Table I. Rotational Barriers of Cations and Carbenes

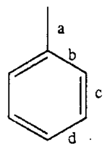
compound	$C_6H_5CH_2^+$	C_6H_5CH	$C_3H_5^+$	C_3H_4
split valence	45.4	11.2	34.3[a]	9.2[c]
higher level			37.7[b]	8.4[d]

[a] HF/3-21G//3-21G.[14] [b] MP2/6-31G**//HF/6-31G*.[15] [c] HF/4-31G.[16] [d] SDQCI//SCF(DZP).[17]

the analogous benzyl cations. Although a similar 90° rotation about an aryl-carbon bond is required in the cyclization of both benzyl and diphenylmethyl 1,5-diradicals[9] the latter cyclize much more easily than the former since rotation about the aryl-carbon bond is facile in the diphenylmethyl system but not for the benzyl radicals. Similarly, earlier reports[10,11] indicate that triphenylmethyl carbocations do undergo intramolecular cyclizations to give the corresponding phthalans. In such systems, steric crowding of the ground state leads to much lower rotational barriers than in the simple benzyl cations included in our study.

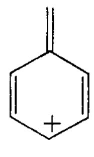
To verify that the divergent intramolecular reactivities of arylcarbenes and benzyl cations arise from the higher rotational barriers in the latter, we have performed ab initio molecular orbital calculations[12] on both the benzyl cation and singlet phenylcarbene, with complete geometry optimizations of planar minima and perpendicular rotation transition states in each case, using the 3-21G basis set.[13]

The rotational barriers from our calculations, together with those reported[14-17] for the allyl cation and vinylcarbene, are shown in Table I. The most relevant features of the geometries of the aromatic species are shown in structure **17**. The rotational barrier calculated for the cation is about 4 times that for the carbene. Our confidence in these values arises from previous studies of the allyl cation and singlet vinylcarbene, which give a similar trend using either split valence basis sets (3-21G or 4-31G)[14,16] or much larger basis sets and inclusion of correlation energy corrections.[15,17,18-23]



17

Planar cation:	a=1.356, b=1.434, c=1.361, d=1.400
Perpendicular cation:	a=1.450, b=1.393, c=1.382, d=1.384
Planar carbene:	a=1.462, b=1.400 (1.398) c=1.378 (1.381), d=1.389 (1.385)
Perpendicular carbene:	a=1.478, b=1.392, c=1.382, d=1.384



18

The origin of this large difference in barriers is revealed by a comparison of the optimized geometries (see structure **17**). In the planar benzyl cation, the exocyclic C–C bond length is 1.357 Å. In the perpendicular form this bond length is 1.450 Å. These bond lengths are very similar to the ones found in polyenes[24] for localized double (1.35 Å) and single (1.48 Å) bonds, respectively. This is indicative of the large extent of conjugation present in the planar form, which is lost upon rotation. The analogous bond length in singlet phenylcarbene is only slightly increased in going from the planar to the perpendicular conformation, from 1.462 to 1.478 Å. The calculated charges also indicate that there exists significant delocalization in the planar cation and little or none in the carbene. Indeed, the planar cation is best represented by structure **18**, while the remaining species are better represented as aromatic compounds.

The exocyclic double bond character in **18** is thus larger than one would expect if the five resonance structures of the cation gave equal contributions. The loss of aromaticity in three resonance structures is compensated by delocalization of the charge on the secondary carbon atoms of the ring, which formally bear a positive charge more favorably than the exocyclic methylene carbon. In the planar carbene, resonance donation from the phenyl group to the vacant p orbital of the carbene occurs only with unfavorable charge separation. Consequently, the exocyclic bond largely retains single-bond character, so that the rotational barrier is low enough to allow the molecule to achieve a nonplanar conformation without difficulty.

Furhter examples of this difference in behavior between arylcarbenes and aryl cations will be reported in due course.

Acknowledgment. We are grateful to the National Science Foundation for financial support of this research.

