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REACTION OF METAL—CARBENE COMPLEXES WITH VINYLLITHIUM REAGENTS

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Summary

The reaction of vinyllithium with $(CO)_5CrC(OCH_3)C_6H_5$ (Ic) at —78° followed by treatment with HCl at —78° gave 43% (*Z*)-1-methoxy-1-phenylpropene (IIIa) and 21% 1,4-dimethoxy-1,4-diphenyl-1,3-butadiene (IVa) and no trace of a vinylphenylcarbene complex or its expected decomposition products. IIIa and IVa are proposed to arise from electrophilic attack at the carbon—carbon double bond of a σ-allylchromium intermediate. The reaction of phenyllithium with $(CO)_5CrC(OCH_3)CH{=}CHC_6H_5$ (V) gave 9% $(CO)_5CrC(OCH_3)CH_2CH(C_6H_5)_2$ (VI) and 17% (*E*)-1-methoxy-1,3-diphenylpropene (VII). Reaction of V with lithium diphenylcuprate gave 30% of the conjugate addition product VI.

Introduction

Transition metal—carbene complexes have been implicated as transient intermediates in the synthesis of cyclopropanes from alkenes [1, 2]. To obtain a better understanding of the way in which transition metals promote the formation of cyclopropanes, it would be highly desirable to have access to a model transition metal—carbene complex which is stable enough to isolate and characterize and which is also reactive towards alkenes to give cyclopropanes. Stable transition metal carbene complexes such as Fischer's $(CO)_5CrC(OCH_3)C_6H_5$ are stabilized by an electron-donating heteroatom (O, N, S) attached to the carbene carbon atom and are unreactive towards simple alkenes [2]*. In an effort to find a less stable and more reactive metal—carbene complex, we previously prepared (diphenylcarbene)pentacarbonyltungsten(0), a carbene complex not stabilized by heteroatoms [4]. Although $(CO)_5WC(C_6H_5)_2$ was found to be less stable than heteroatom-stabilized carbene complexes, reactions with simple alkenes have not yet yielded cyclopropanes.

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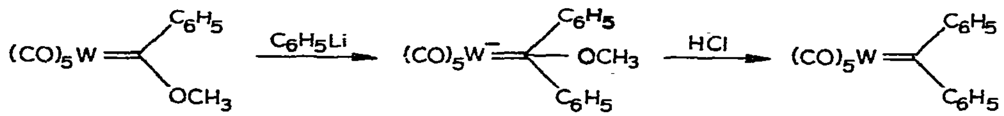
* These complexes have, however, been observed to give cyclopropanes upon reaction with α,β-unsaturated esters and with vinyl ethers [3].



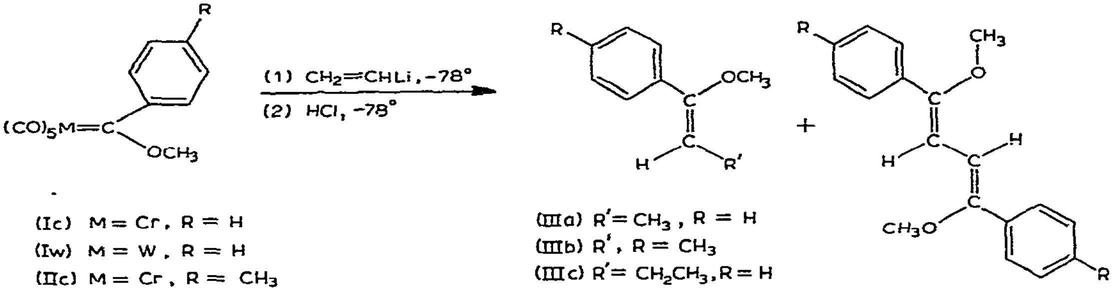
Here we report attempts to prepare vinylphenylcarbene complexes both from the reaction of vinyllithium with phenylmethoxycarbene complexes and from the reaction of phenyllithium with vinylmethoxycarbene complexes. While neither of these approaches have led to a vinylphenylcarbene complex, several interesting reactions discovered in the course of these investigations will be reported here.

