Manganese Carbonyl Compounds as Hydrosilation Catalysts for Organoiron Acyl Complexes

Paul K. Hanna, Brian T. Gregg, and Alan R. Cutler*

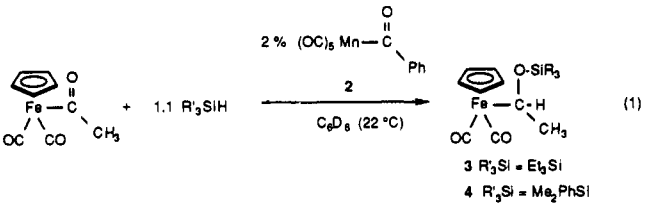
Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12180

Received August 14, 1990

Summary: Manganese acyl complexes $L(CO)_4MnCOR$ [L = CO, R = CH_3, Ph; L = PPh_3, PEt_3, R = CH_3] are effective catalysts (2–5%) for hydrosilating FpCOR compounds [R = CH_3, Ph; Fp = $Fe(CO)_2(\eta^5\text{-}C_5H_5)$] with monohydro-, dihydro-, and trihydrosilanes. Fp(α-siloxyalkyl) complexes $FpCH(CH_3)OSiR'_3$ (SiR'_3 = $SiEt_3$, $SiMe_2Ph$, $SiHPh_2$, $SiHEt_2$), $[FpCH(CH_3)O]_2SiR'_2$ (R' = Et, Ph), $FpCH(Ph)OSiHPh_2$, and $[FpCH(CH_3)O]_3SiPh$ are isolated [after column chromatography on silica gel or on polystyrene (size-exclusion) beads] and fully characterized. Substituted manganese acetyl compounds $L(CO)_4MnCOCH_3$ are extremely active catalysts that quantitatively transform $FpCOCH_3$ and dihydrosilanes R'_2SiH_2 (R' = Et, Ph) to Fp(α-siloxyalkyl) complexes $FpCH(CH_3)OSiHR'_2$. The manganese acetyl catalysts endure (within NMR spectral detection limits) until all of the organoiron acyl substrate is consumed; only then do they undergo rapid hydrosilation. Other manganese complexes, including $(CO)_5MnSiMe_3$, $Mn_2(CO)_{10}$, $(CO)_5MnCH_3$, and $(CO)_5MnCHPh(OSiHR'_2)$, also catalyze the hydrosilation of $FpCOCH_3$.

The rhodium(I)-catalyzed hydrosilation of organotransition-metal acyl complexes recently has been reported,[1] with Wilkinson's compound $(PPh_3)_3RhCl$ catalytically transforming $FpCOCH_3$ [Fp = $Fe(CO)_2(\eta^5\text{-}C_5H_5)$] into either α-siloxyethyl complexes $FpCH(CH_3)OSiHR'_2$ (with R'_2SiH_2, R' = Ph, Et) or $FpCH_2CH_3$ (with $PhSiH_3$).[2] The synthetic usefulness of this procedure for α-siloxyalkyl complexes is limited, however. Trialkylsilanes do not add to $FpCOCH_3$ when $(PPh_3)RhCl$ is used as the catalyst, and dehydrogenative coupling of dihydrosilanes[3] efficiently competes with the hydrosilation of less reactive acyl complexes (e.g., FpCOPh). Isolating analytically pure [(α-diphenylsiloxy)alkyl]Fp compounds (e.g., $FpCH(CH_3)OSiPh_2$ (**5a**) from $FpCOCH_3$) also proved impractical. We now report the synthetic details on using manganese acyl complexes $L(CO)_4MnCOR$ [R = CH_3; L = CO (**1a**), PPh_3 (**1b**), PEt_3 (**1c**); R = Ph, L = CO (**2**)][4] as catalysts for the productive hydrosilation of $FpCOCH_3$ and FpCOPh with monohydro-, dihydro-, and trihydrosilanes.[5]

