition.

Preparation of $\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_3(\text{BrCH}_2\text{CO})$: A solution of $\text{NaMo}(\text{C}_5\text{H}_5)(\text{CO})_3$ was prepared (18) from a mixture of 3.0g of $(\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_3)_2$, excess 1% sodium amalgam, and 100 ml of THF. The solution was cooled to -10°C and treated dropwise with 0.8 ml of bromoacetyl bromide in 5 ml of THF. The reaction mixture was stirred at 0°C for 2 hrs, and the solvent was removed under reduced pressure. The residue was washed with 50 ml of n-pentane, and extracted with 3×30 ml of CH_2Cl_2 and concentrated. Addition of n-hexane followed by cooling afforded 1.1 g of orange crystals (45%, m.p $112-115^\circ\text{C}$).

Preparation of $\text{W}(\text{C}_5\text{H}_5)(\text{CO})_3(\text{BrCH}_2\text{CO})$: A solution of $\text{NaW}(\text{C}_5\text{H}_5)(\text{CO})_3$ was prepared by refluxing $\text{W}(\text{CO})_6$ (3.0 g) with a 20% excess of NaC_5H_5 solution in 150 ml THF for 16 hrs (18). $\text{W}(\text{C}_5\text{H}_5)(\text{CO})_3(\text{BrCH}_2\text{CO})$ was then prepared in a manner similar to $\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_3(\text{BrCH}_2\text{CO})$ from 1.2 ml of bromoacetyl bromide. Orange red crystals (1.0 g) were obtained (31 %, m.p. $118-121^\circ\text{C}$).

Reaction of $\text{NaFe}(\text{C}_5\text{H}_5)(\text{CO})_2$ with BrCH_2COBr : Cyclopentadienyldicarbonyliron (I) dimer, (3.0 g), in 150 ml THF was added to a 1% sodium amalgam to produce $\text{NaFe}(\text{C}_5\text{H}_5)(\text{CO})_2$. The conversion of the dimer to anion was followed by monitoring the absorption band at 1750 cm^{-1} due to the bridge carbonyls. The

Table 1: Infrared and NMR spectra (60 MHz) for metal-bromoacetyl derivatives.

Compound	Metal-CO bands (cm ⁻¹) ^a	Acyl-CO bands (cm ⁻¹) ^a	NMR (δ, ppm) ^b
BrCH ₂ COMo(CO) ₃ C ₅ H ₅	2020s, 1950s 1930s	1645	5.2 (CH ₂) 5.6 (Cp)
BrCH ₂ COW(CO) ₃ C ₅ H ₅	2050s, 1960s 1990s	1630s	5.3 (CH ₂) 5.7 (Cp)

a = KBR Pellets

b = in CS₂

reaction of bromoacetyl bromide (1.3 ml) in 5 ml of THF with NaFe(C₅H₅)(CO)₂ gave mostly the dimer (Fe(C₅H₅)(CO)₂)₂. Extraction of the crude product with petroleum ether (b.p. 30-40°C), followed by chromatography over florisil afforded an orange red powder with low frequency CO band at 1660 and 1750 cm⁻¹. The latter were due to traces of (Fe(C₅H₅)(CO)₂)₂ which could not be removed by recrystallization.

Reaction of Pt(Ph₃P)₄ with BrCH₂COBr: Tetrakis(triphenylphosphine)platinum(0) (0.5 g) was dissolved in 5 ml of dry benzene. 0.2 ml of BrCH₂COBr was added dropwise while stirring for 10 minutes. The pale yellow liquid gradually deposited, upon standing, slightly impure, but quantitative yield of Pt(Ph₃P)₄Br₂.

Thermal decomposition of Mo(C₅H₅)(CO)₃(BrCH₂CO): The compound was placed in a Schlenk flask and heated to 100°C for 1 hour under vacuum. A dark grey product was obtained which was identified as Mo(C₅H₅)(CO)₃Br; NMR (CS₂), δ = 5.5 (Cp); IR (CCl₄), ν(CO) = 2040s, 1908s cm⁻¹.