Results

Reactions of vinylic lithium reagents with arylmethoxycarbene complexes

The addition of 1.1 equivalents of vinyllithium to a red solution of (phenylmethoxycarbene)pentacarbonylchromium(0) (Ic) at −78° gave an orange solution. Treatment of this solution with dry HCl at −78° gave a red solution. The reaction mixture contained neither the anticipated vinylphenylcarbene complex nor its likely thermal decomposition product phenylallene (less than 0.1%). Two vinyl ethers were isolated from the reaction mixture by preparative thin layer chromatography on silica gel. The faster moving vinyl ether was identified as (*Z*)-1-methoxy-1-phenylpropene (IIIa) by NMR, IR and acid-catalyzed hydrolysis to propiophenone. Only one geometric isomer of the vinyl ether was obtained. The yield of propiophenone obtained by direct hydrolysis of the crude reaction mixture was 43%. In addition a second vinyl ether was isolated in 21% yield and identified as 1,4-dimethoxy-1,4-diphenyl-1,3-butadiene (IVa) by IR, NMR, mass spectrum and ceric oxidation to (*E*)-1,2-dibenzoylethene. When the reaction of vinyllithium with Ic was carried out at −78° and then warmed to room temperature without the addition of HCl at −78°, IVa was obtained in 22% yield but none of IIIa was observed.

Similar results were obtained in the reactions of vinyllithium or propenyllithium with arylmethoxycarbene complexes Ic, Iw, and IIc. The results are summarized in Table 1.



(Ic) M = Cr, R = H
(Iw) M = W, R = H
(IIc) M = Cr, R = CH_3

(IIIa) R′ = CH_3, R = H
(IIIb) R′, R = CH_3
(IIIc) R′ = CH_2CH_3, R = H

(IVa) R = H
(IVb) R = CH_3

Reaction of phenyllithium and lithium diphenylcuprate with (styrylmethoxycarbene)pentacarbonylchromium(0)

In an alternative approach to the synthesis of a vinylphenylcarbene complex,

TABLE 1

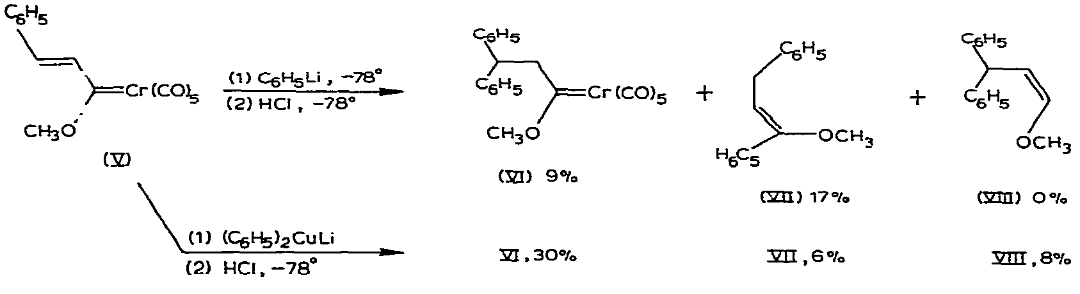
REACTION OF VINYLIC LITHIUM REAGENTS WITH ARYLMETHOXYCARBENE COMPLEXES

Carbene complex	Lithium reagent	Reaction conditions	Yield (%) of vinyl ether [a]	Yield of butadiene [b]
Ic	$CH_2{=}CHLi$	−78°, HCl, −78°	IIIa (43)	IVa (21)
Ic	$CH_2{=}CHLi$	−78°, no HCl		IVa (22)
Iw	$CH_2{=}CHLi$	−78°, HCl, −78°	IIIa (42)	IVa (23)
IIc	$CH_2{=}CHLi$	−78°, HCl, −78°	IIIb (33)	IVb (14)
Ic	$CH_3CH{=}CHLi$ [c]	−78°, HCl, −78°	IIIc (41)	
Iw	$CH_3CH{=}CHLi$ [c]	−78°, HCl, −78°	IIIc (41)	

[a] Determined by GC analysis of the ketones produced upon hydrolysis. [b] Yield of material isolated by thin layer chromatography. [c] 91% *cis*-, 9% *trans*-1-propenyllithium.

