Transfer of ethylidene from .eta.5-C5H5(CO)2Fe:CHMe+ to para-substituted styrenes. Loss of stereochemistry about the C.alpha.-C.beta. double bond of cis-.beta.-deuterio-p-methoxystyrene

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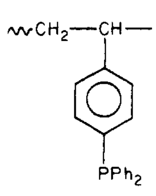

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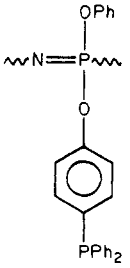

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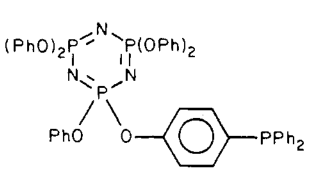

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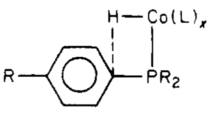
tinuation of our studies in the area of polymer-supported hydroformylation catalyst systems.[8] We find that the cobalt catalysts derived from **1**, **2**, and **3** lose catalytic activity with time, due both to loss of cobalt and loss of tertiary phosphine functionality. Thus exposure of Co$_2$(CO)$_8$ bound to **1**, **2**, or **3** to hydroformylation conditions (190 °C; heptane or toluene solvent; 2000 psig of 1:1 CO/H$_2$) resulted in substantial loss of phosphine functionality (microanalysis of the used catalyst revealed 15–25% loss of P in 28 h for **1** and 30% loss of P in 48 h for **2**; ^{31}P NMR revealed 50% loss of pendant phosphorus from **3** in 48 h). In addition, the catalyst derived from **1** yielded $^1/_2$ mol of benzene per mol of cobalt after 48 h.

In an analogous fashion GC analysis of hydroformylation reaction mixtures with or without 1-hexene substrate, catalyzed by the homogeneous systems Co$_2$(CO)$_8$/8PR$_3$ (R = Ph, CH$_2$Ph), also revealed a release of benzene or toluene.[9] If the reactions are carried out without the 1-hexene substrate, diarylphosphine, R$_2$PH (R = Ph, *p*-MeC$_6$H$_4$, CH$_2$Ph), can be detected by ^{31}P NMR.[10,11] We believe that this represents the first direct detection of R$_2$PH generated by a PPh$_3$-ligated catalyst system.

Several possible intermediates (**4**, **5**, **6**) can be proposed for the metal-catalyzed P–C bond cleavage. Three possibilities seem plausible: (1) simple electrophilic substitution via an intermediate such as **4**, (2) "oxidative addition" of the phosphorus–aryl bond via an intermediate such as **5**, or (3) *o*-metalation and subsequent hydrogenolysis of an intermediate such as **6**.[12] The production of benzene or toluene does not distinguish between these three possibilities; however, close examination of a hydroformylation reaction catalyzed by Co$_2$(CO)$_8$/8P(*p*-MeC$_6$H$_4$)$_3$ revealed the formation of *p*-methylbenzyl alcohol[13] but no *m*-methyl product. We feel that an oxidative-addition mechanism could be operative for these reactions in which para-specific CO insertion occurs. Whether a cobalt–phenyl intermediate is responsible for the production of benzene or toluene is at this point unknown.[12]



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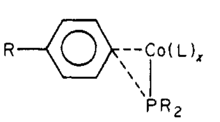

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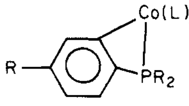

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These findings appear to be relevant to other homogeneous triarylphosphine-modified catalyst systems. We have recently reported the quantitative formation of benzene during RuCl$_2$(PPh$_3$)$_3$-catalyzed conversion of primary to secondary amines,[14] and Crabtree has detected 0.8 mol of fluorobenzene per mol of Ir during his studies on cyclohexane dehydrogenation catalyzed by [IrH$_2$S$_2$L$_2$]SbF$_6$ (S = Me$_2$CO, L = PPh$_3$) at 150 °C.[15] Our results using phosphinated polystyrene as an "immobilization" medium for Co$_2$(CO)$_8$ raise questions about previous reports of the recycling of such hydroformylation catalysts.[16]

In conclusion we wish to note that the detection of triarylphosphine decomposition and/or loss of functionality on heterogenized support materials is a much more common reaction than had been previously thought. It is clear that this decompostion pathway is possible for any reaction involving transition-metal–triarylphosphine catalysis.[18]

Acknowledgment. We thank The Dow Chemical Co. for its support of the work at The Pennsylvania State University. We also thank Professors Crabtree and Tanaka for communication of their results prior to publication.

