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Kinetic and Mechanistic Studies on the Formation and Reactions of Early-Transition-Metal–Ketene Complexes

Julienne M. Galante, Joseph W. Bruno,* and Paulette N. Hazin

Hall-Atwater Laboratories, Wesleyan University, Middletown, Connecticut 06457

Kirsten Folting and John C. Huffman

Molecular Structure Center, Indiana University, Bloomington, Indiana 47405

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A series of complexes of vanadocene or molybdenocene with unsymmetrical ketenes were prepared, either by reaction of the various ketenes with vanadocene itself or by reaction with the molybdenocene phosphine complex $(C_5H_5)_2Mo(PEt_3)$. All of the complexes exhibited the expected ketene C=O bonding mode, and all reactions were very specific in their formation of the facial isomer with metallocene fragment located on the side of the smaller ketene substituent. Kinetic studies were used to assess the sensitivity of the incoming vanadocene to steric and electronic effects, with the latter found to dominate. Kinetic studies and activation parameters for reaction of $Cp_2Mo(PEt_3)$ with EtPhC=C=O indicated a second-order associative mechanism, proposed to involve a nucleophilic attack of the metal center on the ketene central carbon in the rate-limiting step. Lastly, reactions of the bound ketenes with nucleophiles (alkyllithiums or Grignard reagents) proceeded readily to either ketone or aldehyde enolates (the latter via transfer of a β-hydride from the alkyl); the clean production of only *Z* enolates from the unsymmetrical ketenes is indicative of a metal-mediated internal attack of nucleophile on the bound ketene.

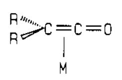
Introduction

There have been a number of possible mechanisms suggested for the Fischer–Tropsch conversion of synthesis gas (CO/H_2) to hydrocarbons.[1] Key experiments by Petit[2] provide convincing evidence for the combination of methylene fragments on the catalyst, and recent surface studies have established that a nickel catalyst surface supports a variety of highly mobile unsaturated fragments such as alkyls, alkylidenes, alkylidynes, hydrides, etc.[3] Further, a typical Flory–Schulz distribution of hydrocarbons is normally seen with catalyst metals which are known to adsorb CO dissociatively.[4] An alternative mechanistic hypothesis which is also consistent with this dissociative adsorption involves the production of surface bound ketenes, and Ruechardt and Schrauzer showed that the reaction of $Ni(CO)_4$ and CH_2N_2 produces ketenes.[5] Since that time, a number of groups have reported reactions modeling such a process. These usually involve the reaction of a metal alkylidene with CO (eq 1)[6-16] or the reaction of a metal carbonyl with an alkylidene source such as diazoalkane (eq 2).[17]

$$L_nM{=}CR_2 + CO \rightarrow L_nM(R_2C{=}C{=}O) \qquad (1)$$

$$L_nM{-}CO + R_2C{=}N{=}N \rightarrow L_nM(R_2C{=}C{=}O) + N_2 \qquad (2)$$

While the studies noted above provide precedents for the proposed Fischer–Tropsch ketene forming reaction, less is known about the subsequent behavior of complexed ketenes. They are known to bind to transition-metal centers via complexation of either the C=C bond (A) or the C=O bond (B), and complexed ketenes have been observed to react with either water or hydrogen to give acid[6] or aldehyde,[12a] respectively. Moreover, both Geoffroy[12] and Mayr[16] have shown that C=C bound ketenes are strong π acceptors; an equilibrium such as that represented in eq 3 is driven to the right when the ancillary ligands L_n allow the metal center to donate electron density to the ketene.



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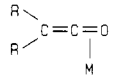

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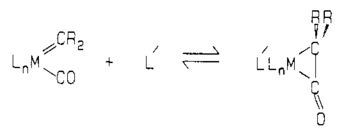
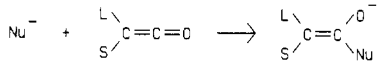


(3)

Less is known about the binding properties of C=O bound ketenes and about the tendency of bound ketenes in general to participate in subsequent C–C bond forming reactions. Free ketenes are well-known to react with nucleophiles at the central carbon, yielding enolates.[18] Earlier theoretical studies showed that the ketene LUMO (the frontier orbital of interest in a nucleophilic attack) is localized in the plane containing the two ketene substituents,[19] and thus an incoming nucleophile would be expected to adopt an approach trajectory which is in this plane. Recent work[18] has indicated that this is so and that unsymmetrical ketenes show a high selectivity for attack on the side of the smaller alkyl substituent (eq 4, where



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L and S = large and small alkyl groups, respectively). Hence, in reactions with methyllithium, the ratios of Z:E enolates are as follows: EtMeC=C=O, 1.7:1; *i*-PrMeC=C=O, 7.0:1; and MePhC=C=O, ca. 99:1.[18] Since the binding properties of C=O bound ketenes are of great interest, we were encouraged to look at the reactions of unsymmetrical ketenes with nucleophilic electron-rich metal centers in the hope of determining the selectivity ratios obtained and more about the electronics of ketene binding. Moreover, we hoped that the unsymmetrical nature of the ketenes might allow some insights into any subsequent reactions of bound ketenes with nucleophiles. As such, we required a metal center that would cleanly form C=O bound ketene adducts; vanadocene has been shown to form a number of such adducts with aldehydes[20] and heterocumulenes.[21,22] Herein we report the results of our kinetic and mechanistic studies on vanadocene and molybdenocene complexes of unsymmetrical ketenes.

Experimental Section

General Considerations. Proton NMR spectra were obtained on a Varian XL-400 FT-NMR. Solution infrared spectra were determined in a 0.05-mm path length liquid cell on a Perkin-Elmer M1500 FT-IR spectrophotometer. Magnetic susceptibilities were measured on a Johnson-Matthey magnetic susceptibility balance using ca. 250 mg of sample. Gas chromatograph–mass spectra were obtained on a Hewlett Packard GC (5890)–MS (5988A) system using a 50-ft. capillary column.

Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN.