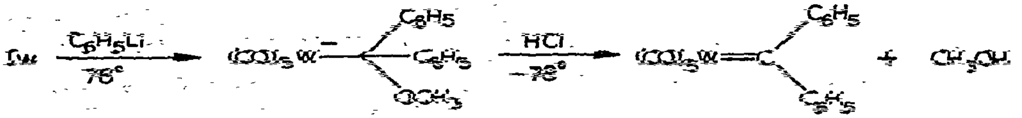
the reaction of phenyllithium with (styrylmethoxycarbene)pentacarbonylchromium(0) (V), was investigated. Addition of one equivalent of phenyllithium to a deep red ether solution of V at −78° produced an orange solution. This solution was then treated with HCl in ether at −78° and warmed to room temperature. Neither a vinylphenylcarbene complex nor its expected decomposition product 1,3-diphenylallene (< 0.5%) could be detected in the reaction mixture. Thin-layer chromatography of the reaction mixture gave an inseparable mixture of (2,2-diphenylethylmethoxycarbene)pentacarbonylchromium(0) (VI) and (*E*)-1-methoxy-1,3-diphenylpropene (VII). Hydrolysis of enol ether VII gave 3-phenylpropiophenone (17% yield by gas chromatography) which was isolated by TLC and identified by spectral comparison with an authentic sample. Carbene complex VI was obtained in 9% yield from the hydrolysis reaction mixture and was identified by its IR, NMR and mass spectral properties and by ceric ion oxidation [5] to methyl 3,3-diphenylpropionate.

Reaction of lithium diphenylcuprate with carbene complex V gave an increased yield (30%) of carbene complex VI, the product of conjugate addition. In addition, the cuprate reaction gave a 6% yield of VII and an 8% yield of a new vinyl ether product (*Z*)-1-methoxy-3,3-diphenylpropene (VIII), which was identified by spectroscopy and by hydrolysis to 3,3-diphenylpropanal.



Discussion

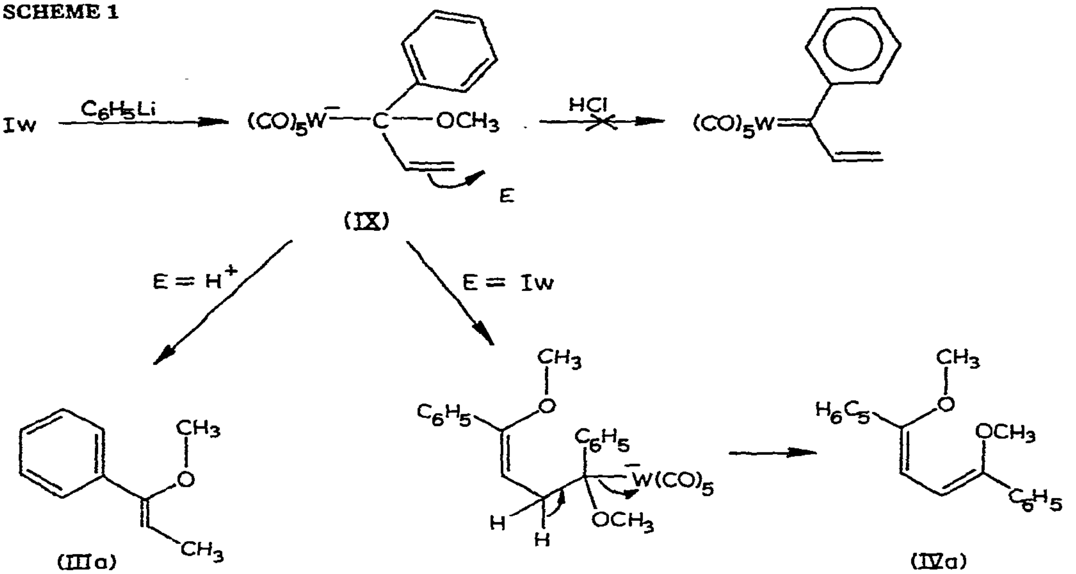
Our attempted synthesis of a vinylphenylcarbene complex was modelled after our successful synthesis of $(CO)_5WC(C_6H_5)_2$ [4]. The reaction of Iw with phenyllithium at −78° gave a thermally unstable adduct from which methanol could be eliminated upon treatment with HCl at −78°.