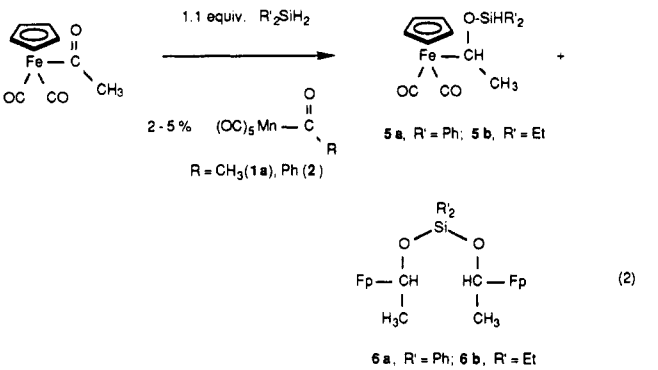
Treatment of $FpCOCH_3$ in benzene-d_6 with 1.1 equiv of either Et_3SiH or $PhMe_2SiH$ and $(CO)_5MnCOPh$ (**2**) (3%) as the catalyst quantitatively affords the α-siloxyethyl compounds **3** and **4** (eq 1), as ascertained by ^1H and



(1)

^{13}C NMR spectral monitoring. These stable products are isolated in >90% yield after chromatography on a short column of deactivated silica gel or by size-exclusion chromatography[6] (Table I).

Both manganese acetyl (**1a**) and benzoyl (**2**) complexes catalyze the hydrosilation of $FpCOCH_3$ with dihydrosilanes R'_2SiH_2 (R' = Et, Ph) (eq 2), although mixtures of



(2)

mono-Fp and bis-Fp α-siloxyethyl products (**5a**/**6a**, **5b**/**6b**) quantitatively form. Figure 1, a ^1H NMR spectrum of a typical Ph_2SiH_2 hydrosilation experiment, exemplifies the cleanliness of this reaction. Distinguishing absorptions for **5a** include a Cp singlet (δ 4.12) and methyl doublet (δ 1.81), whereas **6a** (two diastereomers) exhibits a pair of Cp sin-

(1) (a) Crawford, E. J.; Hanna, P. K.; Cutler, A. R. *J. Am. Chem. Soc.* **1989**, *111*, 6891. (b) Cutler, A. R.; Hanna, P. K.; Vites, J. C. *Chem. Rev.* **1988**, *88*, 1363. (c) Akita, M.; Mitani, O.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 527.

(2) Rh(I)-catalyzed hydrosilation of organic ketones in contrast provides only silyl ethers,[2a] with hydrosilane reactivity decreasing, $PhSiH_3 > R'_2SiH_2 > R'_3SiH$.[2b] (a) Reviews: Ojima, I.; Hirai, K. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1985; Vol. 5, p 103. Corriu, R. J. P.; Guerin, C.; Moreau, J. J. E. *Top. Stereochem.* **1984**, *15*, 45. Brunner, H. *Top. Stereochem.* **1988**, *18*, 129; *Synthesis* **1988**, 645. Chaloner, P. A. *Handbook of Coordination Catalysis in Organic Chemistry*; Butterworths: Boston, 1986; Chapter 7.2. Dickson, R. S. *Homogeneous Catalysis with Compounds of Rhodium and Iridium*; D. Reidel Publishing Co.: Boston, 1985; Chapter 3.11. (b) Ojima, I.; Nihonyanagi, M.; Kogure, M.; Kumagai, M.; Horiuchi, S.; Nakatsugawa, K. *J. Organomet. Chem.* **1975**, *94*, 449. Ojima, I.; Kogure, T.; Kumagai, M.; Horiuchi, S.; Sato, T. *Ibid.* **1976**, *122*, 83. Ojima, I.; Kogure, T. *Organometallics* **1982**, *1*, 1390. Hayashi, T.; Yamamoto, K.; Kumada, M. *J. Organomet. Chem.* **1976**, *113*, 127. Kolb, I.; Hetflejs, T. *Coll. Czech. Chem. Commun.* **1980**, *45*, 2224. Semmelhack, M. F.; Misra, R. N. *J. Org. Chem.* **1982**, *47*, 2469.

