formed directly from **4** and **2** whereas the PMe_3 analogue to **5** was prepared by Stone et al. in a two-step process by reacting **4** with a source of $Pt(PMe_3)_2$[0] followed by protonation of the isolated μ-alkylidyne cluster with $HBF_4 \cdot Et_2O$.[8]

The results of eq 1 and 2 indicate that **2** (and possibly related complexes) might be *generally* useful reagents for preparing clusters from compounds containing unsaturated bonds at appropriate locations by either *formal* insertion or proton transfer reactions. These reactions complement the recent extensive cluster chemistry of Stone[10] with the important difference that in this method *the "addition" of the Pt–H bond to the reactant complex changes the identity of the eventual bridging ligand.* A study of the reactions of **2** (and related species) with other alkylidyne complexes and other compounds containing unsaturated bonds is being pursued.

Acknowledgment. C.M.L. thanks the National Science Foundation (Grant No. CHE-8106140), the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the University Research Council of Vanderbilt University for support of this research.

Registry No. **2**, 84623-75-6; **4**, 60260-15-3; **5**, 92145-08-9; Pt, 7440-06-4; W, 7440-33-7.

(10) (a) Stone, F. G. A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 89–99. (b) Stone, F. G. A. In "Organometallic Compounds"; Shapiro, B. L., Ed.; Texas A&M University Press: College Station, TX, 1983; pp 1–28. (c) Stone, F. G. A. In "Inorganic Chemistry: Toward the 21st Century"; Chisholm, M. H., Ed.; American Chemical Society: Washington, D.C., 1983; *Acs Symp. Ser. No. 211*, pp 383–397.

Stereoselective Additions to the Alkoxycarbene Cations $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(=CROMe)]^+$ (R = H, Et)

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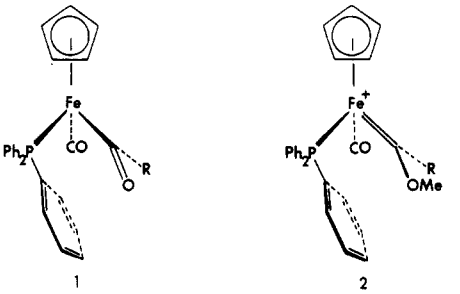
Summary: Nucleophilic addition reactions to the cations $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(=CROMe)]^+$ (R = H, Et) are highly stereoselective. The product diastereoisomers $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(CHEtOMe)]$ undergo epimerization in methanol prior to formation of (*E*)-$[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(CH=CHMe)]$.

We have recently presented a series of guidelines concerning the reactivity of ligands bound to the $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)$ moiety.[1] In particular, it was predicted, by analogy with the acyl complexes **1**, that the alkoxycarbene cations **2** should exist in the anti (O–O) conformation and that high stereoselectivities should be seen in their reactions with nucleophiles.

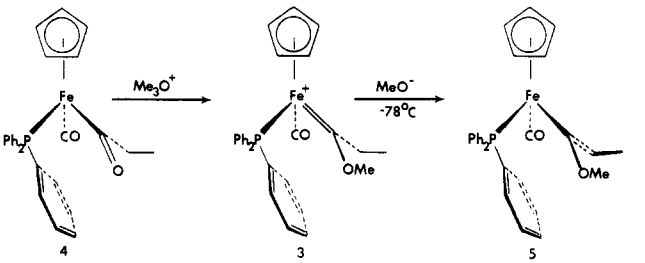
Several reports of the hydride reductions of cations **2** have appeared with little stereoselectivity apparently being observed.[2,3] More surprising was the reported observation that borohydride in the presence of methoxide smoothly



1 2

reduced **3** without deprotonation to the corresponding methoxyvinyl complexes[3] especially since we have recently found that this deprotonation is extremely facile.[4] We report here a reexamination of the reduction of complex **3** together with a more extensive description of its reactivity and reduction products.