All manipulations were carried out under an atmosphere of either nitrogen or argon. Both gases were dried and deoxygenated by passage through columns of Linde 4A molecular sieves and activated BTS catalyst. Solutions were handled by using standard Schlenk methods, and solids were transferred in a Vacuum Atmospheres Corp. glovebox. Benzene, hexane, tetrahydrofuran, and diethyl ether were purchased from J.T. Baker and distilled from sodium benzophenone ketyl under nitrogen. Vanadocene was prepared from VCl_3 and sodium cyclopentadienide via the method of Fischer and Vigourex.[23] $(C_5H_5)_2MoH_2$ was prepared via the standard procedure[24] and converted to $(C_5H_5)_2Mo(PEt_3)$ photolytically,[25] using a Hanovia 450-W medium-pressure mercury lamp to irradiate the dihydride in the presence of 10 equiv of PEt_3 at 0 °C (benzene solution). Commercial diphenylacetic acid and 2-phenylbutanoic acid (Aldrich) were converted to the corresponding acid chlorides with thionyl chloride, and the latter converted to the ketenes via deprotonation with triethylamine.[26] Aldrich 2-phenylpropanal was converted to the acid via permanganate oxidation[27] and then converted to the ketene similarly. Commercial 3,3-dimethylbutanoic acid (Aldrich) was converted to 2-bromo-3,3-dimethylbutanoyl bromide via the method of Smith and Norton;[28] the latter was converted to *tert*-butylketene via zinc reduction.[29] Ketenes were filtered from byproduct ($[NEt_3H][Cl]$ or $ZnBr_2$) and used as solutions in the appropriate solvent.

Table I. Crystal Data for 2

empirical formula	$C_{19}H_{18}OV$
color of cryst	green-brown
cryst dimens, mm	0.25 × 0.25 × 0.25
space group	$R3c$
cell dimens (−159 °C; 30 reflctns)	
$a = b = c$, Å	14.642 (8)
$\alpha = \beta = \gamma$, deg	63.08 (3)
Z (molecules/cell)	6
V, Å^3	2370.99
d(calcd), g cm^{-3}	1.317
wavelength, Å	0.710 69
mol wt	313.29
linear abs coeff	6.021

Vanadocene Ketene Complexes. These were prepared in a manner similar to that used by Floriani.[22] In a typical reaction, 1.0 g (5.5 mmol) of vanadocene was dissolved in 20 mL of hexane; to this was added ethylphenylketene (1.1 equiv in 10 mL of hexane) via syringe. The solution was stirred for a few minutes (during which time it turned from violet to dark green) and then allowed to stand undisturbed overnight at 0 °C. Dark green-black microcrystals of $(C_5H_5)_2V(O{=}C{=}CEtPh)$ (1) precipitated and were filtered under nitrogen and dried in vacuo: yield 78%; IR (Nujol) 1621 (m), 1582 (s) cm^{-1}; Magnetic moment, $\mu_{eff} = 1.81\ \mu_B$; ^1H NMR (C_6D_6) 6.8 (s, br), 4.8 (s, br), 4.2 (s, v br), 3.0 ppm (s, br). Anal. Calcd for $C_{20}H_{20}OV$: C, 72.39; H, 6.11. Found: C, 72.45; H, 6.05. The related complex $(C_5H_5)_2V(O{=}C{=}CMePh)$ (2) was prepared similarly: yield 85%; IR (Nujol) 1623 (m), 1581 (s) cm^{-1}; magnetic moment, $\mu_{eff} = 1.73\ \mu_B$; ^1H NMR (C_6D_6) 7.9 (s, v. br), 6.8 (s, br), 4.8 (s, br), 4.4 ppm (s, v br). Anal. Calcd for $C_{19}H_{18}OV$: C, 71.92; H, 5.72. Found: C, 71.69; H, 5.85.

$(C_5H_5)_2Mo(O{=}C{=}CPhEt)$. In a typical reaction, 0.5 g (1.48 mmol) of $(C_5H_5)_2Mo(PEt_3)$ was dissolved in 40 mL of benzene and 1 equiv of EtPhC=C=O (in 10 mL of benzene) was added via syringe. The solution was stirred for 5 h at ambient temperature, the volume reduced by half in vacuo, and 10 mL hexane added. Upon standing, a light brown powder precipitated and was filtered and dried in vacuo: IR (Nujol) 1629 (m), 1587 (s) cm^{-1}; ^1H NMR (C_6D_6) 6.9–7.15 (m, phenyl), 4.45 (s, C_5H_5), 2.0 (q, CH_2), 0.9 ppm (t, CH_3). Analyses were consistently low in C and H, although spectra indicated a pure compound.

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X-ray Crystallography. Suitable crystals of 2 were obtained by slow cooling of a 1:4 toluene–hexane solution. A small, nearly equidimensional crystal was transferred to the goniostat by using standard inert atmosphere techniques and then cooled to −159 °C. A systematic search of a limited hemisphere of reciprocal space yielded a set of reflections that exhibited threefold symmetry and could be indexed by using a rhombohedral lattice. The systematic extinctions of *hhh* for $h = 2n + 1$ and of *hhl* for $l = 2n + 1$ identified the possible space groups as *R*3*c* or *R*3*barc*. The choice of the noncentrosymmetric group *R*3*c* was confirmed by the solution and refinement of the structure. A sixfold redundant data set was collected over the range $0 \leq 2\theta \leq 45°$, but standard reflections measured every 300 reflections indicated that a section of the data was unsable due to either crystal movement or laboratory temperature fluctuations. The indicated section was removed, and a total of 4640 reflections were processed in the usual manner. After equivalent relections were averaged, a unique set of 1003 reflections remained; of these, 869 met the criterion of $F \geq 3.0\ \sigma(F)$. The structure was solved by a combination of direct methods and Fourier techniques. The vanadium atom was located in the *E* map, and the remaining non-hydrogen atoms were located in successive Fourier maps. After initial refinement all hydrogen atoms were located in a difference map. The full-matrix least-squares refinement was completed by using anisotropic thermal parameters on all non-hydrogen atoms and isotropic parameters on the hydrogen atoms. The final *R* was 0.029, and the final difference map was essentially featureless, the largest peak being 0.22 e/Å^3. Crystal data are collected in Table I.

