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Conjugate Addition of Carbene Anions to α,β-Unsaturated Carbonyl Compounds

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The reaction of (2-oxacyclopentylidene)pentacarbonylchromium, **1**, with 1 equiv of base and methyl vinyl ketone followed by acidic workup gives a 41% yield of monoalkylated material **3**. The reaction of **1** with excess methyl vinyl ketone in the presence of a catalytic amount of base gives a 36% yield of **4**, the product of dialkylation followed by aldol condensation. The reactions of the anion of **1** with 2-cyclohexenone, *trans*-3-penten-2-one, *trans*-4-phenylbuten-2-one, and methyl *trans*-2-butenoate gave diastereomeric mixtures of monoalkylated adducts. The reactions of carbene anions with acetyl chloride, bromine, and ethylene sulfide are also reported.

Introduction

The evolution of metal–carbene complexes into useful reagents for organic synthesis[1,2] requires the development of general synthetic methods for the preparation of a wide variety of metal–carbene complexes. Recently, we demonstrated that anions generated α to the carbene carbon of metal–carbene complexes are synthetically useful intermediates for the elaboration of metal–carbene complexes.[3-7] These carbene anions are readily generated from metal–carbene complexes using convenient bases such as $NaOCH_3$ or n-BuLi.[7-9] Carbene complexes are remarkably acidic; in THF, $(CO)_5CrC(OCH_3)CH_3$ is as acidic as p-cyanophenol, which has a pK_a of 8 in water.[9] The high thermodynamic stability of carbene anions provides a driving force for the addition of a nucleophile to the carbon–carbon double bond of vinylcarbene complexes and thus makes vinylcarbene complexes excellent Michael acceptors.[10-13]

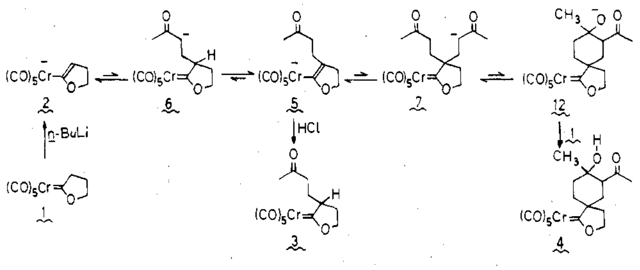
In spite of their high thermodynamic stability, carbene anions are moderately reactive toward electrophiles such as epoxides,[4] α-bromo esters,[4] aldehydes,[3] and chloromethyl methyl ether.[5] Here we report the reactions of carbene anions toward α,β-unsaturated carbonyl compounds.

Results and Discussion

Stoichiometric Reaction of Methyl Vinyl Ketone with the Anion of 1. The reaction of (2-oxacyclopentylidene)pentacarbonylchromium(0), **1**, with methyl vinyl ketone was studied extensively to define the course of the conjugate addition reaction. Reaction of the anion **2** (generated by addition of 1 equiv of n-BuLi to **1** at −78 °C) with methyl vinyl ketone in THF at 0 °C for 1 h gave 41% of the conjugate addition product **3** and 4% of recovered **1** after treatment with HCl. No dialkylated product **4** (vide infra) was observed.

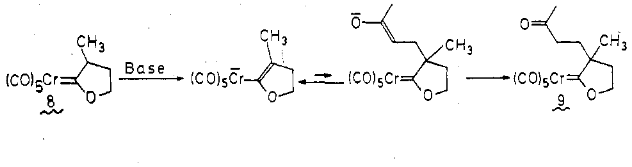
When a similar reaction mixture was quenched with DCl, the monoaddition product **3** was found by NMR to be 43% deuterated at the position α to the carbene carbon atom; no deuterium incorporation α to the ketone was detected. The incomplete deuterium incorporation at the carbon α to the carbene carbon of **3** is probably due to partial washing out of the label on silica gel TLC during isolation; the rapid exchange of protons on the carbon α to the carbene carbon atom of **1** has been observed previously.[7-9,14] These results indicate that carbene anion **5** is the major species present before acidic workup (Scheme I). Carbene complex **1** and p-cyanophenol have comparable acidities in THF,[7,9] and it is therefore not surprising that carbene anion **5** greatly predominates over enolate anion **6** at equilibrium.

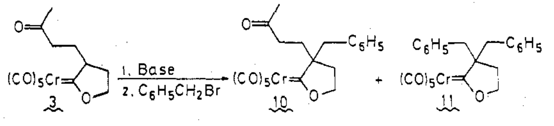
Scheme I



The conversion of carbene anion **2** to alkylated carbene anion **5** indicates that the Michael addition reaction is *favorable if an anion of comparable stability is the net product.* The absence of dialkylated materials such as **4** in the stoichiometric reaction could well be due to the reversible formation of the dialkylated anion **7** which is less stable than **5** since an enolate anion is substantially less stable than a carbene anion.

The above explanation implies that a tertiary carbene anion will not react with a Michael acceptor to give an addition product. Indeed, reaction of the anion of **8** with methyl vinyl