Treatment of the acyl complex **4** with trimethyloxonium tetrafluoroborate generated cation **3**.[5] An X-ray crystallographic analysis of **3**[6] showed that as expected[1] the oxygens were anti and one face of the alkoxycarbene ligand was shielded by the proximate phenyl group of the triphenylphosphine ligand. Treatment of **3** with sodium methoxide quantitatively generated the methoxyvinyl complex **5** (*E*:*Z* = 1:100).



4 3 5

In our hands reduction of cation **3** with a variety of hydride reagents (e.g., $LiAlH_4$, $NaBH_4$) in tetrahydrofuran is very stereoselective with the two diastereoisomers **6** and **7** being produced in the ratio 15:1 ($NaBH_4$, −100 °C). The ratio of **6**:**7** dropped to 12:1 when this reduction was performed at −78 °C. The major diastereoisomer is assigned as **6** on the assumption that hydride adds to the unhindered face of the carbene **3** in the anti (O–O) conformation.[1] Diastereoisomer **6** could be isolated pure by crystallization.[7] With use of the literature procedure[3] of adding a dichloromethane solution of **3** to $NaBH_4$/NaOMe in methanol, a mixture of the reduced products **6** and **7** together with the deprotonated product **5** was obtained in the ratio 8.5:1:4.5, respectively (lit.[3] **6**:**7** = 3:1). Hindered

(1) Davies, S. G.; Seeman, J. I. *Tetrahedron Lett.* **1984**, 1845.
(2) Bodnar, T.; Cutler, A. R. *J. Organomet. Chem.* **1981**, *213*, C31.
(3) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258.
(4) Baird, G. J.; Davies, S. G.; Jones, R. H.; Prout, K.; Warner, P. *J. Chem. Soc., Chem. Commun.* **1984**, 745.
(5) Reaction carried out by using the procedure of: Green, M. L. H.; Mitchard, L. C.; Swanick, M. G. *J. Chem. Soc. A* **1971**, 794.
(6) Jones, R. H.; Prout, K., unpublished results.
(7) 300-MHz ^1H NMR (C_6D_6): **5**, δ 7.7–6.95 (15 H, m, aryl H), 5.30 (1 H, dq, J_{PH} = 5.2 Hz, J_{HH} = 6.3 Hz, vinylic H), 4.36 (5 H, d, J_{PH} = 0.9 Hz, C_5H_5), 2.94 (3 H, s, OCH_3), 2.24 (3 H, d, J_{HH} = 6.4 Hz, CH_3); **6**, 7.6–7.0 (15 H, m, aryl H), 4.40 (5 H, d, J_{PH} = 1.0 Hz, C_5H_5), 4.02 (1 H, ddd, *J* = 10, 3, 1 Hz, FeCH), 3.46 (3 H, s, OCH_3), 2.3 and 2.0 (2 H, m, m, CH_2), 0.91 (3 H, t, *J* = 7.5 Hz, CH_3); **7**, 7.7–7.0 (15 H, m, aryl H), 4.39 (5 H, d, J_{PH} = 1.0 Hz, C_5H_5), 3.90 (1 H, ddd, *J* = 4.6, 8.2, 10 Hz, FeCH), 2.92 (3 H, s, OCH_3), 2.35 and 1.92 (2 H, m, m, CH_2), 1.20 (3 H, t, *J* = 7.5 Hz, CH_3); **11**, 7.6–7.0 (15 H, m, aryl H), 6.90 (1 H, ddq, *J* = 6.7, 15.2, 1.4 Hz), 5.74 (1 H, ddq, *J* = 2.5, 15.2, 5.9 Hz), 4.19 (5 H, d, *J* = 1.0 Hz, C_5H_5), 2.02 (3 H, ddd, *J* = 5.9, 1.4, 1.4 Hz, CH_3). 62.90-MHz ^{13}C NMR (C_6D_6): **5**, δ 222.7 (d, J_{PC} = 33.5 Hz, CO), 177.5 (d, J_{PC} = 24 Hz, Fe–C), 103.57 (=CH), 84.63 (C_5H_5), 55.05 (OCH_3), 17.13 (CH_3); **6**, 223.9 (d, J_{PC} = 33.4 Hz, CO), 89.7 (d, J_{PC} = 16.6 Hz, Fe–C), 85.6 (C_5H_5), 58.90 (OCH_3), 41.05 (CH_2), 15.64 (CH_3); **7**, 222.7 (d, J_{PC} = 33 Hz, CO), 89.82 (d, J_{PC} = 19 Hz, Fe–C), 85.77 (C_5H_5), 59.34 (OCH_3), 36.47 (CH_2), 14.56 (CH_3); **11**, 222.6 (d, J_{PC} = 31.3 Hz, CO), 138.3 (d, J_{PC} = 29.9 Hz, Fe–C), 137.8 (=C), 84.8 (C_5H_5), 25.4 (CH_3). Anal. Calcd for $C_{28}H_{29}FeO_2P$ (**6**): C, 69.43; H, 6.04; P, 6.39. Found: C, 69.41; H, 6.06; P, 6.64.