Reactions with Nucelophiles. In a typical reaction, 0.05 g of isolated, microcrystalline $(C_5H_5)_2V(O{=}C{=}CRPh)$ (R = Me, Et) was dissolved in 10 mL of THF. The resulting dark green solution was added via dropping funnel to a −78 °C THF solution containing 2.5 equiv of alkyllithium or Grignard reagent. The resulting solution was stirred at −78 °C for ca. 15 min, at which time a solution IR spectrum indicated complete conversion of starting ketene complex. Three equivalents of Me_3SiCl were added via syringe, and the solution was stirred at room temperature for 2 h. The solvent was then removed in vacuo and the oily residue extracted with 5 mL of hexane. The hexane solution was exposed to air to quench any organovanadium species present, stirred over a small amount of neutral alumina, and then filtered to yield a clear, colorless solution used for GC–MS analysis. The identities of the silyl enol ethers were confirmed by alternate literature syntheses[18a] and GC–MS coinjection, and control experiments indicated that they were tolerant of the workup conditions.

Kinetic Studies. For reactions of ketenes and vanodocene, these studies were carried out in benzene at 30 °C. A stock solution of $(C_5H_5)_2V$ in benzene was prepared, as was one of the requisite ketene in benzene. Necessary amounts of the two solutions were pipetted together into neat benzene, the resulting reaction was stirred, and an aliquot was added to the solution IR cells. Reactions were carried out with large excesses (5–10-fold) of vanadocene so that a pseudo-first-order loss of the very intense ketene IR band (2100 cm^{-1}) could be monitored. All rate constants quoted are the average of at least three independent runs.

Kinetic studies on the diamagnetic $(C_5H_5)_2Mo(PEt_3)$ were carried out by using ^{1}H NMR to monitor the conversion of the molybdenocene cyclopentadienyl resonance from that of the phosphine complex (4.05 ppm) to that of $(C_5H_5)_2Mo(O{=}C{=}CEtPh)$ (4.45 ppm). Stock solutions were prepared in C_6D_6 and handled as described above.

Results and Discussion

Syntheses and Properties. The reactions between sublimed vanadocene and freshly generated ethylphenyl- and methylphenylketenes proceeded smoothly as reported by Floriani[22] in his synthesis of the diphenylketene complex 3 (eq 5). We found that the alkyl-substituted de-

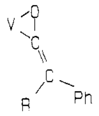
$$(C_5H_5)_2V + PhRC{=}C{=}O \xrightarrow[C_6H_{14}]{} (C_5H_5)_2V(O{=}C{=}CPhR) \quad (5)$$

1: R = Et
2: R = Me
3: R = Ph

rivatives 1 and 2 were considerably more soluble and tended to oil out of aromatic solvents but could be obtained as microcrystals from hexane. They are green-black solids that dissolve in common organic solvents to give green solutions. The compounds are air-sensitive both in the solid state and in solution. They also are found to exhibit magnetic moments which are close to the spin-only value (1.73 μ_B) expected for one unpaired spin. While (d^3) vanadocene is known to have a ^{4}A ground state, acceptor ligands are also known to lead to spin pairing.[30] The resulting doublet systems usually have magnetic moments which show little evidence of orbital contributions to that observed moment.[30] Of practical utility is the fact that, once formed, these complexes are quite stable in the absence of air. As such, they represent a means of "storing" ketenes, which are multiply unsaturated and hence capable of undergoing a number of useful C–C bond-forming reactions. Since free ketenes themselves undergo [2 + 2] cycloadditions,[31] it is fortunate that the complexation reactions are able to compete with dimerization.

Infrared spectroscopy is particularly informative regarding the bonding exhibited in transition-metal–ketene complexes. Free ketenes give rise to two strong IR bands at 2100 and 1600 cm^{-1}. In C=C bound complexes the band due to the "ketone-like" unbound C=O occurs at ca. 1750 cm^{-1} and is relatively strong, whereas C=O bound ketenes normally exhibit much weaker bands at ca. 1620 cm^{-1}.[22] The complexes whose preparation is described above exhibit bands due to the bound ketenes at 1621 (1) or 1623 (2) cm^{-1} (with no trace of any C=C bound complex at ca. 1750 cm^{-1}), as did the analogue 3 which was structurally characterized (and seen to exhibit C=O bonding) by Floriani.[22]

The infrared spectra described above are useful from another standpoint as well. Since the unsymmetrical ketene ligands are C=O bound, they have the potential to exhibit two isomeric binding modes with the alkyl substituent toward or away from the metal center (C or D below). We were interested in determining if vana-



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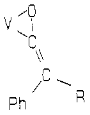

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docene behaved like incoming organic nucleophiles; its' large size relative to carbanionic nucleophiles might be expected to lead to even greater steric differentiation, assuming an approach trajectory located in the same plane as those of the organic nucleophiles. While the spectra do not allow for a differentiation between the two, the sharp single bands for the bound ketene do strongly suggest that only one of the possible isomers is formed. It is also of interest to compare the NMR spectra obtained for the two paramagnetic vanadocene complexes 1 and 2. These were obtained so as to ascertain the magnitude of the effects of the unpaired electron on the various molecular substituents and therefore their disposition relative to the vanadium center. For both complexes the spectra showed identical broad features at 4.8 and 4.2–4.4 ppm (highly broadened), as well as extra resonances for the alkyl (Et or Me) ketene substituent (see Experimental Section). The two resonances noted above are attributed to the ortho and

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para protons of the phenyl groups of the two ketene moieties. The fact that the cyclopentadienyl protons of free vanadocene (^{4}A ground state) are known to resonate 315 ppm downfield from TMS[33] prompted us to look over a wide spectral width for additional signals, but none were detected. These observations indicate that the ketene phenyl groups in the two complexes are experiencing nearly identical magnetic environments in the two complexes and that the geometries (either C or D above) are therefore the same for both.

