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Chemistry at the Alkyne–Carbene Intersection: A Metallacyclobutene–η^3-Vinylcarbene Equilibration

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Ⓢ *Supporting Information*

ABSTRACT: Synthesis of a sterically congested metallacyclobutene complex has led to the first observation of metallacyclobutene–η^3-vinylcarbene equilibration. The structure of the η^3-vinylcarbene complex was elucidated by spectroscopy, HRMS, and *ab initio* computations. The vinylcarbene complex was trapped by reactions with ethyl diazoacetate and $(C_5H_5)Co(PPh_3)_2$ to give cobalt–diene and dicobalt complexes, respectively.

Metallacyclobutene, η^3-vinylcarbene, and η^1-vinylcarbene structures (**I**–**III**) have been widely proposed as intermediates and/or transition states in a number of important metal-catalyzed reactions of alkynes and carbenes, including alkyne polymerization,[1] enyne metathesis,[2] and cyclopropenation,[3] etc.[3,4] (Figure 1). The defining geometric differences for **I**–**III** are the presence of one, two, or three carbon–metal bonds. Interconversions of **I**–**III** have been the subject of extensive speculation in the literature, and direct observations of both metallacyclobutene–η^1-vinylcarbene[5] and η^1-vinylcarbene–η^3-vinylcarbene[6] equilibria have been reported. Here we report the first experimental observation of a metallacyclobutene–η^3-vinylcarbene equilibration.[7] The η^3-vinylcarbene complex is characterized by NMR spectroscopy, HRMS, and *ab initio* quantum chemical computations, and trapped with $(C_5H_5)Co(PPh_3)_2$ and ethyl diazoacetate to give dicobalt and 1,3-diene complexes, respectively.

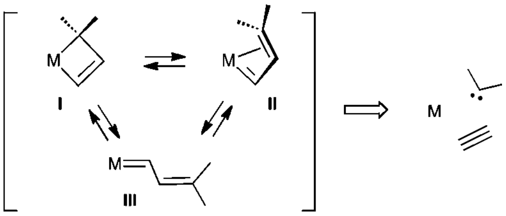
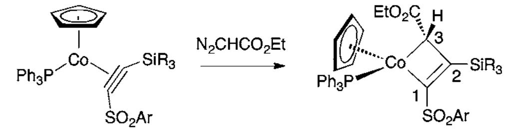


Figure 1. Interconversions of metallacyclobutene (**I**), η^3-vinylcarbene (**II**), and η^1-vinylcarbene (**III**) complexes.

We previously reported the reaction of cobalt–alkyne complex $(C_5H_5)Co(PPh_3)\{\eta^2\text{-}[(Me_3Si)C{\equiv}C(SO_2Ph)]\}$ (**1**-TMS) with ethyl diazoacetate to give the air-stable metallacyclobutene $(C_5H_5)(PPh_3)Co\{\kappa^2\text{-}[C(SO_2Tol){=}C(TMS)CH(CO_2Et)]\}$ (**2**-TMS) (eq 1).[8a] Above 60 °C, **2**-TMS exhibits a rich chemistry, undergoing reactions with carbon monoxide, diazocarbonyls, alkynes, and alkenes to give vinylketene,[8b] 1,3-diene,[8c] cyclopentadiene,[8d] and 1,4-diene products.[8e] These transformations may involve unobserved vinylcarbene intermediates. To facilitate the observation of a vinylcarbene intermediate, we reasoned that increased steric bulk at one of the metallacycle ring substituents would result in dissociation of PPh_3 at lower temperatures. The loss of phosphine (or Cp ring-slippage) is required to move from a two-electron-donor κ^2-propendiyl ligand to a four-electron-donor η^3-vinylcarbene ligand. In addition, one would expect that increased steric congestion might destabilize a planar metallacyclobutene relative to η^1-vinylcarbene and nonplanar η^3-vinylcarbene structures.