(3) Ojima, I.; Inaba, S.-I.; Kogure, T.; Nagai, Y. *J. Organomet. Chem.* **1973**, *55*, C7. Chang, L. S.; Corey, J. Y. *Organometallics* **1989**, *8*, 1855 and references therein.

(4) Treichel, P. M. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Eds.; Pergamon Press: New York, 1982; Vol. 4, Chapter 29.

(5) (a) Manganese carbonyl complexes apparently had not been used as catalyst precursors for the hydrosilation of ketones or alkenes, although $(CO)_5MnSiR_3/Mn_2(CO)_{10}$ systems catalyze alkene hydrosilation and alcohol O-silation. Faltynek, R. A. *J. Organomet. Chem.* **1983**, *258*, C5. Hilal, H. S.; Abu-Eid, M.; Al-Subu, M.; Khalaf, S. *J. Mol. Catal.* **1987**, *39*, 1. Hilal, H. S.; Khalaf, S.; Al-Nouri, M.; Karmi, M. *Ibid.* **1986**, *35*, 137. (b) In contrast, both $Co_2(CO)_8$ and $Co(CO)_4SiR_3$ complexes induce the catalytic hydrosilation of aldehydes and ketones. Kovacs, I.; Sisak, A.; Ungvary, F.; Marko, L. *Organometallics* **1988**, *7*, 1025. Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 837. Murai, S.; Seki, Y. *J. Mol. Catal.* **1987**, *41*, 197.

(6) Standard conditions: Manganese catalyst is added to a benzene-d_6 (600 mg) solution of $FpCOCH_3$ (200 mg) and silane (1.10–1.20 equiv), and within a glovebox, the solution is transferred to a NMR tube. Reaction times increase dramatically with dilution of the reaction mixtures. Chromatography either on Merck silica gel (60–200 mesh; 1 × 10 cm) or on Bio-Rad S-X 12 polystyrene beads (200–400 mesh, molecular weight exclusion 400) using benzene affords **3**–**8** as thermally stable, yellow-brown oils. Spectral data (IR and ^1H, ^{13}C NMR) and the results of acceptable elemental analyses for **3**, **4**, **5a**, **6a**, **6b**, **7**, **8** are deposited as supplementary material. Only **5b** previously had been characterized.[2a,c]