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Unexpected Dissociative Kinetics for CO Exchange in the 17-Electron Complexes Carbonylbis(η^5-pentadienyl)vanadium(II), Carbonyl(η^5-cyclopentadienyl)(η^5-pentadienyl)vanadium(II), and Carbonyl(η^5-cyclopentadienyl)(η^5-2,4-dimethylpentadienyl)vanadium(II)

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Several kinetic studies of 17-electron metal carbonyls such as $V(CO)_6$,[1] $Mn(CO)_5$,[2] $Re(CO)_5$,[3] and $Fe(CO)_3(PR_3)_2^{+}$[4] have

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Table I. Comparison of Rates of CO Exchange at 60.0 °C[a]

$(\eta^5\text{-L})_2$ of $(\eta^5\text{-L})_2V^{13}CO$	ν_{CO},[b] cm^{-1}	A_{iso}^{V}, G	k_1, s^{-1}	k_2, M^{-1} s^{-1}	rel rate[c]
1, $(C_5H_7)_2$	1959	78.7	8.1×10^{-6}	3.8×10^{-3}	1
2, $Cp(C_5H_7)$	1938	63.1	2.7×10^{-4}	5.7×10^{-3}	10
3, $Cp(2,4\text{-}C_7H_{11})$	1935	61.7	3.1×10^{-4}	13×10^{-3}	13
4, Cp_2[d]	1881	27.8	$\sim 10^{-4}$	~800	1.5×10^5
5, Cp_2'[d]	1842	17.7	$\sim 10^{-4}$	~260	5×10^4

[a] In decalin unless otherwise noted. [b] For complexes **1*–5***, $\nu_{^{13}CO}$ are ~45 cm^{-1} lower. [c] Relative rates include both k_1 and k_2 contributions, for reactions under 1 atm of CO. [d] Data extrapolated from activation parameters in toluene.[5] Values for k_1 are rough estimates.

demonstrated rapid associative (S_N2) mechanisms for CO substitution. Recent kinetic studies in our group on the CO-exchange kinetics of the 17-electron complex Cp'_2VCO have shown that this complex also reacts by a rapid associative mechanism.[5] As an extension of these studies, we have been investigating similar processes in analogous 17-electron complexes containing one or two pentadienyl ligands: $(C_5H_7)_2VCO$ (**1**), $Cp(C_5H_7)VCO$ (**2**), and $Cp(2,4\text{-}C_7H_{11})VCO$ (**3**).[6,7] In contrast to the rapid associative kinetic behavior of Cp_2VCO (**4**) and Cp'_2VCO (**5**), the pentadienyl complexes react slowly and with only a small contribution from a ligand-dependent pathway, even though replacement of a cyclopentadienyl ligand by a pentadienyl ligand should favor associative attack through $\eta^5 \rightarrow \eta^3$ ligand transformation.[8-10] The dissociative pathway found for CO substitution in these complexes also contrasts with the behavior expected for 17-electron complexes, for which no kinetically characterized examples of CO dissociation as a rate-determining process have previously been reported.[2,11]

To determine the ^{13}CO exchange kinetics of **1**–**5**, a solution containing the ^{13}CO labeled carbonyl complex (**1***–**5***, respectively) is bubbled with a rapidly recirculating atmosphere of CO or CO/N_2 in a closed, thermostated system. Reaction progress is monitored by the infrared absorbance changes for the carbonyl stretching frequencies accompanying the reaction of eq 1.[12]

$$(\eta^5\text{-L})_2V^{13}CO + CO \rightleftharpoons (\eta^5\text{-L})_2VCO + {}^{13}CO \qquad (1)$$

Observed rate constants follow the McKay equation for isotope exchange reactions (eq 2)[13] where [MCO] = the total concen-

$$k_{obsd}\left[\frac{[MCO]}{C} + 1\right]^{-1} = k_1 + k_2[CO]_{sol} \qquad (2)$$

tration of $(\eta^5\text{-L})_2VCO + (\eta^5\text{-L})_2V^{13}CO$, C = the total moles of $^{12}CO + {}^{13}CO$ in the closed system divided by the volume of solution, and $[CO]_{sol}$ = the solubility of $^{12}CO + {}^{13}CO$ in the solvent at the appropriate temperature and partial pressure of CO.[14] Plots of the quantity on the left-hand side of eq 2 vs. $[CO]_{sol}$ are linear. Slopes of these lines give k_2, the second-order or CO-dependent rate constant, and intercepts give k_1, the first-order or ligand-independent rate constant.