In seeking a diamagnetic analogue of the complexes described above, we chose to pursue the synthesis of molybdenum-ketene complexes. This was more problematic since free molybdenocene does not exist and many of its labile precursors also lead to the formation of dimers and clusters.[34,35] We first attempted to prepare $(C_5H_5)_2Mo$(ketene) by treating the known $(C_5H_5)_2MoH_2$ with excess ketene in the hope that the dihydride would first hydrogenate the ketene to aldehyde (eq 6), which would not be

$$Cp_2MoH_2 + 2EtPhC{=}C{=}O \nrightarrow Cp_2Mo(O{=}C{=}CEtPh) + EtPhCH{-}CHO \quad (6)$$

able to compete effectively with the extra ketene for the molybdenocene transient. This approach was unsuccessful, producing complex product mixtures which we were unable to characterize. We next attempted to prepare ketene complexes by displacing other ligands like CO,[36] side-bound CH_3CN,[37] and diphenylacetylene.[38] However, in all of these cases we found that ketene ligands competed only very poorly with the other π-acceptor ligand.[39] More successful was an attempt to displace the labile σ-bound triethylphosphine in a synthetic reaction depicted in eq 7. This process resulted in a light brown solid from which

$$Cp_2Mo(PEt_3) + EtPhC{=}C{=}O \rightarrow Cp_2Mo(O{=}C{=}CEtPh) + PEt_3 \quad (7)$$

solvent and liberated triethylphosphine could be removed by washing and then drying in vacuo. The infrared was again indicative of only ketene C=O bonding, containing one band at 1629 cm^{-1}. Further, the NMR spectrum contained only one set of resonances for the ketene ethyl group.

Further characterization of the metallocene-ketene isomers requies additional data, particularly with respect to the facial selectivities. As such, we sought crystallographic data to identify the isomer obtained (C or D above) even though the structure of **3** (with $Ph_2C{=}C{=}O$) has been reported;[22] this information has a bearing on the facial selectivities of the nucleophilic reactions to be discussed (vide infra). Slow crystallization of **2** from warm hexane yielded aggregates of small cubic crystals. The resulting ORTEP drawing[40] and atom numbering scheme are depicted in Figure 1, and selected bond lengths and angles are given in Table II. Compound **2** exhibits a gross geometry that is similar to that found for **3**.[22] The C=O ketene binding mode is confirmed, and the compound is seen to adopt geometry C (above) with the vanadocene moiety on the side of the smaller methyl substituent. The phenyl group in **2** is approximately coplanar with the ketene C=C bond. The strong back-bonding interaction is evident from the O-C-C ketene angle of 136.5 (6)°, which compares to the analogous angle found in **3** (135.9 (5)°).[22] Other similarities between **2** and **3** include the C=C bond lengths (1.35 (1) and 1.340 (7) Å, respectively), the O—C bond lengths (1.282 (9) and 1.290 (6) Å), and the V—O bond lengths (2.020 (4) Å for both). The most obvious difference is that the V-C bond is longer in **2** (2.052 (6) Å) than in **3** (2.013 (6) Å). In view of the similarity of the spectra of **1** and **2** (particularly the NMR), we are inclined to assume the same "phenyl outside" geometry for both.

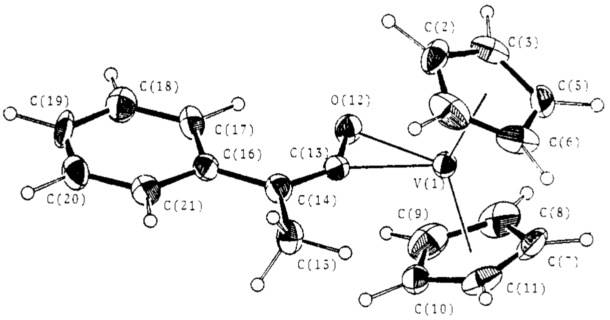

Figure 1. ORTEP view indicating the atom numbering scheme for **2**.

Table II. Bond Lengths (Å) and Angles (deg) for 2[a]

	Bond Lengths		
V-O	2.020 (4)	C(13)-C(14)	1.35 (1)
V-C(13)	2.052 (6)	V-C(Cp)(av)	2.278
O-C(13)	1.282 (9)	V-Cp	1.944 1.955
	Bond Angles		
Cp-V-Cp	139.9	O-C(13)-C(14)	136.5 (6)
C(13)-C(14)-C(15)	118.4 (6)	C(13)-C(14)-C(16)	122.1 (7)
O-V-C(13)	36.7 (2)	V-C(13)-O	70.3 (3)

[a] C(Cp) refers to the cyclopentadienyl carbons; Cp refers to the cyclopentadienyl centroids.

Kinetic Studies. In an effort to learn more about the bonding isomerism in vanadocene ketene complexes and to gather information regarding the relative importance of steric and electronic effects in C=O bound ketenes, we chose to investigate the kinetics of ketene complex formation. Although the color change from violet to dark green suggested that the reaction could be conveniently monitored via ultraviolet-visible techniques, we found it more straightforward to make use of vibrational spectroscopy to follow the loss of the intense ketene stretch at 2100 cm^{-1} as it was replaced by the complex band at ca. 1620 cm^{-1}. Preliminary experiments indicated that second-order kinetics were operative in the reaction, so the concentration of vanadocene was kept high so as to allow for the simple pseudo-first-order loss of the ketene. Indeed, kinetic data taken under conditions of 30° C, ca. 0.0215 M initial ketene concentration (chosen based on the ketene extinction coefficient), and vanadocene concentrations of 0.108 M (fivefold excess) led to plots of ln (ketene) versus time that were linear for at least 3 half-

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(39) (a) After the completion of this work, Okuda and Herberich[39b] reported the use of $(Cp)_2Mo$(stilbene) in the synthesis of a diphenylketene complex. This preparation required 50 °C temperatures, which would cause other ketenes to undergo substantial dimerization. (b) Okuda, J.; Herberich, G. E. *J. Organomet. Chem.* **1987**, *320*, C35–C38.