0276-7333/91/2310-0031$02.50/0

Table I. Hydrosilation of FpCOR Using $(CO)_5Mn$ Complexes as Precatalysts

	FpCOR (mmol/g benzene)		silane (mmol/mmol FpCOR)		Mn precatalyst (% Mn)		reaction time[a]	bis-Fp/mono-Fp[b]	product(s)	yield, %
1	$FpCOCH_3$	(1.52)	Et_3SiH	(1.10)	$(CO)_5MnCOPh$	(2.6)	2		$FpCHCH_3(OSiEt_3)$ (**3**)	90[c]
2		(1.49)		(1.23)	$(CO)_5MnCOCH_3$	(4.2)	11		**3**	95[d]
3		(1.52)	$PhMe_2SiH$	(1.10)	$(CO)_5MnCOPh$	(2.6)	1		$FpCHCH_3(OSiMe_2Ph)$ (**4**)	66[c]
4	FpCOPh	(1.42)	Ph_2SiH_2	(1.30)	$(CO)_5MnCOCH_3$	(20.2)	2		$FpCH(Ph)(OSiHPh_2)$ (**7**)	15[e,f]
5		(0.665)		(1.10)	$(CO)_5MnCOPh$	(2.8)	20		**7**	30[e]
6		(0.665)		(1.10)	$PPh_3(CO)_4MnCOCH_3$	(2.4)	0.5		**7**	92[d,g]
7	$FpCOCH_3$	(1.52)	Ph_2SiH_2	(1.20)	$(CO)_5MnCOCH_3$	(4.6)	4	0.77	$[FpCH(CH_3)O]_2SiPh_2$/ $FpCHCH_3(OSiHPh_2)$ (**6a/5a**)	quant[e]
8		(0.81)		(1.10)	$(CO)_5MnCOCD_3$	(20.2)	2.5	1.01	**6a/5a**	quant[h]
9		(1.14)		(1.10)	$PPh_3(CO)_4MnCOCH_3$	(0.47)	5		**5a**	87[c]
10		(1.14)		(1.17)	$PEt_3(CO)_4MnCOCH_3$	(4.5)	3		**5a**	quant[e]
11		(1.49)		(1.20)	$(CO)_5MnCOPh$	(3.3)	0.33	1.36	**6a/5a**	85[d,i]
12		(1.52)		(1.25)	$(CO)_5MnCH(Ph)OSiHPh_2$	(3.3)	6.0	0.92	**6a/5a**	97[d]
13		(1.52)		(1.19)	$(CO)_5MnCH_3$	(4.2)	0.50	0.23	**6a/5a**	91[d]
14		(1.52)		(1.20)	$(CO)_5MnSiMe_3$	(4.1)	144	0.22	**6a/5a**	94[d]
15		(1.52)		(1.25)	$(CO)_{10}Mn_2$	(3.9)	168	0.22		
16		(1.52)	Et_2SiH_2	(1.24)	$(CO)_5MnCOCH_3$	(3.8)	18	0.82	$FpCH(CH_3)O]_2SiEt_2$/ $FpCHCH_3(OSiHEt_2)$ (**6b/5b**)	91[d]
17		(1.52)		(1.24)	$(CO)_5MnCOPh$	(2.2)	22	0.90	**6b/5b**	94[c]
18		(1.52)	$PhSiH_3$	(1.12)	$(CO)_5MnCOCH_3$	(4.6)	8		$[FpCH(CH_3)O]_2SiHPh$ (**6c**) $FpCHCH_3(OSiH_2Ph)$ (**5c**)	92[e]
									$[FpCH(CH_3)O]_3SiPh$ **8**	68[c]
							12		$FpCH_2CH_3$	

[a] Time in hours required for consumption of FpCOR (^1H NMR spectral monitoring). [b] Ratio of $[FpCHCH_3O]_2SiR'_2$ to $FpCHCH_3(OSiHR'_2)$ estimated by integration of ^1H NMR spectra. [c] Isolated yield after column chromatography on silica gel. [d] Isolated yield after size-exclusion chromtography on Bio-Rad S-X 12. [e] Conversion of FpCOR to product estimated by ^1H NMR spectroscopy; monitoring of reaction establishes continuing product formation over this time interval. [f] <10% consumption of $(CO)_5MnCOCH_3$. [g] No reaction when conducted in the presence of 1 atm of CO. [h] Monitored by ^2H NMR spectroscopy (parallel runs); $(CO)_5MnCOCD_3$ remains intact until all of the $FpCOCH_3$ reacts. Similar results obtain by using 8.4% $(CO)_5MnCOCD_3$. [i] In the presence of 1 atm of CO; an otherwise identical reaction consumes only 85% $FpCOCH_3$ in 2.75 h; **6a/5a** = 1.36, and the half-life increases from 10 min to 1.8 h.

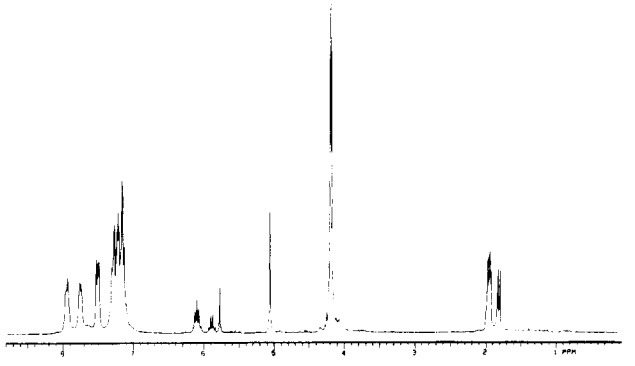


Figure 1. ^1H NMR spectrum (200 MHz) of the hydrosilation reaction: $FpCOCH_3$ (200 mg, 0.909 mmol), Ph_2SiH_2 (200 mg, 1.09 mmol), and $(CO)_5MnCOPh$ (**2**) (10 mg, 3.7%) in 600 mg C_6D_6 (30 min). Residual Ph_2SiH_2, δ 5.10.