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(8) (a) Fellmann, J. D.; Garrou, P. E.; Withers, H. P.; Seyferth, D.; Trafficante, D. D. *Organometallics* **1983**, *28* 818. (b) Dubois, R. A.; Garrou, P. E.; Hartwell, G. E.; Hunter, D. H. *Ibid.* **1984**, *3*, 95.

(9) For R = Ph in the presence of 1-hexene substrate, 0.93 mol of benzene is produced per mol of cobalt after 8 days. For R = CH$_2$Ph, in the absence of substrate, 0.89 mol of toluene is produced per mol of cobalt after only 36 h of reaction. Blank reactions show less than 3% of the benzene could be formed via simple thermal degredation at the reaction temperature.

(10) When 1-hexene is present we believe the R$_2$PH reacts with it to produce R$_2$P(hexyl) which we also observe in minor amounts by ^{31}P NMR. The reverse observation, i.e., phosphido cobalt clusters reacting under CO/H$_2$ with 1-hexene to give R$_2$P(hexyl), has been recently reported.[11]

(11) Harley, A. D.; Guskey, G. J.; Geoffroy, G. L. *Organometallics* **1983**, *2*, 53.

(12) At this point we cannot rule out a radical mechanism. We cannot find radical initiators or scavengers that are stable under our reaction conditions. We are continuing our attempts to examine this possibility.

(13) Although a yield of this alcohol has not yet been determined, we did obtain an 11.5% yield of benzyl alcohol from a similar reaction with Co$_2$(CO)$_8$/8PPh$_3$.

(14) Jung, C. W.; Fellmann, J. D.; Garrou, P. E. *Organometallics* **1983**, *2*, 1042.

(15) Crabtree, R. H., private communication.

(16) For example, close examination of an earlier report[17] in which recycling was carried out contained analytical data that revealed substantial losses of both Co and P after only a few recycles.

(17) Evans, G. O.; Pittman, C. U.; McMillan, R.; Beach, R. T.; Jones, R. J. *J. Organomet. Chem.* **1974**, *67*, 295.

(18) After this publication was submitted we were informed[19] of similar studies which conclude that decomposition during hydroformylation is in the order Rh$_4$(CO)$_{12}$/PPh$_3$ > Ru$_3$(CO)$_{12}$/PPh$_3$ > Ru$_4$(CO)$_{12}$/PBu$_3$ ~ Co$_2$(CO)$_8$/PPh$_3$ > Ru$_3$(CO)$_{12}$/PBu$_3$ > Co$_2$(CO)$_8$/PBu$_3$.

(19) Tanaka, M., private communication.

Transfer of Ethylidene from η^5-C$_5$H$_5$(CO)$_2$Fe=CHCH$_3^+$ to Para-Substituted Styrenes. Loss of Stereochemistry about the C$_\alpha$–C$_\beta$ Double Bond of *cis*-β-Deuterio-*p*-methoxystyrene

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Summary: Transfer of ethylidene from η^5-C$_5$H$_5$(CO)$_2$Fe=CHCH$_3^+$ to a series of para-substituted styrenes gives *cis*- and *trans*-1-(para-substituted phenyl)-2-methylcyclopropanes (X = H, CH_3, OCH_3, F, Cl, and CF_3). With use of the labeled alkene *cis*-β-deuterio-*p*-methoxystyrene, the abnormally low cis/trans ratio for X = *p*-OMe (0.9) is shown to be due to C_α–C_β bond rotation which occurs in an intermediate formed after the transition state. This is the first reported case of loss of alkene stereochemistry upon cyclopropane formation from an electrophilic carbene complex.