(1)

1-*TMS* (Ar = Ph, R = Me)
1-*TIPS* (Ar = Tolyl, R = ^{i}Pr)

2-*TMS* (Ar = Ph, R = Me)
2-*TIPS* (Ar = Tolyl, R = ^{i}Pr)

Despite concern that a more highly congested analogue of **2**-TMS might prove inaccessible, we found that $(C_5H_5)(PPh_3)Co\{\eta^2\text{-}[(TIPS)C{\equiv}C(SO_2Tol)]\}$ (**1**-TIPS; TIPS = iPr_3Si, Tol = $C_6H_4CH_3$) is readily prepared from $(C_5H_5)Co(PPh_3)_2$ and $(TIPS)C{\equiv}C(SO_2Tol)$, and undergoes reaction with ethyl diazoacetate at room temperature to form the highly congested metallacyclobutene $(C_5H_5)(PPh_3)Co\{\kappa^2\text{-}[C(SO_2Tol){=}C(TIPS)CH(CO_2Et)]\}$ (**2**-TIPS) (eq 1). Unlike **2**-TMS, **2**-TIPS is air-sensitive in solution at room temperature. In the ^1H NMR spectrum (C_6D_6) of **2**-TIPS, the C3-hydrogen is observed at δ 2.04 (d, $^3J_{PH}$ = 6.9 Hz), and in the ^{13}C NMR spectrum, propendiyl ligand resonances are observed at δ 134.4 (d, $^2J_{PC}$ = 10.0 Hz, C1), 174.3 (s, C2), and −2.1 (d, $^2J_{PC}$ = 13.1 Hz, C3). In the IR spectra of **2**-TMS and **2**-TIPS the carbonyl stretching frequencies are observed at 1680 and 1684 cm^{-1}, respectively. We attribute these remarkably low energy ester C=O frequencies to hyperconjugation involving the Co–C σ bond and the π* orbital of the carbonyl.[9]

An X-ray-quality crystal of **2**-TIPS was grown from a hexanes/toluene (5:1) solution, and crystallographic analysis confirmed the metallacyclobutene formulation (Figure 2, Table 1). For comparison, crystallographic analysis of **2**-TMS was also carried out. Within the experimental uncertainty, the cobalt–ligand

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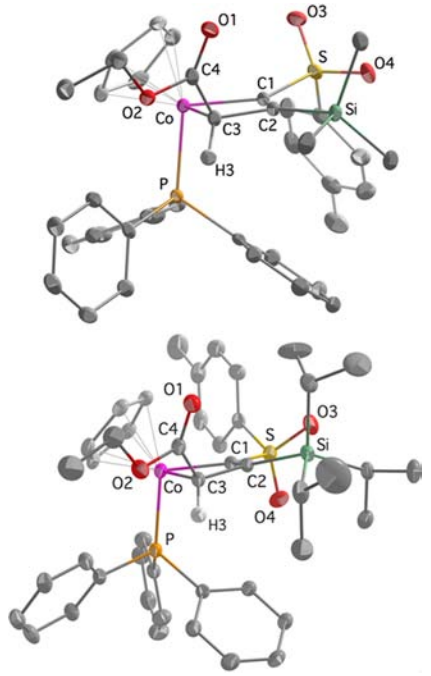


Figure 2. ORTEP drawings of **2**-TMS (top) and **2**-TIPS (bottom). For clarity, the C_5H_5 and tolyl/Ph C-atoms are shown in a lighter color, and most H-atoms have been omitted. For selected bond distance and angle data, see Table 1 and Supporting Information.

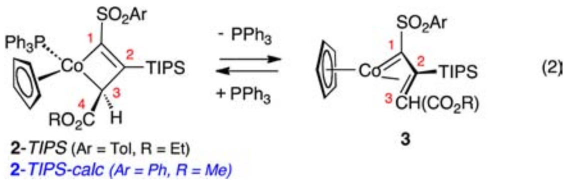
Table 1. Distances (Å) and Angles (deg) for 2-TIPS, 2-TIPS-calc, 3-*E*-calc, 3-*E*-conf-calc, 3-*Z*-calc, and 3-*Z*-conf-calc

	2-TIPS[a]	**2**-TIPS-calc[a]	**3**-E-calc[b]	**3**-E-conf-calc[b]	**3**-Z-calc[b]	**3**-Z-conf-calc[b]
Co−C1	1.938(3)	1.936	1.758	1.759	1.759	1.750
Co−C2	–	–	2.045	2.054	2.059	2.042
Co−C3	2.055(4)	2.078	2.016	2.009	2.024	2.027
C1−C2	1.345(5)	1.349	1.405	1.407	1.412	1.412
C2−C3	1.514(3)	1.518	1.452	1.449	1.462	1.465
C3−C4	1.465(4)	1.476	1.486	1.489	1.481	1.479
C4−O1	1.211(3)	1.220	1.216	1.212	1.218	1.217
Co−P	2.201(2)	2.166	–	–	–	–
C1−S	1.770(3)	1.780	1.766	1.776	1.756	1.765
C2−Si	1.917(4)	1.917	1.914	1.918	1.936	1.928
C1−Co−C3	65.8(1)	66.3	74.9	75.0	74.1	73.6
Co−C1−C2	102.9(2)	102.0	79.7	80.0	80.1	79.6
C1−C2−C3	98.6(2)	99.9	107.4	107.4	105.5	104.4