glets (δ 4.14, 4.15) and methyl doublets (δ 1.97, 1.95).[7] The numerical yields recorded in Table I refer to material isolated after column chromatography; ratios of bis-Fp to mono-Fp adducts were obtained from integration traces of ^1H NMR spectra.[8] Subsequent size-exclusion chromatography provided analytically pure samples of **5a**, **6a**, **5b**, and **6b**.[6]

The manganese acyl catalyzed hydrosilation of $FpCOCH_3$ with dihydrosilanes is characterized by (1) the absence of competing dehydrogenation coupling of dihydrosilanes,[9] (2) the presence of 1 atm of CO inhibiting this reaction (entry 11), and (3) **1a** remaining the only detectable manganese species until at least 90% of the $FpCOCH_3$ reacts. Only then does hydrosilation of **1a** rapidly occur.[9] The results of ^1H and ^2H NMR spectral monitoring of parallel hydrosilation reactions using 8–20% **1a** and $(CO)_5MnCOCD_3$ establish that other manganese intermediates do not build up in detectable concentrations during the hydrosilation of $FpCOCH_3$.[10]

Phosphine-substituted manganese acetyl complexes **1b** and **1c**[11] prove to be especially selective hydrosilation catalysts that transform $FpCOCH_3$ and Ph_2SiH_2 into just the mono-Fp adduct **5a**. Triphenylphoshine-containing

(7) Other diagnostic spectral data: **5a** ^{13}C NMR (C_6D_6) δ 217.73, 217.30 (CO), 86.19, (Cp), 71.34 (FeCH), 35.33 ($FeCHCH_3$); ^1H NMR (C_6D_6) δ 5.87 (q, J = 6.0 Hz, FeCH), 5.77 (s, SiH). **6a** ^{13}C NMR (C_6D_6) δ 217.89, 217.69, 217.55 (CO), 86.20 (Cp), 69.87, 69.75 (FeCH), 36.26, 36.11 ($FeCHCH_3$); ^1H NMR (C_6D_6) δ 6.11, 6.08 (d, J = 6.0 Hz, FeCH).

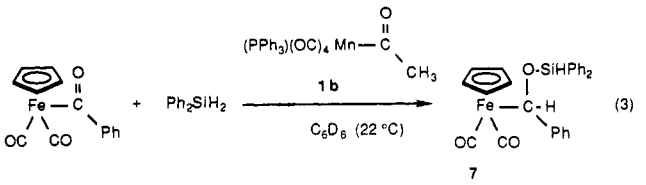
(8) This ratio slowly and continually increases with time, even after the $FpCOCH_3$ is consumed. The bis-Fp/mono-Fp values recorded in Table I correspond to the time when $FpCOCH_3$ is depleted. These reactions occur at the same rates when they are run in the dark.

(9) Treatment of $(CO)_5MnCOCH_3$ (**1a**) or $(CO)_5MnCOPh$ (**2**) in benzene-d_6 with between 1 and 3 equiv of R'_2SiH_2 immediately and quantitatively affords mixtures of $(CO)_5MnCH(OSiHR'_2)CH_3$/ $[(CO)_5MnCH(CH_3)O]_2SiR'_2$ or $(CO)_5MnCH(OSiHR'_2)Ph$. Me_2PhSiH and **1a** afford the fully characterized $(CO)_5MnCH(OSiMe_2Ph)CH_3$. Hanna, P. K.; Gregg, B. T.; Crawford, E. J.; Cutler, A. R. *J. Am. Chem. Soc.*, in press. These solutions do not further transform excess Ph_2SiH_2 over 72 h.