The values for the rate constants k_1 and k_2 for the CO-exchange process for complexes **1**–**3** appear in Table I. Activation parameters for the ligand-independent or dissociative pathway for **1** are $\Delta H_1^{\ddagger} = 28.1 \pm 0.4$ kcal/mol and $\Delta S_1^{\ddagger} = 2 \pm 1$ cal/(mol K). For the ligand-dependent pathway, $\Delta H_2^{\ddagger} = 22.7 \pm 0.4$ kcal/mol and $\Delta S_2^{\ddagger} = -2 \pm 1$ cal/(mol K). The large enthalpy of activation for the ligand-dependent pathway and the similarities in the entropies of activation suggest that this reaction may proceed by a dissociative interchange (Id) mechanism, in which vanadium–carbonyl bond breaking is well advanced in the transition state. Alternatively, activation parameters for the ligand-dependent pathway may support an independent associative reaction involving an energetically unfavorable $\eta^5 \rightarrow \eta^3$ pentadienyl slippage or u-shaped → sickle-shaped ligand rearrangement, either of which could be entropy-favored. Additional studies with other nucleophiles are necessary to more clearly define the nature of the ligand-dependent pathway. Complexes **2** and **3**, as well as $(2,4\text{-}C_7H_{11})_2VCO$, behave similarly, exhibiting somewhat faster rates for the dissociative pathway, with $\Delta H_1^{\ddagger} \cong 26\text{–}29$ kcal/mol, $\Delta S_1^{\ddagger} \cong 3\text{–}11$ cal/(mol K), and similar rates for the ligand-dependent pathway. In these complexes, CO exchange occurs almost exclusively by a dissociative mechanism.

The rates of CO exchange for complexes **4** and **5** appear in Table I for comparison. Previous kinetic studies of the CO-exchange process in Cp'_2VCO showed this complex reacts by a rapid associative process, with kinetic parameters (in toluene) of $\Delta H_2^{\ddagger} = 8.9 \pm 0.7$ kcal/mol and $\Delta S_2^{\ddagger} = -21 \pm 3$ cal/(mol K). No CO dissociative pathway is observed experimentally for the CO exchange of $Cp'VCO$.[5] The complex Cp_2VCO also undergoes rapid associative CO exchange at somewhat faster rates than the more sterically crowded Cp'_2VCO. In striking contrast, *the pentadienyl complexes **1**–**3** react at rates up to 10^5 times slower than the cyclopentadienyl complexes **4** and **5***. Furthermore, these results suggest that replacing one cyclopentadienyl ligand with a pentadienyl ligand is sufficient to "shut-off" associative attack of CO at the 17-electron complex.

Both steric and electronic factors may be important in accounting for the different behavior of the pentadienyl complexes toward CO substitution. Structural studies show significantly shorter V–C distances to pentadienyl compared to cyclopentadienyl ligands.[8,15] Together with the greater girth of the "open" pentadienyl ligand, this leads to severe steric crowding which could hinder associative attack at the metal. However, electronic factors may also be invoked to explain the reduced reactivity of the pentadienyl complexes. The higher carbonyl stretching frequencies (Table I) in **1**–**3** compared to **4** and **5** indicate greater V–CO back-bonding in the latter complexes. The isotropic EPR vanadium hyperfine splitting constants (Table I) suggest electronic similarity between complexes **1**–**3**, which are different from **4** and **5**. In the parent metallocenes, replacement of cyclopentadienyl with 2,4-dimethylpentadienyl ligands results in different electronic ground states.[15] It is possible that different electronic ground states in the 17-electron complexes lead to different vanadium electro-