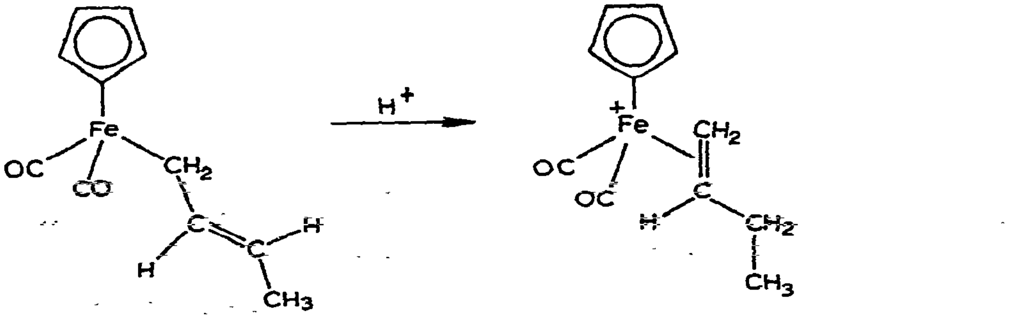
The reaction of vinylic lithium reagents with Iw apparently proceeds in a similar fashion to give adduct IX since HCl treatment at −78° gives products IIIa and IVa which incorporate a new bond from the carbene carbon atom to the added vinyl group. Protonation of adduct IX, however, does not occur at the methoxy group and does not lead to loss of methanol. Neither a phenylvinylcarbene complex nor phenylallene, the product expected from thermal decomposition of a vinylphenylcarbene complex, were observed.

The formation of vinyl ether IIIa and of dimethoxybutadiene IVa can be understood in terms of electrophilic attack at the terminal end of the σ-allyl moiety of anionic adduct IX (See Scheme 1). Terminal protonation of IX leads directly to vinyl ether IIIa. The protonation leads selectively to the formation of only the *Z*-isomer of IIIa. Alternatively, the carbene complex Iw can electrophilically attack the σ-allyl unit of IX and give rise to the dimethoxybutadiene IVa. (The dimethoxybutadiene IVa is obtained even in the absence of HCl work-up).

SCHEME 1



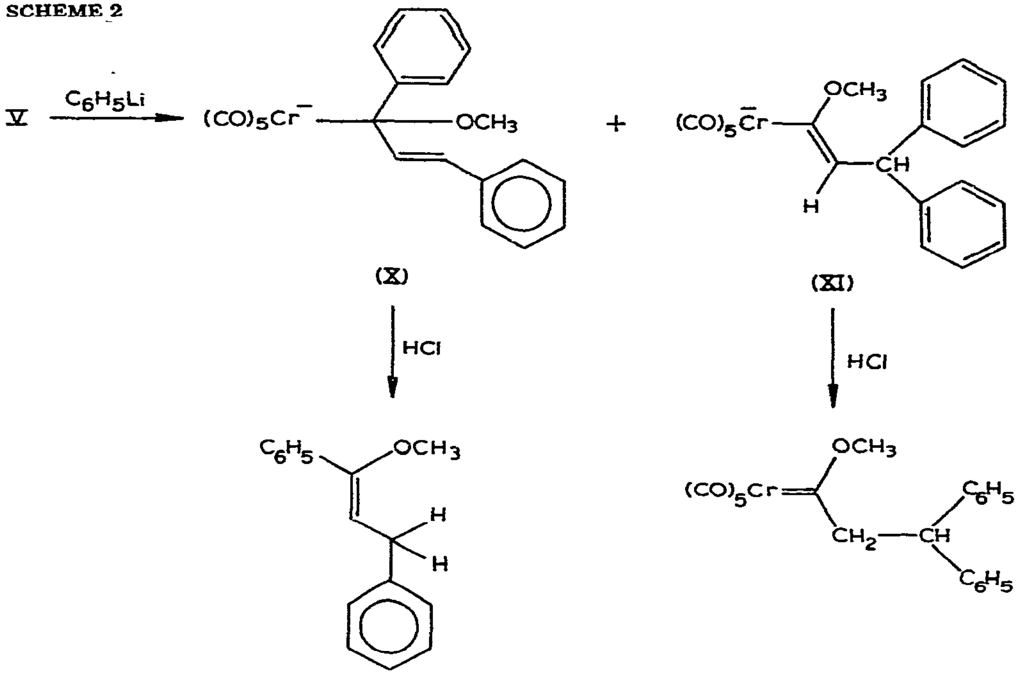
The electrophilic attack at the σ-allyl unit of IX is similar to reactions of σ-allyl iron complexes with H+, TCNE, and DDQ [6].