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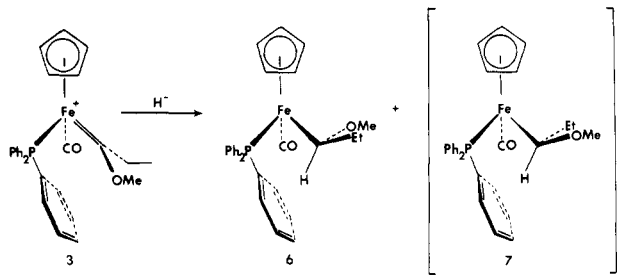
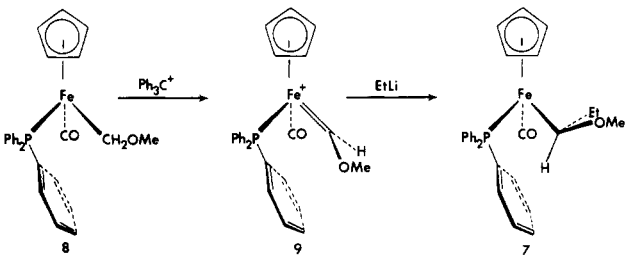
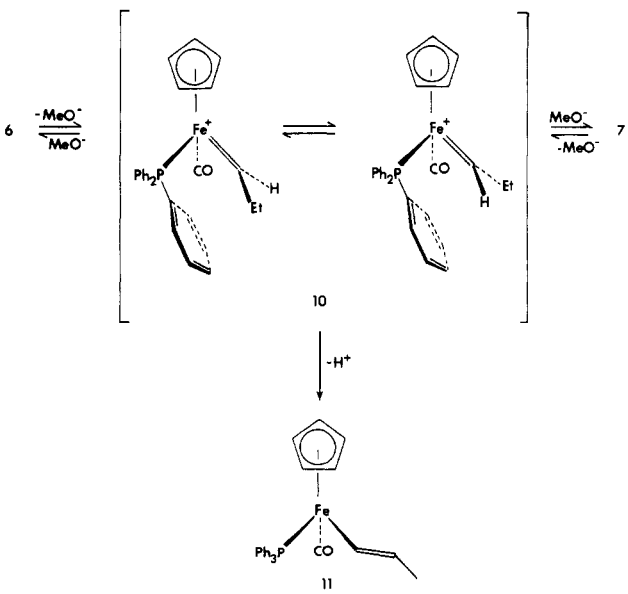
reducing agents such as K[*s*-Bu_3BH] gave only the deprotonated product **5**.[7]



Hydride abstraction from the methoxymethyl complex **8** with the trityl cation generated the carbene cation **9**.[8] Treatment of **9** with ethyllithium in dichloromethane at −78 °C again generated the diastereoisomers **6** and **7**. This time, as expected, **7** was by far the major product (**7**:**6** > 30:1) consistent with attack onto the unhindered face of **9** in the anti (O–O) conformation. Recrystallization gave pure **7**.[7]



Methanol–dichloromethane (1:2) solutions of **6** or **7** at 20 °C undergo epimerization, presumably via reversible loss of methoxide to give the carbene cation **10**. In the presence of methanol-d_4 incorporation of CD_3O into **6** and **7** was observed (CD_2Cl_2/CD_3OD, 2:1; 20 °C; 90% incorporation after 24 h). In methanol solution **6** and **7** slowly undergo methanol loss to generate the stable (*E*)-vinyl complex **11**.