(40) (a) Data were collected and treated as described previously.[40b] (b) Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755–2762.

Table III. Kinetic Results for Reaction (in Benzene, 30 °C) $Cp_2V + PhRC{=}C{=}O \rightarrow Cp_2V(O{=}C{=}CRPh)$

$[Cp_2V]$	ketene	[ketene]	$10^3\ k_{obsd}$,[a] s^{-1}
0.108	PhPh	0.0216	7.57 (1)
0.130	PhPh	0.0216	9.46 (3)
0.108	PhMe	0.0216	6.98 (4)
0.107	PhEt	0.0214	.989 (1)
0.128	PhEt	0.0214	1.19 (9)
0.150	PhEt	0.0214	1.32 (2)
0.171	PhEt	0.0214	1.49 (2)

ketene	k,[b] $M^{-1}\ s^{-1}$
PhPh	8.59×10^{-2}
PhMe	6.47×10^{-2}
PhEt	7.59×10^{-3}

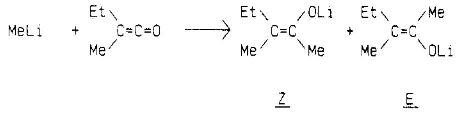
[a] Each k_{obsd} value quoted is the average of at least three separate runs; see text. [b] Second-order rate constants.

lives. This confirmed the first-order dependence of the complexation reaction on ketene concentration. To verify the vanadocene dependence, its concentration was also varied up to ca. eightfold excess and the resulting pseudo-first-order rate constants were determined. Indeed, this reflected a linear dependence of rat constant on vanadocene concentration and verified the straightforward rate law expression given in eq 8, in which k is the second-order

$$\text{rate} = -\frac{d[\text{ketene}]}{dt} = k[\text{ketene}][Cp_2V] \qquad (8)$$

rate constant in $M^{-1}\ s^{-1}$ (determined from pseudo-first-order rate constants divided by [vanadocene]). It should be noted that rate constants were determined from reactions whose ln (ketene) versus time plots exhibited correlation coefficients (r) of ≥ 0.99. The data were derived from the average of at least three such kinetic experiments, each of which behaved in this manner. These average values are given in Table III.

The studies of ketene reactions with organolithium reagents described in the Introduction indicated that the nucleophile does indeed adopt the trajectory suggested by Tidwell[18a,b] and Seebach and Dunitz.[18c,d] With spectral and structural evidence that both ethylphenyl- and methylphenylketene form the same vanadocene complex isomer, it is interesting to compare the steric sensitivity of the vanadium center with that of a common organic nucleophile, methyllithium. Seebach showed that the reaction of MeLi with ethylmethylketene led to a 1.7/1 isomeric mixture, with Z predominant (eq 9).[18c] Assuming irreversible reactions, this corresponds to a free energy difference of ca. 0.4 kcal/mol between the transition states leading to the two products;[41] these two transition states reflect the difference between a Me–Et and a Me–Me interaction in this reaction. When we consider the reactions of vanadocene with ethylphenyl- and methylphenylketene, the interactions of interest are V–Me and V–Et. If we again assume irreversible reactions (as indicated by the spectral monitoring), the rate ratio of 8.5 is indicative of a free energy difference of ca. 1.3 kcal/mol. The magnitude of this greater vanadium sensitivity toward steric differences seems reasonable in light of the imagined size difference between it and the methyl group, and it highlights the potential for achieving high selectivities in metal-mediated ketene bond-forming reactions. This effect should be particularly important when the ketene contains substituents whose size difference is relatively small.



(9)

The relative rates discussed above are ascribed to steric effects since methyl and ethyl are electronically similar. However, with use of the Winstein–Holness A values for the three groups of interest (Me, −1.70 kcal/mol; Et, −1.75 kcal/mol; Ph, −3.0 kcal/mol),[42] it seems unlikely that steric effects can be the cause of the rapid rate of $Ph_2C{=}C{=}O$ complex formation. Instead, it appears that the presence of a second phenyl group serves to enhance the electrophilicity of this ketene and that electronic effects of this type are more important than steric effects. Indeed, preliminary studies indicate that vanadocene complexation of *tert*-butylketene proceeds at a rate slower than any of those in Table III, in spite of the low steric demand of the hydrogen substituent; this also indicates that electronic effects are dominant over steric effects. From this correlation between ketene electrophilicity and vanadocene complexation rate, one might infer that vanadocene functions like other nucleophiles and approaches the ketene central carbon directly; although we are unable to elucidate unambiguously the trajectory of approach for vanadocene, we will address this point in the discussion of molybdenocene complex formation.

The high facial selectivities described above are thought to arise from an approach of the metal center along the side of the ketene moiety. In the case of $(C_5H_5)_2Mo(PEt_3)$, the phosphine ligand is expected to lower the accessibility of the molybdenum center. Although the phosphine might be expected to labilize and allow direct reaction between ketene and $[(C_5H_5)_2Mo]$ transient, three recent reports prompted us to investigate the mechanism of ketene complex formation: divalent group 4[43] and group 5[44] metallocene systems were found to undergo substitution reactions via associative pathways, and a π-acceptor alkyne was observed to undergo associative substitution into an osmium cluster.[45] Initial kinetic runs were carried out by using ^1H NMR to monitor the molybdenum cyclopentadienyl resonances of the two compounds, and the resulting plots of ln $[Cp_2Mo(PEt_3)]$ versus time show decided curvature. Thus the ketene concentration appears in the rate expression, suggesting either a second-order process or the dissociative mechanism indicated in eq 10 and 11. The latter process would be consistent with the

$$(C_5H_5)_2Mo(PEt_3) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [(C_5H_5)_2Mo] + PEt_3 \qquad (10)$$

$$[(C_5H_5)_2Mo] + EtPhC{=}C{=}O \xrightarrow{k_2} (C_5H_5)_2Mo(O{=}C{=}CEtPh) \qquad (11)$$

observation that $Cp_2Mo(PEt_3)$ slowly decomposes in solution to higher order clusters, presumably via loss of a labile phosphine ligand. Mechanisms like this one are readily treated by applying the steady-state approximation,[46] in this case to the molybdenocene concentration. Such a treatment leads naturally to a rate law expression

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(41) Calculated from the expression $\Delta\Delta G^{*} = RT \ln (k_x/k_y)$.