[a] See Figure 2 for atom labeling. [b] See Figure 4 for atom labeling.

bond distances are identical in the two complexes. The greater steric congestion in **2**-TIPS is manifested in a larger four-membered-ring fold angle (the dihedral angle between the C1−Co−C3 and C1−C2−C3 planes) in **2**-TIPS [8.7(7)°] relative to that in **2**-TMS [1(3)°]. The Si atom is displaced 0.17(1) and 0.49(1) Å from the C1−Co−C3 plane in **2**-TMS and **2**-TIPS, respectively. The Co−C(3)−C(4)−O(1) torsion angles in **2**-TMS (87.3(3)°) and **2**-TIPS (89.5(5)°) are ideally disposed for a hyperconjugative interaction involving the Co−C(3) bond and the ester carbonyl.[9]

When a room-temperature benzene-d_6 solution of **2**-TIPS is monitored by ^{1}H NMR spectroscopy, the intensity of the δ 4.32 (C_5H_5) **2**-TIPS resonance slowly decreases with a concomitant increase in the intensity of a new C_5H_5 resonance at δ 4.51 (**3**, s, C_5H_5) (eq 2). After 4 days, a 3:1 ratio of **2**-TIPS:**3** was observed



(K_{eq} = [**3**][PPh_3]/[**2**-TIPS] ≈ 1.0×10^{-3} M; $\Delta G° \approx 4.1$ kcal/mol),[10] and no further changes in that ratio occurred over an additional 3 days. When PPh_3 was added to the solution, the ratio of **2**-TIPS:**3** increased, whereas addition of the phosphine scavenger $Ir(PPh_3)_2(Cl)(N_2)$ (**4**) led to nearly quantitative conversion to **3** and $Ir(H)(Cl)(C_6H_4PPh_2)(PPh_3)_2$ (**5**).[11] Thus, in benzene solution **2**-TIPS and **3**/PPh_3 are in equilibrium at room temperature.

The instability of **3** precluded isolation in pure form, so its structure was established by spectroscopic analysis of samples containing **3** and **5**. In the IR spectrum ($CHCl_3$) of **3**, the carbonyl stretch of the ester is observed at 1698 cm^{-1}. The ν(C═O) stretch assignment was confirmed by comparison to the isotopologue with C-13 enrichment at the carbonyl carbon. The 14 cm^{-1} ν(C═O) shift to higher energy upon going from **2**-TIPS to **3** is consistent with decreased σ(M-C)/π^*(CO) hyperconjugation in the vinylcarbene relative to that in **2**-TIPS.

In addition to the δ 4.51 (C_5H_5) singlet in the ^{1}H NMR spectrum of **3**, characteristic resonances were observed at δ 6.02 (s, 1H, -C*H*CO$_2$-), 3.86 (m, 1H, OC*H*HMe), 3.93 (m, 1H, OCH*H*Me), 1.55 (sept, 3H, TIPS), and 1.17 (d, 18H, TIPS).[12] In the ^{13}C NMR spectrum (benzene-d_6), resonances at δ 251.5 (C1), 91.2 (C2), and 42.1 (C3, $^1J_{CH}$ = 157.6 Hz) were assigned to the propendiyl carbons bound directly to Co.[13] The upfield chemical shifts observed for C2 and C3 are consistent with metal coordination, thereby excluding η^1-vinylcarbene structures.[14,15] The observation of an NOE between the H3 resonance (δ 6.02) and the TIPS primary (δ 1.17) and secondary hydrogen (δ 1.55) resonances is consistent with *E*-stereochemistry in the η^3-vinylcarbene ligand (Figure 3).[16]

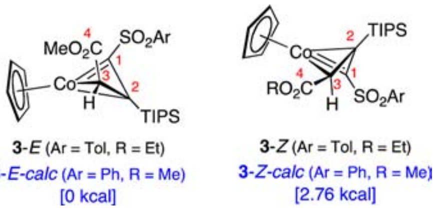


Figure 3. Structures with atom labeling for η^3-vinylcarbenes **3**-*E*, **3**-*Z*, **3**-*E*-calc, and **3**-*Z*-calc.