Photochemical decomposition of M(C₅H₅)(CO)₃(BrCH₂CO) [M = Mo and W]: Exposure of the petroleum ether (b.p. 30-40°C) solution of the compound (M = Mo) for 1 hr to direct sunlight led to the formation of a grey precipitate and an orange solution. Filtration yielded a residue which was largely Mo(C₅H₅)(CO)₃Br. The NMR spectrum showed the expected signal for Mo(C₅H₅)(CO)₃Br, in addition to a new signal at δ = 3.6 ppm which was probably due to the presence of trace amounts of Mo(C₅H₅)(CO)₃(BrCH₂). Similarly the tungsten compound upon exposure to sunlight for 2 hrs led to the isolation of W(C₅H₅)(CO)₃Br containing trace amount of W(C₅H₅)(CO)₃(BrCH₂).

Thermal decomposition of W(C₅H₅)(CO)₃(BrCH₂CO): The compound was placed in Schlenk flask, evacuated and heated to 90°C for one hour. The orange red color of the sample changed to greyish black. The residue was identified as W(C₅H₅)(CO)₃Br. IR in CCl₄, ν(CO) = 1903s, 1950s, 1962s; NMR in CS₂ = 5.6 (Cp).

DISCUSSION

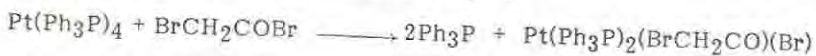
Although a number of bromomethyltransition metal derivatives such as Mo(C₅H₅)(CO)₃(BrCH₂)₂ and W(C₅H₅)(CO)₃(BrCH₂)₂ were obtained in trace quantities, the attempted preparative method for the generation of bromomethyl-metal derivatives did not give satisfactory results. The molybdenum and tungsten bromoacetyl complexes are photosensitive and thermally unstable. Extensive decomposition took place when the experiments were carried out at room temperature. Therefore, all of the synthesis of these bromoacetylmethyl-metal complexes were performed at 0°C, and care was taken to avoid prolonged exposure to light. The complexes are readily soluble in CH₂Cl₂, CS₂, and CCl₄ but they are sparingly soluble in n-pentane and n-hexane.

The attempt to prepare Fe(C₅H₅)(CO)₃(BrCH₂CO) did not give a satisfactory result. Previous investigators also isolated dimers in a related kind of reaction

(16). The quantitative formation of the dimer, $(\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_2)_2$ in the reaction between $\text{NaFeC}_5\text{H}_5(\text{CO})_2$ and BrCH_2COBr suggests that the iron anion is highly reactive (21) (and least selective) and the bromines at both ends of the bromoacetyl bromide are presumably replaced. The resulting product is unstable and decomposes to the dimer.



In the reaction involving BrCH_2COBr and $\text{Pt}(\text{Ph}_3\text{P})_4$, it appears that oxidative addition of the BrCH_2COBr did take place, but the resulting derivatives were unstable under the experimental conditions and decomposed spontaneously to produce the metal bromide species by elimination of Br . β -elimination has been observed previously for a related reaction (22). The formation of ketene was observed by monitoring the IR spectrum of the solution. It was found that a band appeared around 2115 cm^{-1} , grew and then decreased as decomposition proceeded. These facile decompositions (β -bromine elimination) of the bromoacetylmetal derivative can explain why the attempts to make $\text{Pt}(\text{Ph}_3\text{P})_2(\text{BrCH}_2\text{CO})\text{Br}$ gave $\text{Pt}(\text{Ph}_3\text{P})_2\text{Br}_2$.



The decomposition of the bromoacetylmetal complexes also produces carbon monoxide in addition to ketene. It appeared that β -bromine elimination and decarbonylation were simultaneously taking place. The loss of acyl-CO band in the IR spectra after thermal and photochemical decomposition of the complexes constitutes a proof for the loss of carbon monoxide. The data gathered were not sufficient to determine if the bromometal derivatives were produced by β -bromine elimination or by decarbonylation followed by the decomposition of the resulting bromomethylmetal derivatives. In order to determine if β -bromine elimination or decarbonylation is involved, the gaseous products of these reactions must also be analyzed.

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