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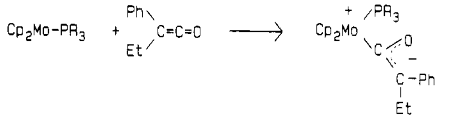
as shown in eq 12, in which the competition between

$$\frac{d[Cp_2Mo(ketene)]}{dt} = \frac{k_1k_2[Cp_2Mo(PEt_3)][ketene]}{k_{-1}[PEt_3] + k_2[ketene]} \qquad (12)$$

phosphine and ketene is indicated in the denominator. This also indicates that if k_2[ketene] ≫ k_{-1}[PEt$_3$], the former term should cancel out of the rate expression, and the reaction reduces to a simple two-step mechanism in which the first step (phoshine dissociation) is rate-limiting; thus, above this competition threshold the ketene concentration should no longer matter. However, we found that a plot of observed rate constant versus ketene concentration was linear (correlation coefficient = 0.991) with a slope of 3.2 (4) × 10^{-2} M^{-1} s^{-1} (30 °C) and an intercept at the origin; even up to 20 equiv of ketene per molybdenocene there was no indication that such a plot was leveling off. This argues against the dissociative mechanism (eq 10 and 11) and favors a second-order process; moreover, the zero intercept indicates that *no* dissociative (first-order) process is operative. As a final confirmation of this, we sought to determine the activation parameters for the process. This was done over the temperature range 0–30 °C; the resulting Eyring plot (ln (k/T vs $1/T$) indicated a value of ΔH^{*} of 13 ± 2 kcal/mol and, more importantly, a value of ΔS^{*} of −25 ± 4 eu. Both are very consistent with an associative process, and we propose the mechanism indicated in eq 13 and 14. In view of the high electrophilicity of free ketenes, the d^4 molybdenum center is postulated to act as a nucleophile. The application of electron-counting formalism to the intermediate allows the assignment of +4 as the molybdenum oxidation state, thereby maintaining an 18-electron count at molybdenum. Subsequent loss of phosphine is accompanied by entry of the ketene oxygen into the coordination sphere. In the synthetic studies the inability of ketene to displace acceptor ligands (alkyne, nitriles, etc.) can be rationalized on the basis that the strongly back-bonding molybdenum center is electron deficient and therefore less nucleophilic (relative to the phosphine-substituted derivative). Most surprising is the observation of associative substitution in a system with such a labile phosphine ligand; again, this is rationalized on the basis of the high ketene electrophilicity. Moreover, the fact that the reaction between Cp$_2$Mo(PEt$_3$) and EtPhC=C=O is faster (k = 3.2 × 10^{-2} M^{-1} s^{-1}) than the analogous reaction with vanadocene (k = 7.59 × 10^{-3} M^{-1} s^{-1}) may be related to the ability of the phosphine ligand to enhance the basicity of the molybdenum center. Also, recent work has indicated that vanadocene faces a substantial activation barrier in its reaction with CO;[44] this is attributed to the need for the Cp ligands to bend back to accommodate the incoming ligand.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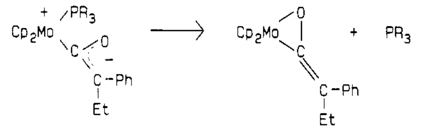
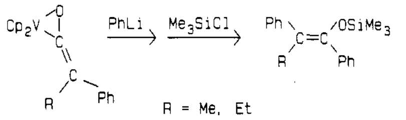

(14)

Reactions with Nucleophiles. We noted above that free ketenes are known to react with nucleophiles at the electrophilic central carbon and that with organolithium reagents this reaction has been used in the stereospecific preparation of Z lithium enolates.[18] However, it is also clear that complexation to vanadium via the C=O bond involves the transfer of substantial electron density into what was the LUMO of the free ketene. Indeed, vanadium-bound ketenes and aldehydes have been shown to exhibit a substantially higher oxygen-centered nucleophilicity than the free ligands.[20,22] Less is known about their ability to react with nucleophiles, however. In fact, there are but a few reports detailing the reactions of bound ketenes with nucleophiles, and these have all been for C=C bound ketenes.[8,12d,e,13] Since the possible involvement of ketenes in C—C bond forming reactions is a potentially important aspect of their intermediacy in the Fischer–Tropsch reaction, it is important to probe the ability of C=O bound ketenes to engage in such a process.

In the reactions of vanadium-bound ketenes with nucleophiles, we used a procedure similar to that used for analogous reactions of free ketenes.[18a] The sample of (C$_5$H$_5$)$_2$V(ketene) used was always isolated as a microcrystalline solid to avoid the possibility of reactions of free ketenes. This compound was dissolved in THF and added in dropwise fashion to a THF solution of the desired nucleophile (organolithium or Grignard reagent) at −78 °C. After being stirred at this temperature, the reaction was quenched with Me$_3$SiCl and then worked up as indicated in the Experimental Section. The resulting silyl enol ethers were analyzed by GC–MS and compared to the products resulting from treatment of free ketene with the same nucleophilic reagent. The use of either MePhC=C=O or EtPhC=C=O complexes leads to the same type of product in all cases. For the nuclephiles PhLi or MeLi, the reactions proceeded to the products indicated in eq 15; both were identified as the Z isomers by analogy with the products obtained from free ketenes. Interestingly, when a similar reaction was carried out by using BuLi as nucleophile, the only ketene-derived product was the *aldehyde* silyl enol ether (eq 16). This suggested a unique behavior for nucleophiles containing β-hydrides, so a similar reaction was carried out with i-PrMgCl. This too led to the formation of the product shown in eq 16, the aldehyde silyl enol ether. A reaction of the free ketene with lithium aluminum hydride followed by Me$_3$SiCl gives the same product, reported to be the Z isomer.[18f] We verified that similar reactions of the free keenes with either i-PrMgCl or BuLi give straightforward production of the expected *ketone* enol silyl ether (e.g. eq 17). As such, it appears that the addition process is mediated by the vanadium center rather than occurring through prior dissociation of ketene (a process for which we have no infrared evidence). This and the observation of Z enolate geometry are consistent with a mechanism involving internal attack of the nucleophile, and two possible pathways are illustrated in Scheme I. In the first mechanistic proposal (a) the incoming nucleophile attacks at the metal center, forcing the metal ketene linkage to open to accommodate it. This is expected to result in a ketene bound to vana-