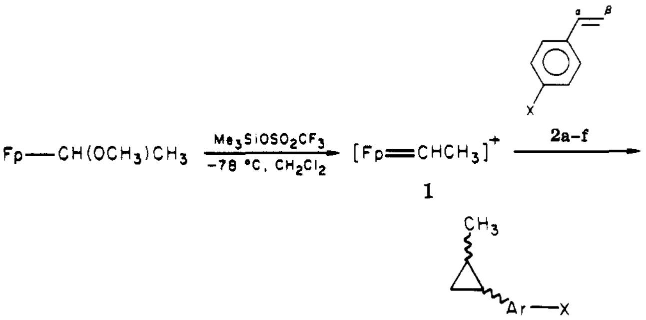
Although the synthetic potential of iron carbene complexes $Fp{=}CRR'^+$ (R = R′ = H[1]; R = H, R′ = aryl[2]; R = H, R′ = CH_3[3-5]; R = R′ = CH_3[6]) for preparation of substituted cyclopropanes from alkenes has been demonstrated,[7] mechanistic details of the transfer reaction and factors controlling stereoselectivity remain unclear. No studies have evaluated the relative importance of steric and electronic properties of the alkene in determining stereoselectivity. We report here (1) the stereoselectivity observed for transfer of ethylidene from $Fp{=}CHCH_3^+$ (**1**) (Fp = η^5-$C_5H_5Fe(CO)_2$) to a series of para-substituted styrenes in which the nucleophilicity of the alkene can be varied without altering the steric properties and (2) the results of transfer to specifically deuterated styrenes which demonstrate that loss of stereochemistry about the carbon–carbon double bond can occur in these reactions.

The reaction of **1**, generated in situ at −78 °C, with a fivefold excess of styrenes **2a**–**2f** was carried out by using previously described procedures.[3] The cis/trans ratios of the resultant 1-aryl-2-methylcyclopropanes (**3**) are summarized in Scheme I.[10]

For cyclopropanes arising from styrenes **2b**–**2f**, the cis/trans ratios all fall within a relatively close range (ca. 5–7) with no evidence that the small variations observed correlate with the electronic character of the substituent. The unusual case was that of **2a** (X = OCH_3) where a cis/trans ratio of 0.9 was observed.

The lack of a smooth variation in the stereoselectivity with a change in para substituents and the strong donor ability of the *p*-OCH_3 group suggested that the low stereoselectivity may occur via formation of a stabilized carbonium ion intermediate capable of rotation around the C_α–C_β bond. to probe this possibility, ethylidene was transferred to specifically labeled *cis*-β-deuterio-*p*-X-styrenes (X = **4a** H, **4b** CH_3, **4c** OCH_3).[11] The deuterium stereochemistry in the resultant cyclopropanes was assessed by ^{1}H and ^{2}H NMR.[13] Results are summarized in Scheme II.

Scheme I



	X	cis/trans
3a	OCH_3	0.9 ± 0.1
b	CH_3	6.0 ± 0.5
c	H	6.5 ± 0.5
d	F	7.0 ± 0.5
e	Cl	6.0 ± 0.5
f	CF_3	5.0 ± 0.5

With styrenes **4a** and **4b** (X = H, CH_3), no scrambling of deuterium is observed in the product cyclopropanes; stereochemistry about the C_α–C_β double bond of these styrenes is completely retained. However, for **4c**, four products were observed, **9c**–**12c**. Cyclopropanes **10c** and **11c** represent systems in which the *p*-anisyl and deuterium stereochemistry is trans and *inverted* relative to **4c**. Clearly, in this case stereochemistry about the original C_α–C_β double bond is not preserved. Interestingly, **11c**, with deuterium stereochemistry inverted, comprises the *major* fraction of the trans isomer. Control experiments establish that (1) residual **4c** remaining after reaction shows no scrambling and that (2) *cis*-1-*p*-anisyl-2-methylcyclopropane is stable to the reaction conditions. Thus, there is an intermediate formed *after* the rate-determining step but before product formation in which loss of stereochemistry about the original C_α–C_β double bond can occur.

The simplest mechanism consistent with the observed results is summarized in Scheme II. Initial cis and trans approaches of the styrenes produce carbonium ions **5** and **8**, respectively. For X = H and CH_3, **5a**–**5b** and **8a**–**8b** are sufficiently short-lived that bond rotation is not competitive with collapse to product cyclopropanes, and deuterium stereochemistry is retained. However, for the more stable *p*-anisyl-substituted ions, **5c** and **8c**, bond rotation is competitive with collapse, and stereochemistry is lost. The major trans isomer (**10c**) must come from cis approach followed by rotation to **6c** and collapse. "Inverted" cis isomer **11c** must arise from formation of **8c**, rotation, and collapse.[14]

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(1) (a) Brandt, S.; Helquist, P. *J. Am. Chem. Soc.* **1979**, *101*, 6473. (b) Jolly, P. W.; Pettit, R. *Ibid.* **1966**, *88*, 5044.