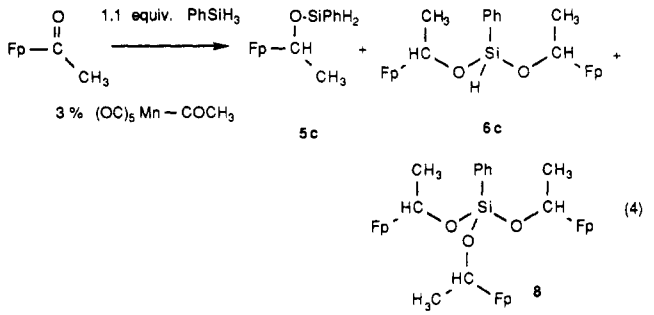
(10) The Fp(acyl) substrate thus blocks hydrosilation of the manganese acyl catalyst; an extreme example appears in Table I, entry 4. $(CO)_5MnCOCH_3$ (**1a**) does not readily promote hydrosilation of FpCOPh, which in turn prevents the otherwise rapid hydrosilation of **1a**.[9]

(11) $(PEt_3)(CO)_4MnCOCH_3$ (**1c**) exists as its trans isomer, whereas **1b** offers an equilibrating cis–trans mixture (1:4.5). We also typically find 5–10% trans $(PPh_3)(CO)_4MnCH_3$ as an unavoidable impurity. Kraihanzel, C. S.; Maples, P. K. *Inorg. Chem.* **1968**, *7*, 1806.

1b also is the most active manganese precatalyst thus far. It expedites the hydrosilation of $FpCOCH_3$ at less than 1% catalyst concentration and of FpCOPh (eq 3) under conditions that other manganese catalysts either are inert (**1a**) or react sluggishly (**2**).



Phenylsilane in the presence of **1a** also hydrosilates $FpCOCH_3$, but the final products are Fp(ethyl) and tris-Fp **8**. Treatment of a 1:1 mixture of $FpCOCH_3$ and $PhSiH_3$ with **1a** as the catalyst (4.6%, entry 18) in C_6D_6 quantitatively produces mixtures of mono-Fp **5c**, bis-Fp **6c**, and tris-Fp **8** α-siloxyethyl compounds within 8 h (eq 4); over



an additional 4–6 h, **5c** and **6c** transform to Fp(ethyl). We assign structures **5c** and **6c** based on the close resemblance of their ^1H and ^{13}C NMR spectral data to that of the (diphenylsiloxy)ethyl compounds **5a** and **6a**. The fully characterized tris-Fp **8** and Fp(ethyl) are isolated by size exclusion chromatography, 26% and 53%, respectively.

Although manganese acyls **1a–c** and **2** are excellent catalysts, the presence of an acyl ligand is not a prerequisite for hydrosilation activity. Both $(CO)_5MnSiMe_3$ and $Mn_2(CO)_{10}$ function as relatively sluggish catalysts toward adding Ph_2SiH_2 (Table I) or Et_2SiH_2 to $FpCOCH_3$. The methyl complex $(CO)_5MnCH_3$, however, qualifies as a more reactive hydrosilation catalyst than **1a**, but it affords a lower **6a**/**5a** ratio of 0.23 that is comparable with those obtained from $(CO)_5MnSiMe_3$ and $Mn_2(CO)_{10}$. The siloxybenzyl compound $(CO)_5MnCHPh(OSiHPh_2)$,[9] which results from mixing **2** with Ph_2SiH_2 (3 min) before adding $FpCOCH_3$, is much less reactive than **2**, and yet it gives an equally high **6a**/**5a** ratio of 0.92.

Manganese alkyl and acyl complexes $L(CO)_4MnCOR$ are far more efficient catalysts than is $(PPh_3)_3RhCl$ for hydrosilating Fp(acetyl) and Fp(benzoyl). Studies in progress are extending their scope and investigating the mechanism[12] of these manganese-catalyzed hydrosilation reactions.