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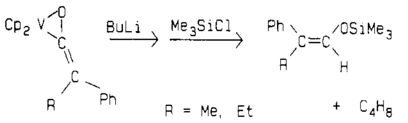
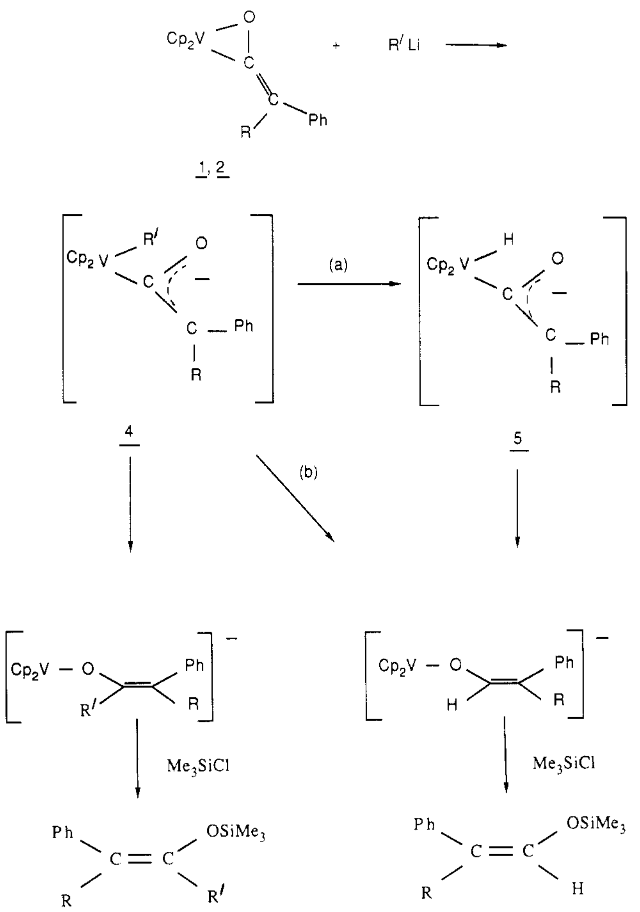


(16)

(17)

Scheme I

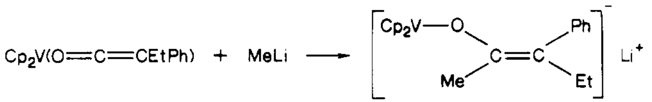


dium only via the central carbon in this formally anionic intermediate (4). We note that this bonding mode for a ketene has ample precedent in CO_2 complexes of anionic (cf. the recent work of Floriani,[47] Cooper,[48] and Cutler[49]) or electron-rich metal centers (cf. the X-ray structures of η^1-bound rhodium[50] and osmium[51] carbon dioxide adducts). Moreover, this intermediate is a metallaenolate and would be expected to maintain its planarity so as to avoid losing the associated allylic-type resonance energy. This is an important aspect of the high facial selectivity observed. At this point, the vanadium-bound alkyl is expected to undergo β-hydride transfer if such a process is available to it. This may proceed as in pathway (a) via elimination of alkene to the indicated hydride species **5**, which exhibits the same ketene-binding mode as the alkyl derivative **4**. These species are expected to have a rather short lifetime, and we have no direct evidence for them. Subsequent coupling of the two vanadium-bound fragments should lead to an enolate, either vanadium- or lithium-bound.

The alternative mechanism (b) in Scheme I involves a direct transfer of the β-hydrogen of the alkyl to the ketene central carbon and is analogous to the semiconcerted process proposed by Teuben in the formation of formates from $(C_5Me_5)_2Ti(Et)$ and carbon dioxide.[52] We consider this possibility because work on related compounds of niobium and tantalum has shown that coordination of an additional ligand will push an alkyl = alkene–hydride equilibrium to the side of the alkyl.[53] In the present work a related effect would rule out the β-hydride elimination proposed above. Since we have no spectral evidence of either **4** or **5** (Scheme I), we are unable to distinguish between the two possibilities.

The two mechanistic pathways converge at the stage of the enolates, depicted as vanadium rather than lithium bound (vide infra). Indeed, we find that the addition of water to the reaction mixture right after addition of the vanadocene–ketene complex leads to formation of either ketone or aldehyde, depending on the nucleophile used. Thus, we believe that the enolate complex is the first intermediate on the pathway with an appreciable lifetime, since a reaction between water and **4** would be expected to give alkane and the carboxylic acid derived from the ketene[31] (none of the latter is observed). Subsequent addition of excess Me_3SiCl (in the absence of water) converts the enolate to the silyl enol ether. We have also considered an alternative mechanism in which incoming nucleophile completely displaces ketene from vanadocene rather than form **4**. However, we discard this possibility for the following reason: we are operating under conditions in which vanadocene–ketene complex is added dropwise to a solution of alkyllithium, so that the latter is present in excess for the entire reaction time. Since the reaction of alkyllithiums with free ketenes is known to be facile, we would expect substantial amounts of *ketone* silyl enol ether to be formed if free ketene were present. However, the reactions of butyllithium and *i*-PrMgCl are very clean in their production of aldehyde silyl enol ether, indicating that little or no free ketene is present. Lastly, the resulting vanadocene is expected to react with Me_3SiCl to undergo oxidation to a V(III) species; such reactions have been studied and are known to be complex.[54] We have not attempted to characterize the vanadium products in this reaction.