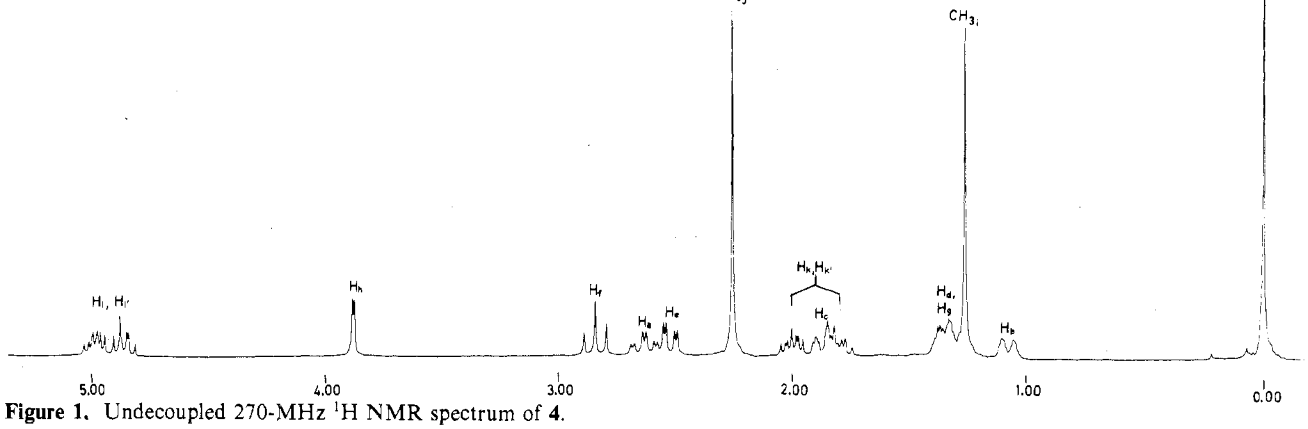
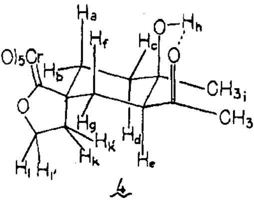


Figure 1. Undecoupled 270-MHz ^{1}H NMR spectrum of **4**.

ketone failed to give an addition product. However, similar addition products can be obtained by alkylation of Michael addition products. For example, reaction of anion of **3** with benzyl bromide gave a 46% yield of alkylated product **10** in addition to 5% of dibenzylated **11**. The above reaction demonstrates that carbene anions are readily and selectively alkylated in the presence of ketone functionalities. Compound **11** probably arises from a sequence of benzylation, retro Michael addition, and benzylation. The observation of **11** demonstrates that the Michael addition of carbene anions to methyl vinyl ketone is a reversible reaction.

Catalytic Reaction of 1 with Methyl Vinyl Ketone. If the failure to observe a dialkylated Michael addition product from the *stoichiometric* reaction of anion **2** with methyl vinyl ketone were due to the *reversible formation of an unstable enolate* (*7*) *or of an unstable alkoxide anion* (***12***), we reasoned that it might be possible to achieve bis Michael addition reactions in the presence of *catalytic* amounts of base. Reaction of **1** with 3 equiv of methyl vinyl ketone in the presence of 0.1 equiv of base led to the exclusive formation of **4** in 36% yield.



4

Compound **4** is the product of dialkylation of **1** by methyl vinyl ketone followed by aldol condensation. When the reaction of **1** with 1 single equiv of methyl vinyl ketone was carried out in the presence of a 0.1 equiv of base, a mixture of starting material **1** (23%), monoalkylated **3** (22%), and dialkylated **4** (17%) was obtained.

The structure of **4** was determined from the infrared spectrum, mass spectrum, and ^{1}H NMR spectrum at 270 MHz (see Figure 1 and Experimental Section). The acetyl group was assigned an equatorial position since H_e was found to be an axial proton with $J_{ef} = 13$ Hz and $J_{eg} = 3.3$ Hz. The assignment of stereochemistry of the hydroxyl-bearing carbon atom was made on the basis of the observed long-range 2.5-Hz coupling of the hydroxyl proton. This is due to W coupling of H_d with the hydrogen-bonded H_h. Irradiation of the multiplet at δ 1.34 (H_d and H_g) caused the OH doublet to collapse to a singlet. The carbene carbon atom is assigned an equatorial configuration since the axial protons H_a and H_f are deshielded by the metal and are shifted downfield to δ 2.63 and 2.84, respectively. It should be pointed out that the assigned structure for **4** is the most stable diastereomer as expected for a product formed under equilibrium conditions.

Table I. Stoichiometric Reactions of Anion **2** with α,β-Unsaturated Carbonyl Compounds

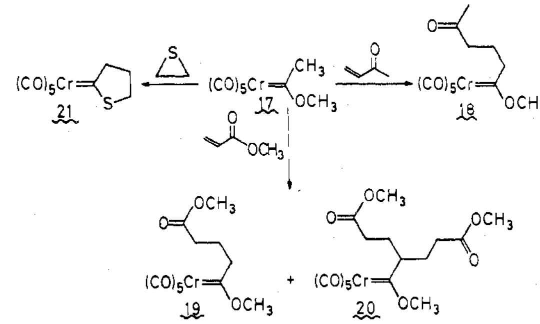
Unsatd carbonyl compd	Mono-addition product	% yield	Ratio of diaster-eomers
CH_2=$CHCOCH_3$	3	41	
trans-CH_3CH=$CHCOCH_3$	13	70	1:1
trans-C_6H_5CH=$CHCOCH_3$	14	60	1:1
2-Cyclohexen-1-one	15	49	
trans-CH_3CH=$CHCO_2CH_3$	16	62	2:1
$(CH_3)_2C$=$CHCOCH_3$		0	

While the addition of methyl vinyl ketone to *stoichiometric* quantities of the anion of **8** led to no apparent reaction, the reaction of **8** with 2 equiv of methyl vinyl ketone in the presence of catalytic (0.1 equiv) amounts of base led to the formation of **9** in 35% yield.

In summary, the stoichiometric reaction of the anion **2** with methyl vinyl ketone leads to the formation of **5**, the anion of the mono adduct, while the base-catalyzed reaction of **1** with methyl vinyl ketone leads to a neutral dialkylated product, **4**. Thus the degree of alkylation of carbene anions can readily be controlled by variation of the reaction conditions.