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(7) (a) Complexes **1**–**3** are readily formed upon exposure of $(\eta^5\text{-L})_2VPR_3$ to a CO atmosphere. The phosphine complexes were synthesized by Robert W. Gedridge and Timothy D. Newbound at the University of Utah. Details will appear in a future publication. (b) Ernst, R. D.; Liu, J.-Z.; Wilson, D. R. *J. Organomet. Chem.* **1983**, *250*, 257–263.

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(12) Solutions of **1***–**3*** in decalin (previously distilled and saturated with the appropriate CO or CO/N_2 gas mixture) were bubbled with a rapidly recirculating atmosphere of CO or CO + N_2 using Matheson calibration gas standards consisting of 99.99% CO, 10.0% CO in N_2, or 1.00% CO in N_2. Aliquots for IR analysis were withdrawn periodically by syringe and monitored on a Nicolet FT-IR spectrophotometer. Plots of either ln $(A_t - A_\infty)$ vs. time for the decrease in absorbance of $(\eta^5\text{-L})_2V^{13}CO$ or ln $(A_\infty - A_t)$ vs. time for the increase in absorbance of $(\eta^5\text{-L})_2VCO$ were linear, and k_{obsd} was obtained as the slope of these lines (correlation coefficient ≥ 0.995 for at least three half-lives). First- and second-order rate constants were then obtained by using eq 2. Similar procedures were used for complexes **4** and **5**, except toluene was used as the solvent.[5]

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philicities in these complexes, with vanadium in complexes **4** and **5** exhibiting greater electrophilicity.

Given the inclination of other 17-electron metal carbonyl complexes to undergo associative ligand displacement reactions, it seems ironic that the incorporation of a pentadienyl ligand, which would be expected to promote associative attack via $\eta^5 \rightarrow \eta^3$ coordination changes, should lead instead to a series of compounds for which much lower rates of substitution are observed and for which the substitutions also take place via dissociative means. Additional kinetic, EPR, and structural studies are under way in attempts to better understand the unexpected behavior of these 17-electron complexes.

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Supplementary Material Available: Table of rate constants and CO concentration dependence for CO exchange in complex **1** (1 page). Ordering information is given on any current masthead page.

Reactions of Alkenylchromium Reagents Prepared from Alkenyl Trifluoromethanesulfonates (Triflates) with Chromium(II) Chloride under Nickel Catalysis

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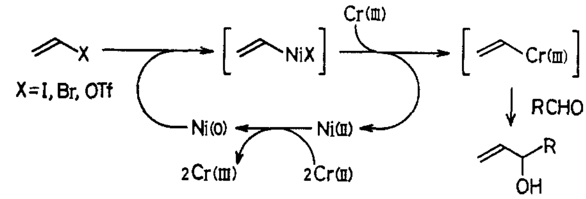
Nucleophilic substitution of an enolate oxygen with an organometallic compound under C(sp^2)–O bond fission has been recently achieved.[1] However, there are few examples of the production of alkenyl anion equivalents from such enolate derivatives as alkenyl triflates.[2] We disclose here reactions of alkenylchromium reagents[3] prepared from alkenyl triflates[4] by reduction with chromium(II) chloride under nickel catalysis.

After our report in 1983 about Grignard-type carbonyl addition of alkenyl halides mediated by $CrCl_2$,[3] we noticed that the success of the reaction heavily depended on the nature of the $CrCl_2$. A certain specimen of $CrCl_2$ purchased[5] was effective and the others[6] failed to give reproducible results. This trouble prompted us to seek a second metal catalyst which might be contained in the effective crop of chromium(II) salt.[7] Analysis of fluorescent X-rays of the special lots revealed that nickel was the major contaminant.[5] Addition of a catalytic amount of $NiCl_2$ to a commercial lot of $CrCl_2$[6] has shown reproducible results as we reported.[3] Moreover, the system has proved to promote the Grignard-type reaction between alkenyl triflates and aldehydes under mild conditions.