Acknowledgment. Support from the Department of Energy, Office of Basic Energy Science, is gratefully acknowledged.

Supplementary Material Available: Table 2, listing ^1H and ^{13}C NMR and IR spectral assignments for **3–7** and microanalytical data (3 pages). Ordering information is given on any current masthead page.

(12) We disfavor a pathway in which the manganese catalyst $Mn(CO)_5(COR)$ loses two terminal carbonyls in order to simultaneously bind silane and $FpCOCH_3$ as $(CO)_3(RCO)Mn(H)(SiR'_3)[O{=}C(CH_3)Fp]$. A plausible working hypothesis is a free-radical mechanism in which a 17-electron species $(CO)_4(RCO)Mn(SiR'_3)$, resulting from hydrogen atom abstraction from the silane oxidative-addition product $(CO)_4(RCO)Mn(H)(SiR'_3)$, associates $FpCOCH_3$. The resulting 19-electron adduct, perhaps having its odd electron partially delocalized on the ligated $FpCOCH_3$, could rearrange to a 17-electron manganese system $(CO)_4(RCO)MnCH(OSiR'_3)Fp$ that shares a μ-siloxyalkylidene ligand with a Fp moiety. Subsequent hydrogen atom transfer to the manganese center and reductive elimination of $FpCH(OSiR'_3)R$ product would regenerate the active catalyst, $(CO)_4MnCOR$.

Acid-Catalyzed Isomerization and Deuterium Exchange of Rhenium Alkene Complexes via In-Place Rotation of an Agostic Alkylrhenium Cation

Charles P. Casey* and Chae S. Yi

Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin 53706

Received August 2, 1990

Summary: $C_5H_5(CO)_2Re(cis\text{-}CH_3CH{=}CHCH_3)$ (**1**) isomerized to a 45:55 equilibrium mixture of **1** and $C_5H_5(CO)_2Re(trans\text{-}CH_3CH{=}CHCH_3)$ (**2**) upon treatment with CF_3CO_2H in CH_2Cl_2. In the isomerization of **1** by CF_3CO_2D, the initially formed **2** was monodeuterated at the vinyl position. Treatment of $C_5H_5(CO)_2Re(CH_2{=}CHCH_2CH_3)$ (**3**) with CF_3CO_2D led only to deuterium exchange of the vinyl hydrogens; no formation of **1** or **2** was observed. These data are consistent with a mechanism involving agostic rhenium alkyl complexes that undergo "in-place rotation" and deprotonation much more rapidly than formation of a free alkylrhenium intermediate.

We have recently devised several new syntheses of $C_5H_5(CO)_2Re$(alkene) complexes from reactions of alkynes with the heterobimetallic dihydride $C_5H_5(CO)_2(H)RePt(H)(PPh_3)_2$,[1] from rearrangement of rhenium carbene complexes,[2] and from reaction of $C_5H_5(CO)_2ReH^-$ with allyl halides[3] that complement previous syntheses from $C_5H_5(CO)_2Re(THF)$ and alkenes.[4] We have begun to explore the reactivity of these rhenium alkene complexes and have found that reaction with $(C_6H_5)_3C^+$ leads to hydride abstraction and formation of (π-allyl)rhenium cations.[5]

(1) Casey, C. P.; Rutter, E. W., Jr. *J. Am. Chem. Soc.* **1989**, *111*, 8917.
(2) Casey, C. P.; Vosejpka, P. C.; Askham, F. R. *J. Am. Chem. Soc.* **1990**, *112*, 3713.
(3) Casey, C. P.; Yi, C. S. Unpublished results.
(4) (a) Sellmann, D.; Kleinschmidt, E. *Z. Naturforsch., B* **1977**, *32B*, 795. (b) Einstein, F. W. B.; Jones, R. H.; Klahn-Oliva, A. H.; Sutton, D. *Organometallics* **1986**, *5*, 2476. (c) Caulton, K. G. *Coord. Chem. Rev.* **1981**, *38*, 1.

0276-7333/91/2310-0033$02.50/0