Reactions of the Anion of 1 with Various Michael Acceptors. The reactions of stoichiometric amounts of anion **2** with various Michael acceptors were investigated to define the scope of the reaction (Scheme II and Table I). α,β-Unsaturated ketones and esters with a single β-alkyl or -aryl substituent reacted with the anion to give good yields of monoaddition products. Two new asymmetric centers are generated in these reactions and mixtures of diastereomers were obtained in all cases. Reaction of the anion **2** with mesityl oxide which has two β-alkyl substituents failed to give a Michael addition product. It is known that β substituents tend to prevent Michael additions to α,β-unsaturated carbonyl compounds.[15]

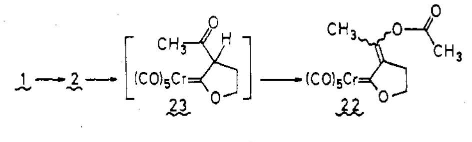
Addition Reactions of the Anion of $(CO)_5CrC(OCH_3)CH_3$. The reactions of $(CO)_5CrC(OCH_3)CH_3$, **17**, with Michael acceptors was briefly investigated. In general, low yields and mixtures of mono and bis adducts were observed. Reaction of the anion of **17** with methyl vinyl ketone gave a 22% yield

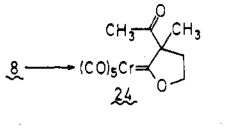


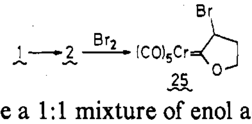
of monoaddition product **18**. Reaction of the anion of **17** with methyl acrylate gave a mixture of 21% monoalkylated **19** and 15% dialkylated **20**.

Miscellaneous Reactions of Carbene Anions with Electrophiles. This opportunity will be taken to present several extensions of our previous work on the reactions of carbene anions with electrophiles. We have previously reported reactions of carbene anions with epoxides;[4] we have now found that ethylene sulfide reacts with the anion of **17** to give the cyclic sulfur-substituted carbene complex **21**.

Earlier we reported that the reaction of $(CO)_5WC(OCH_3)CH_3$ with base followed by acetyl choride gave a 2:1 mixture of *Z*- and *E*-$(CO)_5WC(OCH_3)CH{=}C(CH_3)O_2CCH_3$;[3] these enol acetates were suggested to arise from O-acetylation of an intermediate acetyl-substituted carbene complex. The reaction of the anion of **1** proceeds in a similar manner to give a 1:1 mixture of enol acetates **22**, presumably derived from O-acetylation of **23**. However, acetylation of the anion of **8** gives the α-acetylated carbene complex **24** which cannot easily undergo enolization and formation of an enol acetate. Bromination of the anion of **1** gave a 55% yield of the α-bromo carbene complex **25**.





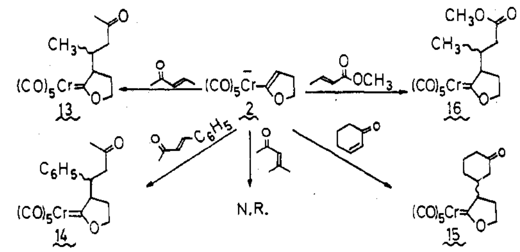


Experimental Section

General Information. All reactions were carried out in flame-dried flasks under a nitrogen atmosphere. Ether and tetrahydrofuran (THF) were distilled from sodium and benzophenone under a nitrogen atmosphere. NMR spectra were taken using a JEOLCO MH-100 or a Bruker WH-270 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 267 infrared spectrometer. Mass spectra were taken using a AEI-902 mass spectrometer at 70 eV. For carbene complexes, the intensities of peaks from successive loss of CO ligands are listed in addition to all peaks with greater than 10% relative intensity. Preparative thin-layer chromatography (TLC) was performed on Merck PF-254 silica gel. A Thomas-Hoover capillary melting point apparatus was used to determine melting points which are uncorrected.

Reaction of the Anion of 1 with Methyl Vinyl Ketone. *n*-BuLi (0.27 mL, 1.43 M, 0.38 mmol) was added to **1** (100 mg, 0.38 mmol) in 10 mL of THF at −78 °C. The solution was warmed to 0 °C and methyl vinyl ketone (50 μL, 0.62 mmol, Aldrich) was injected. After 1 h at 0 °C, HCl in ether (0.15 mL, 2.8 M, 0.42 mmol) was added. Preparative TLC (1:1 hexane–ether) afforded **1** (4 mg, 4% recovery, R_f 0.37) and **3** (52 mg, 41%, R_f 0.22) as a yellow solid: mp 98–100 °C dec; NMR ($CDCl_3$) δ 1.5–1.8 (m, 2 H, CH_2CH_2O), 1.8–2.1 (m, 1 H of $CH_2CH_2C{=}O$), 2.20 (s, 3 H, $CH_3C{=}O$), 2.4–2.7 (m, 3 H, $CH_2C{=}O$ and 1 H of $CH_2CH_2C{=}O$), 3.5 (m, 1 H, $HC{-}C{=}Cr$), 4.90 (t, J = 7.5 Hz, 2 H, CH_2O); IR (hexane) ν_{CO} 2070 (w), 1963 (s), 1990 (w), 1954 (s), 1935 (s) cm^{-1}; exact mass 331.9994 (calcd for $C_{13}H_{12}O_7Cr$ 331.9987); MS [m/e (%)] 332 (3) M^+, 304 (<1) M − 1CO, 276 (2) M − 2CO, 248(1) M − 3CO, 220 (7) M − 4CO, 192 (8) M − 5CO, 156 (11), 154 (26), 113 (11), 99 (34), 96 (21), 86 (100), 83 (17), 80 (15), 71 (10), 69 (21), 67 (11), 55 (30), 53 (15), 52 (46). Anal. Calcd for $C_{13}H_{12}O_7Cr$: C, 47.00; H, 3.64; Cr, 15.65. Found: C, 47.08; H, 3.81; Cr, 15.30.

Scheme II



An experiment similar to the one above was performed using the same amount of reactants. The reaction was quenched after 50 min at 0 °C by adding the reaction mixture dropwise to DCl (0.40 mL, 1.2 M in Et_2O, 0.48 mmol) in 2 mL of THF and stirring for 1 min. Preparative TLC gave **3** which according to NMR contained 43% d_1 in the position α to the carbene carbon. There was no evidence of deuterium incorporation adjacent to the ketone.