To further address the issue of η^3-vinylcarbene stereochemistry, as well as the relative energetics of conformational and constitutional vinylcarbene isomers, we carried out *ab initio* computations at the B97D/Def2-TZVPP level of theory on model complexes in both gas phase and benzene solution environments (Figure 4).[17] The validity of the computed structures is supported by the excellent agreement between the crystallographic and computational data for **2**-TIPS and $(C_5H_5)Co(PPh_3)\{\kappa^2\text{-}[CH(CO_2Me)(TIPS)C{=}C(SO_2Ph)]\}$ (**2**-TIPS-calc; Table 1). The lowest energy vinylcarbene is the *E*-stereoisomer $(\eta^5\text{-}C_5H_5)Co\{\eta^3\text{-}E\text{-}[CH(CO_2Me)C(TIPS){=}C\text{-}$

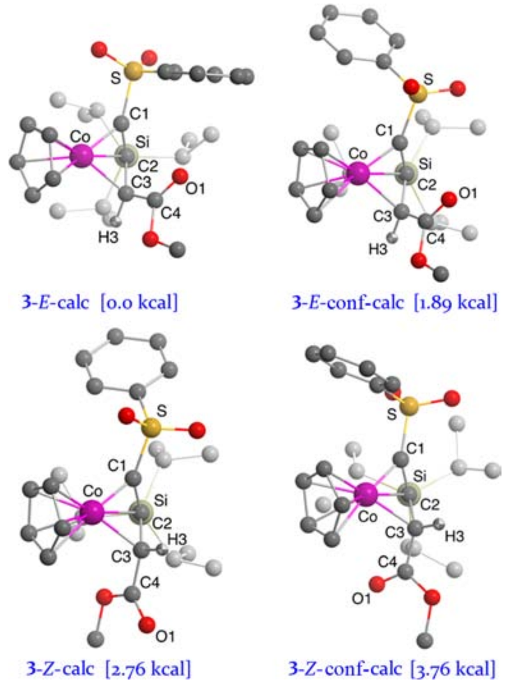


Figure 4. Calculated structures for η^3-vinylcarbene isomers 3-*E*, 3-*E*-conf-calc, 3-*Z*-calc, and 3-*Z*-conf-calc, as viewed down the C2−Si bond. Relative energies are shown in brackets. For clarity the isopropyl C-atoms are shown in lighter color, and all H-atoms but H3 are omitted.

$(SO_2Ph)]\}$ (**3**-*E*-calc, 0.0 kcal), with the lowest energy *Z*-diastereomer, $(\eta^5\text{-}C_5H_5)Co\{\eta^3\text{-}Z\text{-}[CH(CO_2Me)C(TIPS){=}C(SO_2Ph)]\}$ (**3**-*Z*-calc), 2.76 kcal higher in energy. From the calculated energy difference between **3**-*E*-calc and **3**-*Z*-calc one would expect that an equilibrium mixture of the *E*- and *Z*-complexes would result in ~99:1 ratio of the *E*:*Z* isomers, which is consistent with the observation of only a single isomer by ^{1}H NMR spectroscopy. In addition to **3**-*E*-calc and **3**-*Z*-calc, conformers of both the *E*-isomer (**3**-*E*-conf-calc, 1.89 kcal) and the Z-isomer (**3**-*Z*-conf-calc, 3.76 kcal) were located at slightly higher energies (Figure 4). No coordinatively unsaturated η^1-vinylcarbene or metallacyclobutene isomers of **3** were found computationally.[18] The difference in double bond stereochemistry results in pronounced structural differences for **3**-*E*-calc and **3**-*Z*-calc, including 60.8° and 116.1° dihedral angles between the C1−Co−C3 and C1−C2−C3 planes, respectively. This difference in the fold angles is in part a consequence of shorter Co−C2 (Δ = 0.014 Å) and Co−C3 (Δ = 0.008 Å) bonds in **3**-*E*-calc. The calculated H3 chemical shift values for the gas-phase structures of **3**-*E*-calc (δ 5.0) and **3**-*Z*-calc (δ 2.5) are consistent with the assigned *E*-stereochemistry for **3** (exp δ 6.0) and suggest that the significant chemical shift difference for *E*- and *Z*-isomers may prove generally useful for assigning stereochemistry in η^3-vinylcarbene complexes.

