[(η^5-5-*exo*-Phosphoniumylcyclohexa-1,3-diene)Fe(CO)$_3$]X Salts in Enantioselective Synthesis: Wittig Reactivity and Elimination Reactions

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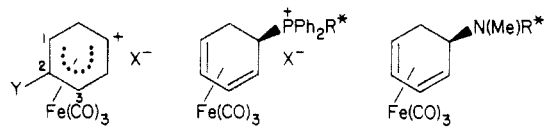
Enantiomerically pure [(2-methoxycyclohexadienyl)Fe(CO)$_3$]PF$_6$ may be converted with retention of configuration to [(2-methoxy-5-alkylcyclohexadienyl)Fe(CO)$_3$]PF$_6$ (alkyl = Me, CH$_2$Ph) by conversion to [(2-methoxy-5-*exo*-phosphoniumylcyclohexadiene)Fe(CO)$_3$]PF$_6$ (phosphoniumyl = PPh$_{3-x}$Me$_x$; x = 0–2) followed by Wittig reaction with RCHO (R = H, Ph) and protonation. The intermediate ylide may be protonated to give [(2-methoxy-5-*endo*-(triphenylphoniumyl)cyclohexadiene)Fe(CO)$_3$]PF$_6$ with inversion of configuration at C-5. Reaction of [(2-methoxy-5-*exo*-(menthyldiphenylphosphoniumyl)cyclohexadiene)Fe(CO)$_3$]BF$_4$ with LiAlD$_4$ also results in inversion at C-5 with elimination of phosphine to give primarily (2-methoxy-5-*endo*-deuteriocyclohexadiene)Fe(CO)$_3$. A small amount of (1-methoxy-6-*endo*-deuteriocyclohexadiene)Fe(CO)$_3$ resulting from a concerted elimination is also isolated. By a similar method, enantiomerically pure (5-*endo*-deuteriocyclohexadiene)Fe(CO)$_3$ may be prepared in which chirality is a consequence only of the isotopic substitution at C-5.

Introduction

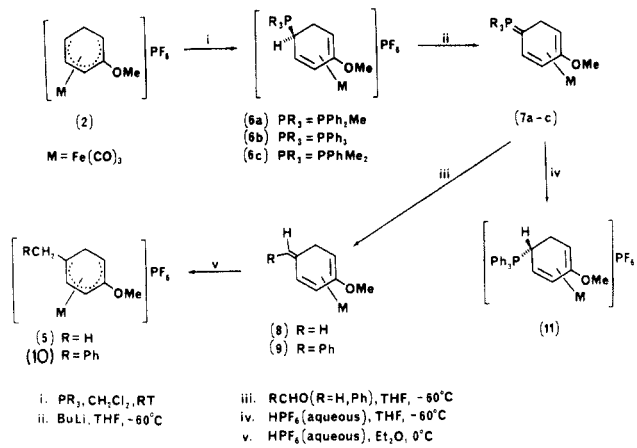
In terms of application to stoichiometric organic synthesis, the utility of the [(η^5-cyclohexadienyl)Fe(CO)$_3$]$^+$ cation (1) and its ring substituted derivatives has been amply demonstrated by the work of Birch[1] and Pearson[2]. It has also been recognized that the potential for enantioselective synthesis exists, since 1- or 2-substituted derivatives of 1 exist as enantiomeric pairs due to the lateral coordination of the metal moiety. Most importantly, nucleophilic attack on enantiomerically pure 1- or 2-substituted cations provides access to a fully resolved asymmetric carbon at the point of nucleophilic attack, due to the stereospecific exo addition of the nucleophile.



1, Y=H
2, Y=OMe
3
4

While the 1-COOH derivative of 1 has been resolved by classical procedures[3], only two generally applicable methods have been reported to date, involving either (a) asymmetric complexation of a prochiral diene with chiral transfer reagents based on (η^4-enone)Fe(CO)$_3$ complexes[4] or (b) a kinetic and/or thermodynamic discrimination in reactions of substituted derivatives of 1 with a deficiency of chiral nucleophile[5]. To date, the levels of enantiomeric enrichment obtained do not form the basis for satisfactory enantioselective syntheses.