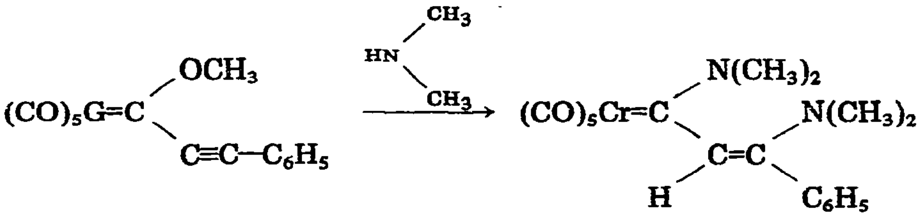
More recently, Giering has reported the electrophilic attack of a cationic carbene complex on a σ-allyl iron compound [7].

The attack of phenyllithium on styrylmethoxycarbene complex V occurs both directly at the carbene carbon atom and conjugately at the carbon—carbon double bond (Scheme 2). Protonation of intermediate adduct X does not lead to loss of methanol and the formation of either a styrylphenylcarbene complex or its expected thermal decomposition product 1,3-diphenylallene. Protonation of X occurs at the σ-allyl unit to give vinyl ether VII. Conjugate addition product XI is the anion of a carbene complex and protonation gives carbene complex VI.

SCHEME 2



The ratio of conjugate addition product VI to direct addition product VII increases from 0.5/1 to 5/1 when lithium diphenylcuprate is employed in the initial reaction with V. Organocopper compounds are well known to give predominantly conjugate addition products on reaction with α,β-unsaturated carbonyl compounds*. The analogy between carbene complexes and esters [1, 2, 9] is thus extended by our results to include similar conjugate addition behavior towards organocopper reagents. The conjugate addition of dimethylamine to an acetylenic carbene complex was previously observed by Fischer [10].



$$(CO)_5G{=}C\begin{matrix}OCH_3\\ C{\equiv}C{-}C_6H_5\end{matrix}\xrightarrow{HN\begin{smallmatrix}CH_3\\ CH_3\end{smallmatrix}}(CO)_5Cr{=}C\begin{matrix}N(CH_3)_2\\ C{=}C\begin{matrix}N(CH_3)_2\\ C_6H_5\end{matrix}\\ H\end{matrix}$$

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* For a review of conjugate addition of organocopper reagents see ref. 8.

Experimental section

NMR spectra were determined using a Jeolco MH-100 spectrometer. Infrared spectra were recorded on a Beckman IR-8 spectrophotometer. Mass spectra were determined using an AEI-902 mass spectrometer, or a Varian CH-7 GC-mass spectrometer. Gas chromatographic analyses were performed using a Hewlett—Packard Model 5750 research chromatograph. Preparative thin-layer chromatography was performed on Merck PF_{254} silica gel. All reactions were carried out under a nitrogen atmosphere. Diethyl ether was distilled from sodium and benzophenone under a nitrogen atmosphere. Carbene complexes Ic, Iw, IIc and $(CO)_5CrC(OCH_3)CH_3$ were prepared by the procedure of Fischer [11, 12]. *cis*-1-propenyllithium (91% *cis*) was prepared and analyzed according to the procedure of Whitesides [13].

Reaction of Ic with vinyllithium

Vinyllithium (0.41 ml, 1.5 *M* in THF, 0.56 mmol, Foote Mineral) was added dropwise to a red solution of Ic (0.15 g, 0.48 mmol) in 20 ml of diethyl ether at —78°. After 30 minutes, the resulting pale-orange solution was treated with dry HCl (0.48 ml, 1.73 *M* in Et_2O, 0.84 mmol) at —78° to give a red solution which was then warmed to room temperature. Preparative thin layer chromatography on silica gel—hexane allowed the isolation of a white solid, m.p. 89—92°, IVa (14 mg, 22%, R_f 0.25) and a colorless oil, IIIa (R_f 0.29).