Base-Catalyzed Reaction of 1 with Methyl Vinyl Ketone. *n*-BuLi (0.025 mL, 1.31 M, 0.033 mmol) was added to **1** (89 mg, 0.34 mmol) in 8 mL of THF at −78 °C. Methyl vinyl ketone (83 μL, 1.03 mmol) was then added, and the solution was warmed to 0 °C. After 1.5 h of stirring, HCl in ether (0.06 mL, 0.69 M, 0.04 mmol) was added. Removal of solvent and preparative TLC (3:1 ether–hexane) gave **4** (49 mg, 36%, R_f 0.18) as a yellow solid: mp 142–146 °C dec; IR (CH_2Cl_2) ν_{CO} 2059 (m), 1982 (w), 1945 (s), 3450 (OH), 1700 cm^{-1}(C═O of ketone); NMR ($CDCl_3$, 270 MHz) δ 4.99 (1 H, H_l, m), 4.86 (1 H, $H_{l'}$, m), {H_k, $H_{k'}$} AB quartet, 3.88 (1 H, H_h, d, J_{hd} = 2.5 Hz, exchanges in D_2O), {H_d, H_g} s, 2.84 (1 H, H_f, dd, J_{fg} = 13 Hz, J_{fe} = 13 Hz), {H_d, H_g} d, J = 13 Hz, {He} d, J = 13 Hz, 2.63 (1 H, H_a, ddd, J_{ad} = 13.5 Hz, J_{ab} = 13.5 Hz, J_{ac} = 3.5 Hz), {H_d, H_g} dd, J = 13.5, 3.5 Hz, {H_b} dd, J = 13.5, 3.5 Hz, {H_c} dd, J = 13.5, 13.5 Hz, 2.51 (1 H, H_e, dd, J_{ef} = 13 Hz, J_{eg} = 3.3 Hz), {H_f} d, J = 3.3 Hz, {H_d, H_g} d, J = 13 Hz, 2.25 (3 H, H_j, s), 2.00 (1 H, H_k, m), 1.81 (1 H, $H_{k'}$, m), {H_l, $H_{l'}$} AB quartet, 1.87 (1 H, H_c, ddd, J_{cd} = 13 Hz, J_{ca} = 3.5 Hz, J_{cb} = 2.5 Hz), {H_d, H_g} dd, J = 3.5, 2.5 Hz, {H_a} dd, J = 13, 2.5 Hz, {H_b} dd, J = 13, 3.5 Hz, 1.34 (2 H, H_d, H_g, m), 1.26 (3 H, H_i, s), 1.07 (1 H, H_b, broad d, J_{ab} = 13.5 Hz), {H_a} broad s; exact mass 402.0387 (calcd for $C_{17}H_{18}CrO_8$ 402.0407); MS [m/e (%)] 402 (8) M^+, 384 (1), 318 (8) M − 3CO, 290 (3) M − 4CO, 272 (2), 262 (28) M − 5CO, 244 (51), 235 (13), 234 (21), 216 (19), 214 (13), 195 (13), 194 (21), 176 (18), 148 (12), 133 (24), 124 (31), 123 (100), 121 (13), 109 (14), 105 (14), 95 (16), 93 (17), 91 (19), 79 (17), 77 (14), 55 (13), 52 (62).

The above procedure was performed using 1 equiv of methyl vinyl ketone. Preparative TLC (3:1 hexane–ether) gave **1** (21 mg, 23%, R_f 0.47), **3** (27 mg, 22%, R_f 0.22), and **4** (24 mg, 17%, R_f 0.17).

Base-Catalyzed Reaction of 8 with Methyl Vinyl Ketone. *n*-BuLi (0.025 mL, 1.31 M, 0.033 mmol; total base 1.52 M, 0.038 mmol) was added to a solution of **8** (87 mg, 0.32 mmol) in 5 mL of THF at −78 °C. Methyl vinyl ketone (51 μL, 0.63 mmol) was added, and the solution was warmed to 0 °C and stirred for 1.5 h. HCl in ether (0.06 mL, 0.69 M, 0.04 mmol) was then added, and preparative TLC (1:1 hexane–ether) gave **9** (39 mg, 35%, R_f 0.19) as an orange oil: IR (CH_2Cl_2) ν_{CO} 2059 (m), 1989 (w), 1946 (s), 1718 cm^{-1} (C═O of ketone); NMR ($CDCl_3$) δ 4.92 (2 H, t, J = 8 Hz, OCH_2), 2.21 (3 H, s, CH_3CO), 2.6–1.9 (4 H, m, CH_2CH_2CO), 1.9–1.6 (2 H, m, OCH_2CH_2), 1.36 (3 H, s, CH_3); exact mass 346.0133 (calcd for $C_{14}H_{14}CrO_7$ 346.0144); MS [m/e (%)] 346 (8) M^+, 290 (10) M − 2CO, 262 (3) M − 3CO, 234 (22) M − 4CO, 206 (38) M − 5CO, 176 (62), 150 (36), 148 (39), 138 (69), 123 (100), 110 (32), 109 (13), 95 (51), 93 (16), 91 (18), 82 (29), 81 (19), 80 (12), 79 (21), 77 (16), 69 (50), 68 (16), 67 (55), 55 (31), 53 (23), 52 (56).

When the above reaction was performed using a stoichiometric amount of base, TLC analysis of the reaction mixture showed only **8**, with no detectable amount of **9**.