Scheme I



We (and others)[6] have recently reported syntheses of pure *R* and *S* forms of the [(2-methoxycyclohexadienyl)-Fe(CO)$_3$]$^+$ cation (2) via chromatographic separation of diastereoisomeric menthyl ethers, together with syntheses of diastereoisomerically pure 3 and 4 which are resolved in terms of the trisubstituted carbon formed on nucleophilic attack of the chiral amine or phosphine. In this article, we describe further transformations of these readily available materials, most notably the conversion of 2 into [(2-methoxy-5-alkylcyclohexadienyl)Fe(CO)$_3$]$^+$ cations with *retention* of configuration, and the nucleophilic substitution of the resolving residue of 3 which proceeds with *inversion* of configuration. Part of this work has been presented as a communication.[7]

Results and Discussion

(a) Preparation of Enantiomerically Pure [(2-Methoxy-5-alkylcyclohexadienyl)Fe(CO)$_3$]PF$_6$ Salts. The [(2-methoxy-5-methylcyclohexadienyl)Fe(CO)$_3$]$^+$ cation (5) is a useful precursor for some advanced intermediates in natural product chemistry[2], undergoing specific nucleophilic addition at the methylated terminus of

(1) Birch, A. J.; Bandara, B. M. R.; Chamberlain, K.; Dahler, P.; Day, A. I.; Jenkins, I. D.; Keely, L. F.; Khor, T. C.; Kretschmer, G.; Liepa, A. J.; Narula, A. S.; Raverty, W. D; Rizzardo, E.; Sell, C.; Stephenson, G. R.; Thompson, B. J.; Williamson, D. H. *Tetrahedron* **1981**, *37* (*Suppl. 1*), 289.
(2) Pearson, A. J. "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 8, Chapter 58.
(3) Birch, A. J.; Bandara, B. M. R. *Tetrahedron Lett.* **1980**, 2981.
(4) Birch, A. J.; Stephenson, G. R. *Tetrahedron Lett.* **1981**, 779. Birch, A. J.; Raverty, W. D.; Stephenson, G. R. *Tetrahedron Lett.* **1980**, 197. Birch, A. J.; Raverty, W. D.; Stephenson, G. R. *J. Org. Chem.* **1981**, *46*, 5166.
(5) Kelly, L. F.; Narula, A. S.; Birch, A. J. *Tetrahedron Lett.* **1979**, 4107. Kelly, L. F.; Narula, A. S.; Birch, A. J. *Tetrahedron* **1982**, *38*, 1813. Atton, J. G.; Kane-Maguire, L. A. P.; Williams, P. A.; Stephenson, G. R. *J. Organomet. Chem.* **1982**, *232*, C5. Evans, D. J.; Kane-Maguire, L. A. P.; Wild, S. B. *J. Organomet. Chem.* **1982**, *232*, C9. Evans, D. J.; Kane-Maguire, L. A. P. *J. Organomet. Chem.* **1982**, *236*, C15.
(6) Howell, J. A. S.; Thomas, M. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1401. Birch, A. J.; Bandara, B. M. R.; Kelly, L. F.; Khor, T. C. *Tetrahedron Lett.* **1983**, *24*, 2491.
(7) Howell, J. A. S.; Thomas, M. J. *J. Organomet. Chem.* **1983**, *247*, C21.

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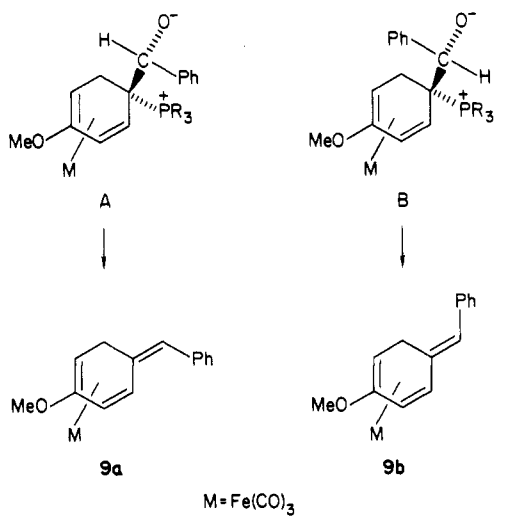
the dienyl ring. We have found that enantiomerically pure **2** may be transformed into **5** by using the Wittig reaction recently described by Lewis et al.[8] Thus, reaction of **2** [(2*S*)-(+)] with PPh_2Me yields the phosphonium salt **6a** [(2*S*,5*S*)-(−)][9] whose spectral characteristics (Table I) are in agreement with exclusive attack at C-5; exo attack on **1** has been demonstrated by a crystallographic determination of the triphenylphosphonium adduct.[10] Proton abstraction with BuLi in THF at −50 °C yielded in situ the deep red ylide **7a** which on treatment with anhydrous formaldehyde and purification yielded the methylenecyclohexadiene complex **8a**. Although stable in solution, a slow decomposition ensues in the pure state from which only traces of $Fe_3(CO)_{12}$ may be isolated. Spectroscopic data, however, are completely consistent with this structure, in particular the ^{13}C resonance at 102.9 ppm (off-resonance triplet) due to the exocyclic methylene carbon. Protonation of **8** using aqueous HPF_6 yields enantiomerically pure **5** [(2*S*,5*R*)-(+)] in an overall 40% yield. The absolute configurations of Scheme I can be written with confidence, since the configurations of **2** and **5** have been established by conversion of enantiomerically enriched samples into natural products known configuration[4].