Acknowledgment. We thank the SERC for studentships (G.J.B. and T.R.M.).

Registry No. **3**, 92219-90-4; **4**, 32611-01-1; (*Z*)-**5**, 91594-50-2; **6**, 83802-10-2; **7**, 83860-17-7; **9**, 69621-15-4; **11**, 92219-91-5.

(8) Cutler, A. R. *J. Am. Chem. Soc.* **1979**, *101*, 604.

Unprecedented Alkyl Migration in an Iron(II) Alkylidene[1]

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Summary: Protonation of $(\eta^5\text{-}C_5H_5)(CO)_2FeCR(1\text{-norbornyl})OC_2H_5$ (R = H or D) with HBF_4 provides $[(\eta^5\text{-}C_5H_5)(CO)_2Fe(exo\text{-}\eta^2\text{-}1\text{-R-bicyclo}[3.2.1]oct\text{-}2\text{-ene})]^+BF_4^-$ (R = H or D) in nearly quantitative yield. No $[(\eta^5\text{-}C_5H_5)(CO)_2Fe(\eta^2\text{-bicyclo}[2.2.2]oct\text{-}2\text{-ene})]^+BF_4^-$ is formed. This regioselective reaction is thought first to form an $[(\eta^5\text{-}C_5H_5)(CO)_2Fe(1\text{-norbornylmethylidene})]^+$, which undergoes an unprecedented ring enlargement to a $[(\eta^5\text{-}C_5H_5)(CO)_2Fe(\eta^2\text{-bicyclooct-1-ene})]^+$ and then rearranges to the final product.

In an effort to form and trap an unstable[2] bridgehead olefin as a π-complex, we have generated and examined the reaction of [Fp(1-norbornylmethylidene)]$^+$ [A, Fp = $(\eta^5\text{-}C_5H_5)(CO)_2Fe$] in acid solution.

Alkylation[3] of the Fp–acyl, **1**,[4] with $Et_3O^+BF_4^-$ in CH_2Cl_2 at 25 °C gives the yellow ethoxycarbene salt **2**[5] in >90% yield. Reduction of **2** in CH_2Cl_2 at −78 °C with a 1 M solution of $LiEt_3BH$ in THF[6] produces the ethoxyalkyl complex **3**[7] as a yellow oil in 65% yield. Protonation of **3** in CH_2Cl_2 at 25 °C with a slight excess of HBF_4 in $Ac_2O/HOAc/CH_2Cl_2$,[8] concentration, and dilution with Et_2O gives an essentially quantitative yield of a yellow, crystalline Fp(η^2-bicyclooctene)$^+BF_4^-$ identical with that[9]

(1) Presented before the 188th National Meeting of the American Chemical Society, Philadelphia, PA, Aug 1984; American Chemical Society: Washington, DC, 1984; Abstract INOR 79.

(2) Maier, W. F.; Schleyer, P. von R. *J. Am. Chem. Soc.* **1981**, *103*, 1891–1900.

(3) Dry, oxygen-free solvents and Schlenk techniques were employed throughout.

(4) **1**: IR (CH_2Cl_2) 2005, 1955, 1640 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.80 (s, 5 H, Cp), 2.21 (b s, 1 H, >CH), 1.49 (m, 10 H, 5 >CH_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 261.6 (>C=O), 215.0 (–C≡O), 86.1 (Cp), 75.3 (C_1), 41.9 (C_4), 35.8 (C_7), 32.3 (C_2, C_6), 29.6 (C_3, C_5); mp 97–99 °C. Anal. Calcd for $C_{15}H_{16}FeO_3$: C, 60.03; H, 5.37. Found: C, 59.91; H, 5.41. We thank John Lever for the original preparation of this compound.