The electrophilic HOMO and nucleophilic LUMO plots for the four lowest energy isomers of **3** indicate that, in the absence of steric effects, the highest probability of attack by an electrophile is at Co, whereas the highest probability for attack by a nucleophile is at C1 (for a representative example see Figure 5). One would therefore expect an electrophile such as $[(C_5H_5)CoL]$ to undergo reaction with **3**-*E* at Co, whereas a nucleophile such as ethyl diazoacetate would attack at C-1. Experimentally this was found to be the case.

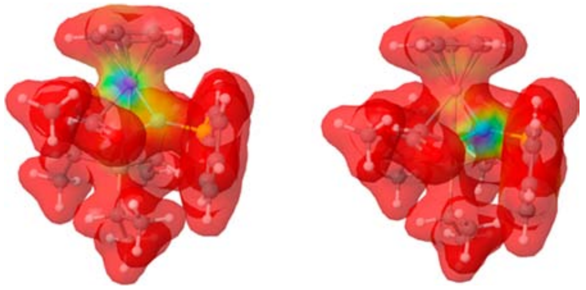


Figure 5. Left: Electrophilic HOMO frontier density plot for **3**-*E*-calc. Right: Nucleophilic LUMO frontier density plot for **3**-*E*-calc. Blue indicates the regions with the highest probability for attack of an electrophile (left) or nucleophile (right) in the absence of steric effects.

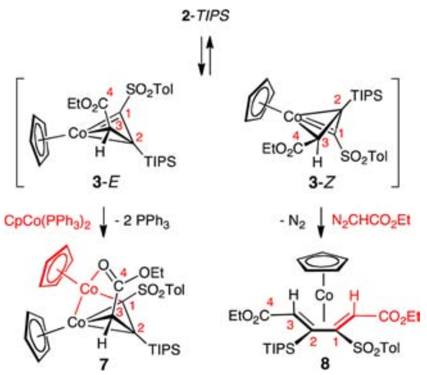


Figure 6. Conversion of **2**-TIPS to dicobalt (**7**) and cobalt−diene (**8**) complexes.

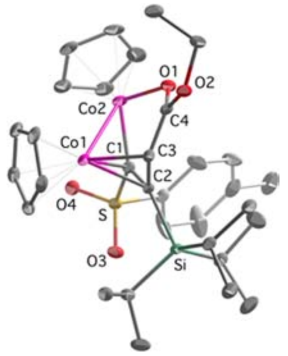


Figure 7. ORTEP drawing for **7**. For clarity the tolyl C-atoms are shown in a lighter color, and H-atoms have been omitted. Selected bond distances (Å): Co1−Co2 2.5661(6), Co1−C1 1.951(2), Co1−C2 2.009(2), Co1−C3 2.000(2).

When a benzene solution of **2**-TIPS was treated with $(C_5H_5)Co(PPh_3)_2$ (**6**) the dicobalt complex **7** was formed in 47% isolated yield over 14 h *at room temperature* (Figure 6). The structure of **7** was established by X-ray crystallography (Figure 7).[10] Of particular note is the observation that the alkene stereochemistry in **3**-*E* is preserved in **7**, consistent with reaction of $[(C_5H_5)Co]$ with **3**-*E* and inconsistent with involvement of **3**-*Z*. Examination of space-filling models indicates that the isopropyl groups block *exo*-approach of an electrophile at the metal−C1 bond in both *E*-conformers. The ester substituent presumably directs *endo*-approach of "CpCoL" by coordination of the ester oxygen to Co.

Room temperature reaction of ethyl diazoacetate with **2**-TIPS led to the formation of a single 1,3-diene complex, **8**, in 37% yield

(Figure 6). For comparison, the less congested metallacycle, **2**-TMS, underwent reaction with ethyl diazoacetate only at elevated temperatures and gave rise to a mixture of three cobalt−diene stereoisomers.[8a,c] X-ray crystallographic analysis of **8** confirms that the diazoester has coupled to C1 of the vinylcarbene intermediate and that the diene stereochemistry is *ZZ*.[19,20] The C2−C3 double bond stereochemistry in **8** is consistent with nucleophilic attack by ethyl diazoacetate at C1 of the *Z*-isomer. Examination of space-filling models indicates that both *endo*-(*syn* to H3) and *exo*-approach of a nucleophile at C1 are hindered in **3**-*E*-calc and **3**-*E*-conf-calc (*exo*-approach by the ^{i}Pr groups and *endo*-approach by the ester), whereas *endo*-approach in the case of **3**-*Z*-calc and **3**-*Z*-conf-calc is relatively unhindered.[21]