Reaction of the Anion of 1 with *trans*-3-Penten-2-one. *n*-BuLi (0.27 mL, 1.43 M, 0.38 mmol) was added to **1** (100 mg, 0.38 mmol) in 10 mL of THF at −78 °C. Following the injection of *trans*-3-penten-2-one (60 μL, 0.615 mmol, Aldrich), the solution was stirred 2.5 h at 25 °C and quenched with HCl in ether (0.15 mL, 2.8 M, 0.42 mmol). Preparative TLC (1:1 hexane–ether) gave **13** (R_f 0.29, 92 mg, 70%) as an orange oil. **13** was found to be a 1:1 mixture of diastereomers by NMR. Some of the coupling constants reported below were determined by decoupling experiments. NMR (270 MHz, $CDCl_3$): δ 0.72 (d, *J* = 6.8 Hz, 3 H, CH_3 of one diastereomer), 1.15 (d, *J* = 6.6 Hz, 3 H, CH_3 of other diastereomer), 2.11 (s, 3 H, $CH_3C{=}O$ of one diastereomer), 2.24 (s, 3 H, $CH_3C{=}O$ of other diastereomer), 1.73–2.04 (m, 4 H, H_b, CH_2CH_2O of both diastereomers), 2.1 (m, 2 H, H_e, CH_2CO of one diastereomer), 2.40–2.59 (ddd, $J_{ee'}$ = 15.8 Hz, J_{de} = 6.8 Hz, $J_{de'}$ = 7.7 Hz, CH_2CO of other diastereomer), 3.39–3.54 (m, 2 H, H_d, $CHCH_3$ of both diastereomers), 3.61–3.68 (ddd, H_c, $CHC{=}Cr$ of one diastereomer), 3.72–3.79 (ddd, J_{cd} = 2.6 Hz, J_{bc} = 4.8, 9.6 Hz, $CHC{=}Cr$ of other diastereomer), 4.93–5.02 (m, 2 H, one diastereotopic H of CH_2O of both diastereomers), 4.81–4.89 (m, 2 H, one diastereotopic H of CH_2O of both diastereomers). IR (hexane): ν_{CO} 2067 (w), 1991 (w), 1965 (s), 1955 (s), 1945 (s, sh), C=O (ketone) 1722 cm^{-1}. Exact mass: 346.0132 (calcd for $C_{14}H_{14}O_7Cr$ 346.0143). MS [*m*/*e* (%)]: 346 (10) M$^+$, 318 (<1) M − 1CO, 290 (7) M − 2CO, 262 (3) M − 3CO, 234 (22) M − 4CO, 206 (47) M − 5CO, 178 (12), 177 (12), 176 (44), 150 (25), 138 (44), 123 (60), 110 (58), 109 (16), 105 (10), 97 (36), 96 (16), 95 (14), 93 (15), 91 (20), 85 (27), 81 (15), 80 (16), 79 (18), 77 (21), 69 (91), 67 (41), 55 (33), 53 (21), 52 (100).

Reaction of the Anion of 1 with *trans*-4-Phenyl-3-buten-2-one. *n*-BuLi (0.27 mL, 1.43 M, 0.38 mmol) was added to **1** (100 mg, 0.38 mmol) in 10 mL of THF at −78 °C. After *trans*-4-phenyl-3-penten-2-one (65 mg, 0.44 mmol, Aldrich) was added, the solution was stirred for 1.5 h at 45 °C and quenched with HCl in ether (0.15 mL, 2.8 M, 0.42 mmol). Preparative TLC (1:1 hexane–ether) yielded a 1:1 ratio of the diastereomers of **14** (107 mg, 69%, R_f 0.11) as an orange oil: NMR (270 MHz, $CDCl_3$) δ 1.76–2.0 (m, 4 H, CH_2CH_2O of both diastereomers), 2.05 (s, 3 H, CH_3 of one diastereomer), 2.19 (s, 3 H, CH_3 of other diastereomer), 2.81–3.04 (m, 4 H, CH_2CO of both diastereomers), 3.86 (m, 1 H, $CH{-}C{=}Cr$ of one diastereomer), 4.12 (m, 1 H, $CH{-}C{=}Cr$ of other diastereomer), 4.38 (dt, *J* = 3, 8 Hz, CHC_6H_5 of 1 diastereomer), 4.56 and 4.86 (m, 4 H, CH_2O of both diastereomers), 4.69 (td, *J* = 3, 12 Hz, 1 H, CHC_6H_5 of one diastereomer), 6.96–7.4 (m, 10 H, C_6H_5 of both diastereomers); IR (hexane) ν_{CO} 2066 (w), 1994 (w), 1967 (s), 1954 (s), 1941 (s), C=O (ketone) 1718 cm^{-1}; exact mass 408.0289 (calcd for $C_{18}H_{16}O_7Cr$ 408.0300); MS [*m*/*e* (%)] 268 (5) M − 5CO, 159 (5), 131 (3), 121 (4), 91 (5), 88 (11), 86 (67), 84 (100), 77 (3), 52 (4), 49 (14), 47 (23).

Reaction of the Anion of 1 with 2-Cyclohexen-1-one. *n*-BuLi (0.27 mL, 1.43 M, 0.38 mmol) was added to **1** (100 mg, 0.38 mmol) in 10 mL of THF at −78 °C. The solution was warmed to 25 °C and 2-cyclohexen-1-one (41 mg, 0.43 mmol) was injected. The solution was stirred at 25 °C for 1.5 h and at 40 °C for 1 h and quenched with HCl in ether (0.15 mL, 2.8 M, 0.42 mmol). Preparative TLC (1:1 hexane–ether) gave **1** (9 mg, 9% recovery, R_f 0.50) and **15** (67 mg, 49%, R_f = 0.10) as an orange oil: NMR ($CDCl_3$) δ 1.1–1.4 (m, 2 H of cyclohexanone ring), 1.5–2.6 (m, 8 H, CH_2CH_2O and 6 H of cyclohexanone ring), 2.8–3.2 (m, 1 H of $CH_2C{=}O$), 3.5–3.9 (m, 1 H, $HC{-}C{=}Cr$), 4.8–5.1 (m, 2 H, CH_2O); IR (hexane) ν_{CO} 2068 (w), 1992 (w), 1969 (s), 1956 (s), 1943 (s), C=O (ketone) 1728 cm^{-1}; exact mass 358.0150 (calcd for $C_{15}H_{14}O_7Cr$ 358.0143); MS [*m*/*e* (%)] 358 (11) M$^+$, 330 (<1) M − 1CO, 302 (1) M − 2CO, 274 (6) M − 3CO, 246 (18) M − 4CO, 218 (73) M − 5CO, 192 (54), 165 (54), 154 (41), 123 (50), 121 (54), 119 (41), 97 (91), 96 (77), 91 (86), 88 (100), 79 (45), 67 (50), 55 (77), 52 (73).