(2) (a) Brookhart, M.; Humphrey, M. B.; Kratzer, H.; Nelson, G. O. *J. Am. Chem. Soc.* **1980**, *102*, 7802. (b) Nelson, G. O.; Brookhart, M. *Ibid.* **1977**, *99*, 6099.

(3) (a) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1981**, *103*, 979. (b) Brookhart, M.; Tucker, J. R.; Husk, G. R. *Ibid.* **1983**, *105*, 258.

(4) Kremer, K. A. M.; Helquist, P.; Kerber, R. C. *J. Am. Chem. Soc.* **1981**, *103*, 1862.

(5) Bodnar, T.; Cutler, A. *J. Organomet. Chem.* **1981**, *213*, C31.

(6) (a) Casey, C. P.; Miles, W. H.; Tukada, H.; O'Connor, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 3761. (b) Kremer, K. A. M.; Kuo, G.-H.; O'Connor, E. J.; Helquist, P.; Kerber, R. C. *Ibid.* **1982**, *104*, 6119.

(7) Other stable electrophilic transition-metal–carbene complexes which transfer the carbene ligand to alkenes to yield cyclopropanes include $(CO)_5W{=}CHPh$[8] and $Cp(CO)_2(L)M{=}CH_2^+$ (M = Mo, W; L = PPh_3, PEt_3).[9]

(8) Casey, C. P.; Shusterman, A. J.; Polichnowski, S. W.; Jones, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 7282.

(9) Brookhart, M.; Kegley, S. E.; Husk, G. R. *Organometallics* **1982**, *1*, 760.

(10) Triplicate runs were carried out and isomer ratios and yields determined by GC. Transfer yields were X = OCH_3 (50%), CH_3 (75%), F (83%) H (70%), Cl (35%), CF_3 (ca. 10%). Where X = CF_3, yields are clearly low due to substantial deactivation by CF_3; however, since products are stable under the reaction conditions the cis/trans ratios still accurately reflect differences in free energies of activation for cis and trans product formation.

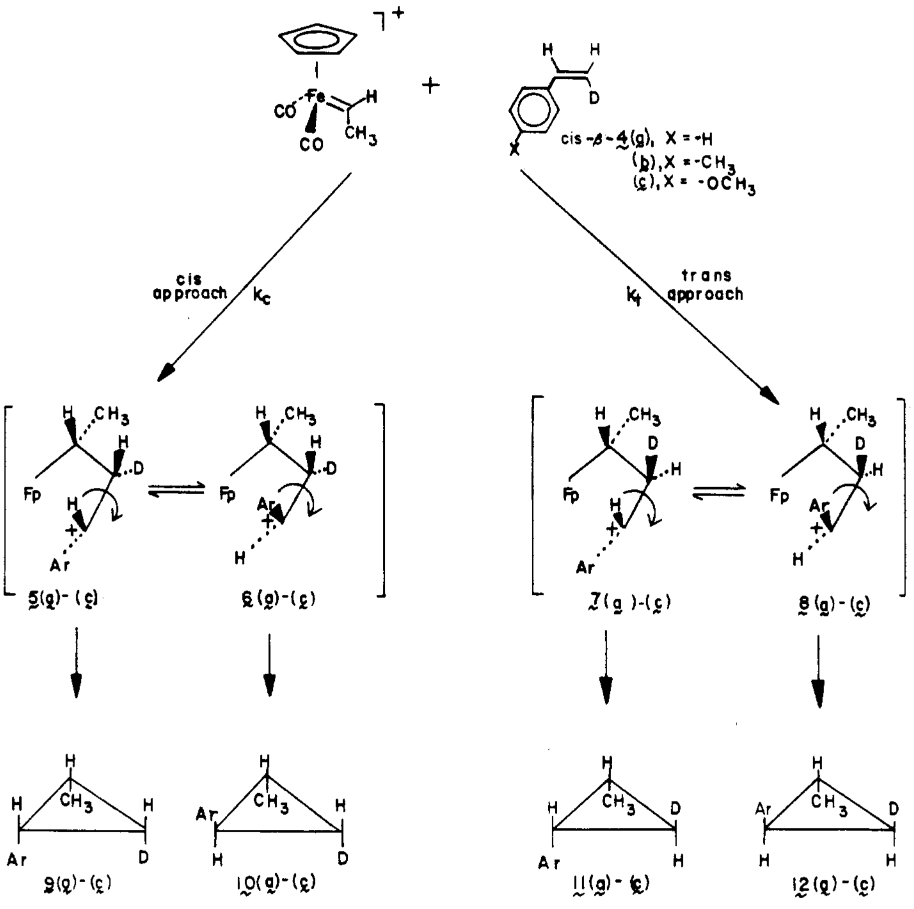
(11) The labeled styrenes **3a**–**3c** were prepared via diisobutylaluminum hydride reduction of the corresponding deuterated acetylenes.[12]