In summary, the first experimental observation of a metallacyclobutene−η^3-vinylcarbene equilibration has been documented by a combination of spectroscopic, computational, and reactivity studies. The relative energetics and steric parameters of the computed η^3-vinylcarbene structures are fully consistent with the experimental results, including trapping of **3** by both an electrophile and a nucleophile. These results implicate η^3-vinylcarbenes as key reactive intermediates in the chemistry of cobaltacyclobutenes **2**-TMS and **2**-TIPS, and suggest that η^3-vinylcarbenes may play a pivotal role in the reactions of other metallacyclobutene and vinylcarbene complexes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental and computational details and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(10) Due to overlapping resonances in the ^{1}H NMR spectrum, the concentration of free PPh_3 is approximate, which results in only approximate values for K_{eq} and $\Delta G°$.

(11) The phosphine scavengers CuCl and $AuCl(PPh_3)$ proved less satisfactory than **4**. In solution $Ir(PPh_3)_3Cl$ has been shown to convert to **5**: Bennett, M. A.; Milner, D. L. *J. Am. Chem. Soc.* **1969**, *91*, 6983.

(12) For comparison, the η^3-vinylcarbene ligand in $[(C_5H_5)(CO)_2W\{\eta^3\text{-}(CPhCPh{=}CHTol)\}]BF_4$ exhibits a vinyl hydrogen resonance at δ 6.05 in the ^{1}H NMR spectrum: Garrett, K. E.; Sheridan, J. B.; Pourreau, D. B.; Feng, W. C.; Geoffroy, G. L.; Staley, D. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 8383.

(13) The δ 42.1 chemical shift assignment was confirmed by the synthesis of $(\eta^5\text{-}C_5H_5)Co\{\eta^3\text{-}[^{13}CH(CO_2Et)(TMS)C{\equiv}C(SO_2Ph)]\}$ from **2**-TIPS and $N_2{}^{13}CH(CO_2Et)$, followed by treatment with **4**. The δ 6.02 resonance in the ^{1}H NMR spectrum of **3** correlated with the δ 42.1 carbon resonance in a 2D-HSQC NMR spectrum, and with the δ 91.7 and 251.5 carbon resonances in a 2D-HMBC spectrum.

(14) The η^1-vinylcarbene complex $\{\eta^5,\eta^1\text{-}[C_5H_4CH_2CH_2P(^tBu)_2]\}\text{-}Co({=}C^1HC^2H{=}C^3Ph_2)]$ exhibits carbon chemical shifts at δ 199.5 (C^1), 155.9 (C^2), and 123.6 (C^3): Foerstner, J.; Kakoschke, A.; Stellfeldt, D.; Butenschön, H.; Wartchow, R. *Organometallics* **1998**, *17*, 893.

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(16) The *E*/*Z* assignment in these η^3-vinylcarbene complexes is defined by the C4−C3−C2−Si dihedral angle. For **3**-*E*-calc and **3**-*Z*-calc this torsion angle is 132° and −28°, respectively.

(17) Energies shown in Figures 3 and 4 are from solution (C_6H_6) environment calculations. For gas-phase values see SI.

(18) Two additional η^3-vinylcarbene conformers of **3**-*Z*-calc and an η^1-vinylcarbene complex with the ester oxygen coordinated to Co (**3**-*C*,*O*-calc) were located > 6.5 kcal higher in energy than **3**-*E*-calc (see SI for details).

(19) For nucleophilic attack of diazoalkanes and diazoesters at a η^1-carbene carbon to generate alkene products see: (a) Casey, C. P.; Bertz, S. H.; Burkhardt, T. J. *Tetrahedron Lett.* **1973**, *16*, 1421. (b) Collman, J. P.; Rose, E.; Venburg, G. D. *J. Chem. Soc., Chem. Commun.* **1993**, 934.

(20) The regioselectivity observed in the formation of **8** is consistent with the regioselectivity of related metallacyclobutene reactions reported in ref 8c.

(21) It is not possible to conclusively rule out involvement of higher energy vinylcarbene isomers in the reactions of **3**; however, the significant energy difference between the Figure 4 vinylcarbenes and higher energy isomers and the stereoselectivity observed in the reactions of **3** are most consistent with the involvement of **3**-*E* and **3**-*Z*.