Reaction of the Anion of 1 with Methyl *trans*-2-Butenoate. *n*-BuLi (0.27 mL, 1.4 M, 0.38 mmol) was added to **1** (100 mg, 0.38 mmol) in 10 mL of THF at −78 °C and the solution warmed to 25 °C. Methyl *trans*-2-butenoate (50 μL, 0.47 mmol) was injected and the solution was stirred for 2 h at 25 °C and quenched with HCl in ether (0.15 mL, 2.8 M, 0.42 mmol). Preparative TLC (1:1 hexane–ether) gave **1** (11 mg, 11% recovery, R_f 0.27) and **16** (86 mg, 62%, R_f 0.18) as an orange oil. The product is a 2:1 mixture of diastereomers as determined by NMR. NMR ($CDCl_3$): δ 0.80 (d, *J* = 7 Hz, CH_3 of major diastereomer), 1.14 (d, *J* = 7 Hz, CH_3 of minor diastereomer), 1.8–2.1 (m, CH_2CH_2O and $CHCH_3$ of both diastereomers), 2.48 (m, one diastereotopic H of $CH_2CO_2CH_3$ of both diastereomers), 2.4–3 (m, $HCC{=}Cr$ and one diastereotopic H of $CH_2CO_2CH_3$ of both diastereomers), 3.83 (s, OCH_3 of major isomer), 3.77 (s, OCH_3 of minor isomer), 4.9–5.2 (m, CH_2O of both diastereomers). IR (hexane): ν_{CO} 2066 (w), 1990 (w), 1963 (sh, s), 1955 (s), 1942 (s), C=O (ester) 1745 cm^{-1}. Exact mass: 362.0100 (calcd for $C_{14}H_{14}O_8Cr$ 362.0092). MS [*m*/*e* (%)]: 362 (15) M$^+$, 334 (<1) M − 1CO, 306 (2) M − 2CO, 278 (2) M − 3CO, 250 (20) M − 4CO, 222 (84) M − 5CO, 194 (23), 166 (45), 99 (13), 97 (24), 86 (19), 80 (12), 69 (24), 55 (12), 52 (100).

Reaction of the Anion of 3 with Benzyl Bromide. Potassium *tert*-butoxide (37 mg, 0.33 mmol) was added to **3** (97 mg, 0.29 mmol) in 10 mL of THF at 0 °C. After 10 min, benzyl bromide (54 μL, 0.45 mmol) was injected and the solution stirred 1 h at 25 °C. Preparative TLC (1:1 hexane–ether) afforded (5,5-dibenzyl-2-oxacyclopentylidene)pentacarbonylchromium(0), **11**[7] (7 mg, 5%, R_f 0.54), and **10** (57 mg, 46%, R_f 0.21) as an orange oil. Compound **10**: NMR ($CDCl_3$) δ 1.4–1.7 (m, 1 H of diastereotopic CH_2CH_2O), 2.09 (s, 3 H, $CH_3C{=}O$), 1.8–2.4 (m, 5 H, $CH_2CH_2C{=}O$ and 1 H of diastereotopic CH_2CH_2O), 2.80 (d, *J* = 13.5 Hz, 1 H of diastereotopic $CH_2C_6H_5$), 3.30 (d, *J* = 13.5 Hz, 1 H of diastereotopic $CH_2C_6H_5$), 4.4–4.9 (m, 2 H, CH_2O), 7.0–7.4 (m, 5 H, C_6H_5); IR (hexane) ν_{CO} 2067 (w), 1991 (w), 1964 (s), 1953 (s), 1940 (s), C=O (ketone) 1727 cm^{-1}; exact mass 422.0449 (calcd for $C_{20}H_{18}O_7Cr$ 422.0456); MS [*m*/*e* (%)] 422 (1) M$^+$, 394 (<1) M − 1CO, 366 (<1) M − 2CO, 338 (3) M − 3CO, 282 (9) M − 5CO, 176 (39), 175 (20), 129 (10), 123 (54), 92 (18), 91 (100), 83 (32), 77 (11), 74 (16), 59 (26), 55 (15), 52 (18).

Reaction of the Anion of 17 with Methyl Vinyl Ketone. *n*-BuLi (0.37 mL, 0.60 mmol) was added to **17** (150 mg, 0.60 mmol) in 10 mL of THF at −78 °C. Freshly distilled methyl vinyl ketone (76 μL, 0.92 mmol) was injected. The solution was stirred at 0 °C for 2 h and quenched with HCl in ether (0.25 mL, 2.8 M, 0.70 mmol). Preparative TLC (2:1 hexane–ether) gave **17** (18 mg, 12% recovery, R_f 0.32) and **18** (42 mg, 19%, R_f 0.18) as an orange oil. NMR ($CDCl_3$): δ 1.75 (quintet, *J* = 7.5 Hz, 2 H), 2.12 (s, 3 H, $CH_3C{=}O$), 2.42 (t, *J* = 7.5 Hz, 2 H, $CH_2C{=}O$), 3.32 (t, *J* = 7.5 Hz, 2 H, $CH_2C{=}Cr$), 4.78 (s, 3 H, OCH_3). IR (hexane): ν_{CO} 2065 (w), 1987 (w), 1965 (sh, s), 1950 (s), C=O (ketone) 1725 cm^{-1}. Exact mass: 319.9988 (calcd for $C_{12}H_{12}O_7Cr$ 319.9987). MS [*m*/*e* (%)]: 320(5), 264 (4) M − 2CO, 208 (13) M − 4CO, 180 (15) M − 5CO, 137 (28), 115 (100), 113 (23), 112 (24), 111 (32), 109 (22), 97 (23), 95 (11), 85 (15), 81 (15), 80 (15), 74 (16), 59 (33), 55 (25), 52 (35).