The structure of IVa was assigned on the basis of spectral data: NMR ($CDCl_3$) δ 3.71 (s, 6H, OCH_3), 6.63 (s, 2H, HC=C), 7.55 (m, 10H, C_6H_5); IR (CCl_4) 3077, 2941, 2850, 1594, 1491, 1444, 1310, 1294, 1274, 1070 (CH_3O), 696 cm^{-1}; UV (hexane) 237 nm (ε 9700), 330 (ε 26000)); mass spectrum *m/e* (rel. intensity) 266 (80), 251 (21), 236 (17), 220 (12), 191 (17), 133 (10), 115 (15), 106 (10), 105 (100), 91 (9), 77 (72), 51 (11); exact mass, 266.1309 (calcd. for $C_{18}H_{18}O_2$, 266.1307). Oxidation of IVa (6 mg, 0.025 mmol) with excess ceric ammonium nitrate (75 mg) in acetone for 20 minutes gave dibenzoylethene (4.5 mg, 85%) which was isolated by preparative thin-layer chromatography (R_f 0.20 on silica gel—pentane) and identified by comparison of IR and NMR spectra with those of an authentic sample.

The structure of IIIa was determined by spectral methods. The NMR spectrum was in good agreement with that reported for (*Z*)-1-methoxy-1-phenylpropene [14] and none of the (*E*)-isomer was detected: NMR (CCl_4) δ 1.76 (d, *J* 7Hz, 3H, CH_3CH=C), 3.50 (s, 3H, OCH_3), 5.28 (q, *J* 7Hz, 1H. HC=C), 7.31 (m, 5H, C_6H_5). The yield of IIIa was determined to be greater than 43% by direct hydrolysis of the crude reaction mixture by addition of wet HCl in Et_2O and VPC analysis (6′ × 1/8″ 10% UC-W98 column, n-$C_{12}H_{26}$ internal standard) of the propiophenone formed.

Reactions of Iw and IIc with vinyllithium and cis-1-propenyllithium

Similar procedures were followed to give the results summarized in Table 1. The products were identified by spectral means.

IIIb: NMR δ 1.72 (d, *J* 7 Hz, 3H, CH_3CH=C), 2.30 (s, 3H, CH_3Ar), 3.41 (s, 3H, OCH_3), 5.09 (q, *J* 7 Hz, HC=C), 6.93 (d, *J* 8 Hz, 2H), 7.12 (d, *J* 8 Hz, 2H). IR (thin film) 3030, 2933, 2855, 1655, 1509, 1436, 1315, 1262, 1073, 825, 803 cm^{-1}. IIIb was hydrolyzed to 1-(4-tolyl)-1-propanone which was identified by spectral comparisons with an authentic sample.

IIIc: NMR (CCl_4) δ 1.06 (t, *J* 7 Hz, 3H, CH_2CH_3), 2.32 (quintet, *J* 7 Hz, 2H, $CH_2C=C$), 3.57 (s, 3H, OCH_3), 5.38 (t, *J* 7 Hz, 1H, HC=C), 7.46 (m, 5H, C_6H_5)*. IR (thin film) 3030, 2966, 1648, 1447, 1332, 1297, 1276, 1238, 1077, 770, 697 cm^{-1}. IIIc was hydrolyzed to give butyrophenone which was identified by spectral comparisons with an authentic sample.

IVb: NMR (CCl_4) δ 2.32 (s, 6H, CH_3Ar), 3.54 (s, 6H, OCH_3), 6.26 (s, 2H, HC=C), 6.98 (d, *J* 8 Hz, 4H, Ar), 7.24 (d, *J* 8 Hz, 4H, Ar). IR (CS_2) 3050, 3000, 2941, 2840, 1312, 1298, 1274, 1070, 821 cm^{-1}.

(Styrylmethoxycarbene)pentacarbonylchromium(0), V

V was prepared by the condensation of the anion of $(CO)_5CrC(OCH_3)CH_3$ with benzaldehyde [16]. n-Butyllithium (7.6 ml, 1.74 *M* in hexane, 13 mmol, Foote Mineral) was added to a solution of $(CO)_5CrC(OCH_3)CH_3$ (3.0 g, 12 mmol) in 100 ml diethyl ether at —78°. After 2 minutes, benzaldehyde (1.30 g, 12 mmol) was added at —78°. The solution was stirred at 0° for 15 minutes, washed with 40 ml water, dried (Na_2SO_4) and concentrated. Column chromatography (silica gel—hexane) gave deep red crystals of V (2.12 g, 52%, m.p. 73—76°). NMR (CS_2) δ 4.74 (s, 3H, OCH_3), 6.83 (d, *J* 16 Hz, 1H, $C_6H_5CH=CH$), 7.35 (m, 5H, C_6H_5), 7.81 (d, *J* 16 Hz, 1H, $C_6H_5CH=CH$). IR (CS_2) 2053, 1980, 1946 cm^{-1}.