As a means of characterizing any enolates formed as either vanadium or lithium bound, the reaction mixture (in eq 18) was studied by IR prior to the addition of Me_3SiCl. This was then compared to an analogous reaction of free ketene + MeLi. The latter reaction is expected to give rise to an O-bound lithium enolate that is probably dimeric in nature, based on literature precedent.[55] Indeed, this solution exhibited three IR bands (1603 (s)8 1597 (sh), and 1559 (w) cm^{-1}) very similar to those reported in the



(18)

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literature for other lithium enolates.[55] The reaction in eq 18, however, gave a similar but not identical spectrum with bands at 1602 (w), 1579 (s), and 1559 (m) cm^{-1}. Differences were observed both in band positions and in relative intensities. This indicates that the reaction in eq 18 does not simply give loss of vanadocene and a lithium enolate; there are enough similarities in the band positions, however, to prompt us to assign the spectrum to the vanadium enolate. A monomeric formulation is indicated for clarity in eq 18, but this species is very likely dimeric or oligomeric in solution. Its lifetime in solution (hours at room temperature) precludes further structural analysis, although it is isolable as a free-flowing black powder. When analogous infrared studies were carried out for the addition of BuLi to vanadocene ketene, they showed no evidence for an intermediate vanadium hydride (as in **5**, Scheme I); this corroborates the suggestion that vanadium enolate is the first long-lived species on the reaction path.

Conclusions. The studies described herein were undertaken to gain a more complete understanding of the ability of ketenes to bind to transition-metal centers via C=O complexation. They indicate that the formation of such complexes with unsymmetrical ketenes occurs wth a very high degree of facial selectivity, higher than that exhibited by smaller organic nucleophiles. However, the associative substitution of the triethylphosphine ligand on molybdenocene suggests that such reactions go via a straightforward attack by the electron-rich metal center at the ketene central carbon; in that sense, the metallic nucleophiles appear to behave in a manner similar to carbon nucleophiles. Further, it is clear that even though such bonding should place a substantial amount of electron density in the ketene LUMO, C=O bound ketenes are still capable of undergoing nucleophilic attack. The use of unsymmetrical ketenes allos us to define this as an internal attack mediated by the metal. This is particularly important with respect to any potential Fischer–Tropsch ketene C–C and C–H bond-forming reactions, since incoming hydrides or alkyls would presumably also be delivered from the surface of the catalyst. Subsequent attack of the resulting enolate nucleophiles on other ketenes could form the basis for an anionic ketene polymerization leading to several C–C bond formations; the anionic polymerization of ketenes has been reported.[56] However, this does not address the question of whether there is a sufficient population of ketenes on the catalyst surface to support such a polymerization process, and this issue remains in doubt. Likewise, there may be some synthetic use for the vanadocene enolates reported herein since other metallocene enolates undergo highly stereospecific Aldol condensations with aldehydes;[57] the reactions described herein constitute one means of preparing such enolates with high *Z* specificity. Lastly, we note that we have observed behavior by later transition-metal–ketene complexes similar to that reported here, and these results will be communicated separately.

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Registry No. 1, 113161-87-8; **2**, 113161-88-9; **3**, 76173-79-0; O=C=CEtPh, 20452-67-9; Cp_2V, 1277-47-0; O=C=CMePh, 3156-07-8; $Cp_2Mo(PEt_3)$, 63672-65-1; Cp_2Mo(O=C=CPhEt), 113161-89-0; O=C=CPh_2, 525-06-4.

Supplementary Material Available: Drawings of **2** and tables of crystal and diffractometer data, bond distances, bond angles, and positional and thermal parameters (12 pages); a listing of observed and calculated structure factors (3 pages). Ordering information is given on any current masthead page.

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Carbon–Carbon Bond-Forming Reactions of Cobaltacyclopentene/Cobaltaoxanorbornadiene Complexes with Isocyanides, Carbon Monoxide, and Alkynes

Maryrose Scozzafava and Alan M. Stolzenberg*

Department of Chemistry, Brandeis University, Waltham, Massachusetts 02254

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Reaction of $(\eta^5\text{-}C_5H_5)\overline{Co[C(R)C(CO_2CH_3)CH(CO_2CH_3)C}H(CO_2CH_3)][P(C_6H_5)_3]$ ($R = C_6H_5$, **2a**; $R = CO_2CH_3$, **2b**) with isocyanides, CO, and diphenylacetylene (DPA) afforded 1-amino-1,3-cyclopentadienes, cyclopent-2-enones, and $(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}1,3\text{-cyclohexadiene})$ complexes, respectively. The related [2.2.1]-metallabicyclic cobaltaoxanorbornadiene complexes **1a** and **1b** reacted with the same reagents to afford identical products. Reactions with isocyanides and CO proceeded in two distinct steps: (1) coordination of the reactant to cobalt to form a new ligand-substituted cobaltacyclopentene complex and (2) insertion of the reactant into the metallacycle, followed by reductive elimination. Intermediates were not detected in the reactions with DPA. However, the isolation of isomeric η^4-*cis*-5,6-dicarbomethoxy-1,3-cyclohexadiene complexes with CpCo coordinated on different faces of the diene suggested the intermediacy of a metallacycloheptadiene complex. Kinetic measurements established that the reaction of **1a** with DPA was first order with respect to both reagents. A rate constant for the reaction of **2a** with DPA was calculated from our data and the known equilibrium constant between **2a**, **1a**, and $P(C_6H_5)_3$. The agreement of the calculated rate with a published rate for the reaction confirmed that **1a** is the kinetically significant intermediate in the carbon–carbon bond-forming reactions of **2a**.

The participation of metallacyclic complexes in carbon–carbon bond-forming reactions has created extensive interest in these complexes.[1] Our interest in the reactivity of metallacyclopent-2-ene complexes[2,3] has been prompted

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