Scheme I



A mixture of anhydrous $CrCl_2$ (0.49 g, 4.0 mmol)[6] and a catalytic amount of $NiCl_2$ (2.6 mg, 0.020 mmol) in dry, oxygen-free dimethylformamide (DMF, 10 mL) was stirred at 25 °C for 10 min under argon atmosphere. To the reagent at 25 °C was added a solution of benzaldehyde (0.11 g, 1.0 mmol) in DMF (5 mL) and a solution of alkenyl triflate **1** (0.63 g, 2.0 mmol) in DMF (5 mL) successively. After stirring at 25 °C for 1 h, the reaction mixture was diluted with ether (20 mL), poured into water (20 mL), and extracted with ether repeatedly. The combined extracts were dried (Na_2SO_4) and concentrated. Purification by silica gel column chromatography provided 0.23 g (83%) of the desired allylic alcohols **2** as a colorless oil. Under the same conditions, 1-iodo-1-cyclohexene also reacted with the aldehyde to give the adduct in 74% yields (Table I, run 11), while 1-(trimethylsiloxy)-1-cyclohexene and 1-cyclohexenyl diethyl phosphate remained unchanged with 83%[8] and 98% recovery, respectively. Yields of the coupling reaction between triflate **1** and benzaldehyde with such potential catalysts[9] (5 mol % of $CrCl_2$) in DMF at 25 °C for 12 h are as follows: $MnCl_2$, <1%; $FeCl_3$, 9%; $CoCl_2$, 16%; CuCl, <1%; $PdCl_2$,[10] <1%.[11] In general, high solubility of $CrCl_2$ is essential to promote the reaction smoothly. Little or no reaction occurs in ether or THF. DMF is the most effective solvent.

The examples of the Grignard-type addition of alkenyl triflates to aldehydes with the combination of $CrCl_2$ and $NiCl_2$ are shown in Table I. In the case of α,β-unsaturated aldehyde, 1,2-addition products are produced mainly (runs 4 and 10).[3,12] The alkenylchromium reagents have aldehyde-selectivity[13] (runs 5–7) similarly to allyl-[14] and alkynylchromium ones.[15] Steric factors of double bonds influence the reaction markedly. Triflates **4** and **6**, whose substituents of double bonds possess trans position of OTf group, reacted smoothly (runs 14 and 17). In contrast, treatment of a triflate having a cis substituent with the $CrCl_2$–$NiCl_2$ system resulted in recovery of the starting triflate even at 60 °C (run 13) or in cis–trans isomerization–coupling reaction sequence (run 15).[16] As seen in Table I, regiochemistry of double bonds is maintained during the coupling reaction. Since alkenyl triflates can be obtained regioselectively from ketones,[1b,17] the new

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(6) Anhydrous $CrCl_2$ free from nickel salts[9] was purchased from either Aldrich Co. (90% purity) or Rare Metallic Co. (99.99% purity).

(7) Professor Yoshito Kishi kindly informed us that he also encountered the problem and found the same effect of nickel independently. He employed the combination of chromium and nickel in the total synthesis of palytoxin. See, Jin, H.; Uenishi, J.; Christ, W. J.; Kishi, Y. *J. Am. Chem. Soc.*, in press.

(8) GLPC (3% Silicone OV-17, 1.5 m) yield.

(9) The absence of Ni was confirmed by fluorescent X-rays analysis.

(10) Reduction of triflate **1** to 1-dodecene took place in 64% yield based on the triflate **1**.

(11) Decomposition of triflate **1** leading to 1-dodecyne and/or 1,2-dodecadiene proceeded at the same time with these catalysts.

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(16) The cis–trans isomerization of double bond could occur during oxidative addition of triflate **4** to nickel(0). See ref 18a.

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