Reaction of phenyllithium with V

Phenyllithium (3.6 ml, 0.25 *M*, 0.89 mmol) was added by syringe to a solution of V (300 mg, 0.89 mmol) in diethyl ether at —78°. After 10 minutes at —78°, HCl in diethyl ether (1.50 ml, 1.38 *M*, 2.07 mmol) was added. Preparative thin-layer chromatography (silica gel—hexane) allowed the isolation of a mixture (R_f 0.22) of carbene complex VI and vinyl ether VII. The NMR spectrum (CS_2) indicated a 4.3/1 mixture of VII/VI; resonances due to vinyl ether VII appeared at δ 3.48 (s, CH_3O), 3.52 (d, $CH_2HC=C$), 5.32 (t, *J* 7 Hz, $CH_2CH=C$), 7.2 (m, C_6H_5).

Since the mixture of VI and VII could not be separated, in a separate parallel experiment the crude reaction mixture was hydrolyzed by the addition of 0.10 ml water and stirring for 4 h at 25°. Preparative thin-layer chromatography (silica gel—hexane) allowed the isolation of pure carbene complex VI (33 mg, 9%, R_f 0.22). NMR (CS_2) δ 4.07 (d, *J* 7 Hz, 2H, $CHCH_2$), 4.47 (t, *J* 7 Hz, 1H, $CHCH_2$), 4.56 (s, 3H, OCH_3), 7.08 (m, 10H, C_6H_5); IR (CS_2) 2063 s, 1989 s, 1955 cm^{-1}; exact mass, 416.0333 (calcd. for $C_{21}H_{16}O_6Cr$, 416.0350). VI was further characterized by ceric ammonium nitrate oxidation to methyl 3,3-diphenylpropionate (95% yield) which was identified by comparison of its IR and NMR spectra with those of an authentic sample.

The hydrolysis reaction mixture also contained 1,3-diphenyl-1-propanone (17% yield measured by gas chromatography, 20″ × 1/8″ 10% UC-W98 column, n-$C_{16}H_{34}$ internal standard) which was isolated in 13%-yield by thin-layer chromatography (R_f 0.16) and identified by spectral comparison with an authentic sample.

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* The NMR spectrum is in agreement with that reported by Casey et al. [15].

Reaction of lithium diphenylcuprate with V

A solution of $LiCu(C_6H_5)_2 \cdot PBu_3$ was prepared by the addition of phenyllithium (1.21 ml, 1.66 *M*, 2.0 mmol) to a solution of $[Cu(PBu_3)]_4$ (391 mg, 1.0 meq) in 10 ml diethyl ether at −78° and was transferred by cannula to an ether solution of V (300 mg, 0.89 mmol) at −78°. After 15 minutes at −78°, HCl in diethyl ether (2.60 ml, 1.87 *M*, 4.86 mmol) was added. Preparative thin-layer chromatography (silica gel—hexane) allowed the isolation of a mixture (R_f 0.22) of carbene complex VI, tri-n-butylphosphine and two methylvinyl ethers VII and VIII tentatively identified on the basis of the NMR spectrum of the mixture.

In a separate identical experiment, the crude reaction mixture was directly hydrolyzed by the addition of 0.30 ml H_2O and stirring for 15 hours. Thin-layer chromatography (silica gel—hexane) gave VI (106 mg, 30%, R_f 0.20). In addition, gas chromatography (20″ × 1/8″ 10% UC-W98 column, $n\text{-}C_{16}H_{34}$ internal standard) demonstrated the presence of 1,3-diphenyl-1-propanone (6%) and 3,3-diphenylpropanal (8%) which was identified by comparison of VPC retention time and mass spectrum (CH-7 GC—mass spectrometer) with those of an authentic sample.

Acknowledgement

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