(5) **2**: IR (CH_2Cl_2) 2057, 2010 cm^{-1}; ^{1}H NMR (CD_2Cl_2, −10 °C) δ 5.42 (s, 5 H, Cp), 5.30 (q, J = 7.5 Hz, 2 H, OCH_2CH_3), 2.40 (b s, 1 H, >CH), 1.90–1.32 (b m, 13 H, CH_3 + 5 >CH_2); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −10 °C) δ 342.9 (C_8), 209.4 (–C≡O), 88.2 (Cp), 83.9 (C_9), 78.7 (C_1), 44.7 (C_4), 37.3 (C_7), 35.4 (C_2, C_6), 30.0 (C_3, C_5), 14.7 (C_{10}).

(6) Bodnar, T.; Cutler, A. *J. Organomet. Chem.* **1981**, *213* C31–C36.

(7) **3**: (a) IR (CH_2Cl_2) 1995, 1937 cm^{-1}; ^{1}H NMR ($CDCl_3$, −10 °C) δ 5.10 (s, 1 H, FpC*H*(OR)C<), 4.80 (s, 5 H, Cp), 3.57 (d of q, $J_{ac} \approx 6.6$ Hz, $J_{ab} \approx 2$ Hz, 1 H, >C*OC*H*^{a}H^{b}CH$_3^c$), 3.26 (d of q, $J_{bc} \approx 6.6$ Hz, $J_{ba} \approx 2$ Hz, 1 H, >C*OCH^a*H*^{b}CH$_3^c$), 2.11 (b s, 1 H, >CH), ~1.9–0.9 (b m, ~10 H, 5 >CH_2) superimposed upon a triplet at 1.07, $J_{cb} \approx J_{ca} = 6.6$ Hz, ~3 H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, −20 °C)[7b] δ 218.9, 216.8 (–C≡O), 85.9 (Cp), 85.3 (C_8), 65.8 (C_9), 61.6 (C_1), 45.1 (C_7), 36.6, 35.1 (C_2, C_6), 32.2 (C_4), 31.1, 30.4(C_3, C_5), 15.4 (C_{10}); MS m/e 330 [M]$^+$·, 302 [M − CO]$^+$·, 274 [M − 2CO]$^+$·, 153 [M − Fp]$^+$·. (b) These ^{13}C assignments were made by using the refocused "insensitive nucleus enhancement through polarization transfer" (INEPT) technique [Morris, G. A.; Freeman, R. *J. Am. Chem. Soc.* **1979**, *101*, 760–762].

(8) (a) Jolly, P. W.; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 5044–5045. (b) Green, M. L. H.; Ishaq, M.; Whiteley, R. N. *J. Chem. Soc. A* **1967**, 1508–1515.

(9) **4**: IR (CH_2Cl_2) 2079, 2038 cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 5.50 [b s, ~5 H, Cp superimposed on an ~1 H multiplet at ~5.4–5.5 due to Fp$^+$(η^2-=C(3)*H*CH$_2$–)], 5.30 [s, 1 H, Fp$^+$(η^2-C(2)*H*=)], 2.73 (m, 1 H, >C(1)*H*), 2.48 (perturbed d, 1 H, =CHC(4)*H*(endo)HCH<), 2.05–2.25 (m, 3 H, >C(5)*H* superimposed upon –C(6)H*H*(exo)C(7)H*H*(exo)–), ~1.86 (m, 2 H, –C(6)*H*(endo)HC(7)(endo)H–), 1.45 (m, 1 H, =CHC(4)H*H*(exo)CH<), 1.39 (br, perturbed doublet, $J \approx$ ' 16 Hz, 1 H, >C(8)*H*(anti)H), 0.58 (d, J = 16 Hz, 1 H, >C(8)H*H*(syn); $^{13}C\{^1H\}$ N 1 R (CD_2Cl_2, −10 °C)[7b] δ 211.1, 210.8 (–C≡O), 89.1 (Cp), 86.6 (C_2), 76.4 (C_3), 38.8 (C_1), 35.1 (C_8), 33.4 (C_4), 32.5 (C_5), 32.3, 30.5 (C_6, C_7); mp 92.5–93.5 °C dec. Anal. Calcd. for $C_{15}H_{17}O_2FeBF_4$: C, 48.44; H, 4.61. Found: 48.09, H, 4.66.

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