Reaction of the Anion of 17 with Methyl Acrylate. *n*-BuLi (0.37 mL, 1.62 M, 0.60 mmol) was added to **17** (150 mg, 0.60 mmol) in 10 mL of THF at −78 °C. The solution was warmed to 0 °C and methyl acrylate (65 μL, 0.72 mmol) was injected followed by stirring for 2 h at 0 °C and addition of HCl in ether (0.25 mL, 2.8 M, 0.70 mmol) at −78 °C. Preparative TLC (3:1 hexane–ether) gave **17** (16 mg, 11% recovery, R_f 0.39), **19** (38 mg, 21%, R_f 0.17), and **20** (34 mg, 15%, R_f 0.06).

Compound **19** was obtained as an orange oil: NMR ($CDCl_3$) δ 1.82 (quintet, *J* = 7.5 Hz, 2 H), 2.33 (t, *J* = 7.5 Hz, $CH_2CO_2CH_3$), 3.40 (t, *J* = 7.5 Hz, 2 H, $CH_2C{=}Cr$), 3.70 (s, 3 H, CO_2CH_3), 4.82 (s, 3 H, OCH_3); IR (hexane) ν_{CO} 2067 (w), 1987 (m), 1951 (s), C=O (ester) 1750 cm^{-1}; exact mass 335.9942 (calcd for $C_{12}H_{12}O_8Cr$ 335.9936); MS [*m*/*e* (%)] 336 (10) M$^+$, 280 (5) M − 2CO, 252 (4) M − 3CO, 224 (25) M − 4CO, 196 (59) M − 5CO, 181 (27), 154 (18), 153 (100), 125 (35), 115 (36), 95 (15), 83 (25), 80 (20), 71 (32), 58 (19), 55 (27), 52 (60).

Compound **20** was isolated as an orange oil: NMR ($CDCl_3$) δ 1.4–2.0 (m, 4 H, $CHCH_2$), 2.30 (m, 4 H, $CH_2CO_2CH_3$), 3.66 (s, 6 H, CO_2CH_3), 4.0 (m, 1 H, $HC{-}C{=}Cr$), 4.80 (s, 3 H, OCH_3); IR (hexane) ν_{CO} 2066 (w), 1986 (w), 1966 (m), 1951 (s) cm^{-1}; exact mass 422.0307 (calcd for $C_{16}H_{18}O_{10}Cr$ 422.0303); MS [*m*/*e* (%)] 422 (1), 215 (74), 214 (24), 187 (15), 186 (69), 160 (17), 155 (43), 154 (20), 141 (39), 128 (34), 127 (100), 123 (48), 100 (58), 95 (24), 86 (23), 85 (74), 84 (33), 71 (37), 67 (33), 59 (65), 55 (70).

(2-Thiacyclopentylidene)pentacarbonylchromium(0), 21. *n*-BuLi (0.30 mL, 1.6 M total base, 0.48 mmol) was added to **17** (120 mg, 0.48 mmol) in 10 mL of THF at −78 °C. Ethylene sulfide (35 μL, 0.60 mmol) was injected followed by stirring for 30 min at 30–35 °C and quenching with HCl in ether (0.13 mL, 2.8 M, 0.36 mmol). Preparative TLC (hexane, two elutions) gave **17** (27% recovery, R_f 0.35) and **21** (16 mg, 12%, R_f 0.18) as a red-orange oil: NMR ($CDCl_3$) δ 2.23 (quintet, *J* = 6.5 Hz, 2 H), 3.34 (t, *J* = 6.5 Hz, 2

H, $CH_2C{=}Cr$), 4.00 (t, $J = 6.5$ Hz, 2 H, CH_2S); IR (hexane) ν_{CO} 2061 (w), 1959 (s, b) cm^{-1}; exact mass 277.9331 (calcd for $C_9H_5O_5SCr$ 277.9340); MS [*m/e* (%)] 278 (28), 194 (15) M – 3CO, 178 (12), 166 (40) M – 4CO, 162 (23), 138 (100) M – 5CO, 119 (23), 111 (27), 110 (46), 105 (35), 102 (42), 97 (27), 86 (29), 85 (61), 83 (35), 81 (31), 79 (35), 69 (46), 52 (96).

Reaction of the Anion of 1 with Acetyl Chloride. *n*-BuLi (0.31 mL, 1.65 M, 0.51 mmol) was added to **1** (125 mg, 0.48 mmol) in 10 mL of THF at –78 °C. After 5 min, acetyl chloride (60 μL, 0.84 mmol) was injected followed by warming to 25 °C and stirring for 50 min. Removal of solvent and preparative TLC (1:1 hexane–ether) gave **1** (49 mg, 39% recovery, R_f 0.35) and **22** (70 mg, 43%, R_f 0.25). NMR indicated that **22** was a 1:1 mixture of the *Z* and *E* isomers; the mixture was isolated as a red solid and could not be separated by preparative TLC: NMR (CS_2) δ 2.17 (s, $CH_3C{=}O$), 2.24 (bs, $CH_3C{=}C$), 2.35 (s, $CH_3C{=}O$), 2.82 (s, $CH_3C{=}C$), 2.66 (m, $CH_2C{=}C$ of both isomers), 4.70 (two overlapping triplets, $J = 7$ Hz, CH_2O of both isomers); IR (hexane) ν_{CO} 2058 (m), 1985 (m), 1950 (sh, s), 1944 (s), C=O (enol acetate) 1775 cm^{-1}; exact mass 345.9773 (calcd for $C_{13}H_{10}O_8Cr$ 345.9779); MS [*m/e* (%)] 346 (14), 234 (19) M – 4CO, 206 (34) M – 5CO, 178 (65), 176 (21), 163 (50), 150 (50), 139 (19), 135 (15), 128 (69), 121 (18), 113 (35), 111 (32), 82 (14), 80 (19), 69 (34), 67 (31), 52 (100).