(12) (a) Eisch, J. J.; Kaska, W. C. *J. Am. Chem. Soc.* **1966**, *88*, 2213. (b) Berson, J. A.; Cortês, D.; Arney, J. S.; Wood, J. T. *Ibid.* **1978**, *100*, 3855. (c) Casey, C. P.; Scheck, D. M.; Shusterman, A. J. *Ibid.* **1979**, *101*, 4233.

(13) See supplementary material.

(14) Although we have no proof for their intervention, it is possible that metallacyclic intermediates are formed during these reactions. Several possibilities exist. For example, cis and trans metallacycles may be formed which can open and equilibrate via benzylic carbonium ions or lead, via reductive elimination, to cyclopropane products. With this scheme, equilibration of metallacycles would be favored for the carbonium ion stabilized *p*-anisyl system. However for **2b**–**2f**, reductive elimination is required to be more rapid than metallacyclic equilibration.

Scheme II



X				
(a)H	87%	None obsvd (<2%)	None obsvd (<2%)	13%
(b)CH_3	85%	None obsvd (<2%)	None obsvd (<2%)	15%
(c)OCH_3	41%	40%	6%	13%

For styrenes **4a**–**4c** where C_α–C_β stereochemistry is retained, this cis/trans product ratio is determined by what can be termed the cis/trans approach ratio, k_c/k_t (see Scheme II). For the p-OCH_3 system, the observed cis/trans product ratio does not reflect the approach ratio since **5c** ⇌ **6c** and **8c** ⇌ **7c** equilibration occurs. However, if it is assumed that there is no interconversion of these sets with one another,[15] then the cis/trans approach ratio for the p-anisyl system can be calculated as (**9c** + **10c**)/(**11c** + **12c**) = 4.3, a value similar to the approach ratios for **2b**–**2f**. This fact implies a similarity in the transition-state structures for all of the reactions of **1** with substituted styrenes.

The results of this study show (1) the cis/trans approach ratios for the reaction of a series of substituted styrenes with **1** are relatively insensitive to a wide range of para substituents, and thus k_c/k_t appears to be determined largely by steric factors; (2) when alkenes bearing substituents capable of stabilizing a carbonium ion are employed, loss of stereochemistry about the alkene double bond can occur, presumably via a stabilized carbonium ion intermediate. This is the first case where loss of stereochemistry of the alkene has been demonstrated for such transfer reactions, and this suggests that assumption of stereochemical integrity of the alkene in cyclopropanation reactions using electrophilic transition-metal carbenes must be made with caution.

Acknowledgment. Acknowledgment is made to the U.S. Army Research Office and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Supplementary Material Available: Tables of ^1H and ^2H NMR data for the substituted cyclopropanes (2 pages). Ordering information is given on any current masthead page.

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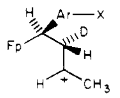
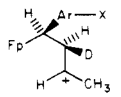
[15] It is important to note that interconversion between the intermediates from the cis manifold (**5** and **6**) and those from the trans manifold (**7** and **8**) does not occur via the unstable secondary carbonium ions **13a** and **13b**; i.e., the relative stereochemistry of methyl and D is fixed.



13a



13b

Additionally, it is evident that the relative rates of bond rotation (**5c** ⇌ **6c** and **7c** ⇌ **8c**) and cyclopropane formation are competitive, as indicated by the nonequivalence of the product ratios (**9c**:**10c** ≠ **11c**:**12c**).