Reaction of the Anion of 8 with Acetyl Chloride. *n*-BuLi (0.62 mL, 1.61 M, 1.0 mmol) was added to **8** (250 mg, 0.91 mmol) in 15 mL of THF at –78 °C. Acetyl chloride (78 μL, 1.1 mmol) was injected followed by stirring for 30 min at –78 °C and 30 min at 25 °C. Preparative TLC (1:1 pentane–ether) gave **8** (35 mg, 14% recovery, R_f 0.30) and **24** (189 mg, 65%, R_f 0.08) as a yellow solid: mp 59–61 °C; NMR ($CDCl_3$) δ 1.75 (s, 3 H, CH_3), 1.7–2 (m, 1 diastereotopic H of CH_2CH_2O), 2.2–2.5 (m, 1 diastereotopic H of CH_2CH_2O), 2.32 (s, 3 H, $CH_3C{=}O$), 5.01 (m, 2 H, CH_2O); IR (hexane) ν_{CO} 2064 (w), 1993 (w), 1962 (s), 1953 (s), 1926 (m) cm^{-1}; exact mass 317.9815 (calcd for $C_{12}H_{10}O_7Cr$ 317.9830); MS [*m/e* (%)] 318 (1) M^+, 290 (8) M – 1CO, 262(3) M – 2CO, 234 (5) M – 3CO, 206 (11) M – 4CO, 178 (21) M – 5CO, 126 (12), 123 (12), 111 (5), 83 (6), 80 (6), 55 (7), 52 (7), 43 (15), 28 (100).

Reaction of the Anion of 1 with Bromine. *n*-BuLi (0.28 mL, 1.50 M, 0.42 mmol) was added to **1** (100 mg, 0.38 mmol) in 10 mL of THF at –78 °C. Bromine (24 μL, 0.42 mmol) was added dropwise and the reaction was stirred 5 min at –78 °C and 10 min at 25 °C. Preparative TLC (2:1 hexane–ether) gave α-bromo-γ-butyrolactone (10 mg, 16%, R_f 0.10), which was identified by comparison of its IR spectrum with that of an authentic sample, and **25** (71 mg, 55%, R_f = 0.25) as a red-orange oil: NMR (CS_2) δ 2.38 (m, 2 H, CH_2CH_2O), 4.88 (m, 2 H, CH_2O), 5.50 (m, 1 H, CHBr); IR (hexane) ν_{CO} 2068 (w), 1997 (w), 1969 (s), 1960 (s), 1946 (s) cm^{-1}; exact mass 339.8662 (calcd for $C_9H_5BrO_6Cr$ 339.8673); MS [*m/e* (%)] 340 (3) M^+, 312 (0.5) M – 1CO, 256 (1) M – 3CO, 228 (3) M – 4CO, 200 (4) M – 5CO, 170 (4), 149 (5), 138 (5), 121 (6), 120 (4), 97 (5), 91 (8), 82 (93), 81 (31), 80 (100), 69 (6), 52 (18).

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Registry No. **1**, 54040-15-2; **3**, 64082-32-2; **4**, 64082-31-1; **8**, 54040-17-4; **9**, 64082-30-0; **13**, diastereomer 1, 64129-90-4; **13**, diastereomer 2, 64082-29-7; **14**, diastereomer 1, 64130-28-5; **14**, diastereomer 2, 64082-28-6; **15**, 64082-27-5; **16**, diastereomer 1, 64129-89-1; **16**, diastereomer 2, 64082-26-4; **11**, 61989-11-5; **10**, 64082-25-3; **17**, 20540-69-6; **18**, 64091-77-6; **19**, 64091-76-5; **20**, 64091-75-4; **21**, 64103-52-2; **22** (*Z* isomer), 64130-26-3; **22** (*E* isomer), 64091-74-3; **24**, 64091-86-7; **25**, 64091-85-6; methyl vinyl ketone, 78-94-4; *trans*-$CH_3CH{=}CHCOCH_3$, 3102-33-8; *trans*-$C_6H_5CH{=}CHCOCH_3$, 1896-62-4; 2-cyclohexen-1-one, 930-68-7; *trans*-$CH_3CH{=}CHCO_2CH_3$, 623-43-8; benzyl bromide, 100-39-0; methyl acrylate, 96-33-3; ethylene sulfide, 420-12-2; acetyl chloride, 75-36-5; Br_2, 7726-95-6; α-bromo-α-butyrolactone, 5061-21-2.

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Metal Atom–Metal Cluster Chemistry. 1. Alkane Matrices

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The optical spectra (200–700 nm) of vanadium atoms isolated in a series of normal, branched, and cyclic alkanes have been recorded over a temperature range between 10 K and approximately half the melting point of the matrix material. The atomic spectra are less well defined in alkane matrices than in argon matrices, but matrix-induced frequency shifts from gas-phase values are smaller and they tend to decrease with increasing chain length of the normal alkane matrix material. The temperature at which metal atom diffusion becomes appreciable in these matrices, during controlled matrix warm-up, correlates roughly with one-third of the melting point of the matrix material. The influence of the matrix material on the extent to which divanadium forms on the surface of the matrix during deposition is considered in terms of a steady-state model for the deposition process. Under similar deposition conditions, alkane matrices are more efficient than argon matrices for isolation of atoms over diatomic and higher polyatomic molecules, and the isolation efficiency increases with increasing chain length of the normal alkane matrix material.

Introduction

In recent years there has been much interest expressed in the effects of low-temperature matrix environments on the optical spectra of metal atoms. These effects, which often result in substantial differences between gas-phase and matrix spectra, include frequency shifts from gas-phase values and splitting of single gas-phase lines.[1] Matrix-induced changes in atomic optical spectra are of particular interest in so far as they relate to studies in the area of metal atom matrix chemistry. As ultraviolet–visible spectroscopy is of basic importance in this area, it is desirable to clearly establish atomic spectra in different matrix environments. Atomic spectral features may then be more readily distinguished from

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