The reaction may be extended by using benzaldehyde and the enantiomerically pure triphenylphosphonium salt **6b** [(2*S*,5*S*)-(−)] to the preparation of enantiomerically pure [(2-methoxy-5-benzylcyclohexadienyl)Fe(CO)$_3$]PF_6 (**10**) [(2*S*,5*R*)-(+)].

In contrast to **8**, the phenyl-substituted methylenecyclohexadiene complex is a completely stable, sublimable yellow solid. Both ^1H and ^{13}C spectra (Table I) show clearly the presence of the two geometric isomers **9a** and **9b** which are inseparable by chromatography. The geometry of **9** depends on the initial orientation adopted by the aldehyde in the intermediate betaine A or B. Molecular models indicate considerably less steric strain in A, and therefore the major isomer of **9** is assigned structure **9a**.



The ratio of **9a**:**9b** is dependent on the phosphonium salt used. Thus, in the case of **6b**, only a trace (≤1%) of the minor isomer is formed, whereas for the phosphines of smaller cone angle used in **6a** and **6c**, the observed ratio is 9:1. Some degree of steric influence of the methoxy-substituent is also evident, as it has been reported[8] that the unsubstituted analogue of **6b** yields a similar mixture of isomers, but in the ratio of 4:1. Complex **10** may be easily deprotonated by using Et_2N-*i*-Pr to regenerate **8a**,**b** in a 9:1 ratio of isomers. Indeed, the facility of this deprotonation precludes the resolution of 5-alkyl-substituted complexes of this type via reaction with chiral amines or alkoxides.

The yield of both **8** and **9** is also sensitive to the phosphonium salt used [PPh_3 (65%) ≥ PPh_2Me (39%) ≥ $PPhMe_2$ (22%) for production of **9**]. Although alkyl substitution usually increases ylide reactivity, this is mainly manifested in this reaction in an increased thermal instability. Thus, although **7b** reacts most slowly, its greater thermal stability provides the higher yield; only decomposition of the ylide was observed on reaction with ketones.

In contrast, addition of aliphatic aldehydes to the deep red ylide **7b** formed from racemic **6b** results in an immediate color change to light yellow. Purification yields a material identical with that obtained by direct addition of aqueous HPF_6 to the ylide, implying an α-proton abstraction on reaction with aliphatic aldehydes. Microanalysis and spectroscopic data show that the product is the endo triphenylphosphonium salt **11**, contaminated with a trace (5%) of the starting salt **6b**. Protonation of the ylide thus probably occurs exclusively at the exo face and results in inversion of configuration at C-5. The small amount of **6b** isolated is most likely a remnant of an initial incomplete conversion to the ylide **7b**, although a small amount of endo protonation cannot be excluded. Pure samples of the endo salt can be obtained by utilizing its much greater solubility in acetone and ether solvents.

Although identical in their infrared spectra, the exo and endo isomers exhibit different ^{31}P NMR resonances and are quite distinctive in their ^{13}C NMR spectra. Although both exo and endo isomers have been isolated from direct reaction of the seven-membered ring [(cycloheptadienyl)Fe(CO)$_3$]PF_6 with phosphines,[11] the above represents the first preparation of an *endo* isomer in the six-membered ring series. It is interesting that although the ^{13}C NMR spectra of the exo and endo phosphonium salts of the seven-membered ring complex are almost superposable, the ^{13}C spectra of **6b** and **11** differ substantially, particularly in a reversal of the chemical shift order for the two sp^3 ring carbons and in J(P–C) values for the ring carbons. This implies a substantially greater change in ring geometry for the exo and endo isomers of the six-membered ring complex.

(b) The Stereochemistry of Phosphine Elimination Using $LiAlD_4$. Complexes such as **3** and **4**, in their pure diastereoisomeric forms, have a potential for further use, in that nucleophilic displacement of the phosphine or amine residue can potentially yield single enantiomers of defined configuration at C-5. As a prelude to a study of the generality of this reaction, we report here on the elimination of phosphine from **3a** and **3b** to establish (a) whether the elimination occurs with retention or inversion at C-5 and (b) whether the reaction involves a direct and/or a concerted elimination.

Reaction of **3b** (Scheme II) (as a 1:1 diastereoisomeric mixture) with $LiAlD_4$ in THF proceeds to yield a 9:1 mixture of the labeled 2-methoxy and 1-methoxy complexes **12** and **13** which can be separated by preparative TLC. The 400-MHz ^1H NMR spectra (CH_2 region only) of **12**, of unlabeled (2-methoxycyclohexadiene)Fe(CO)$_3$, and of the monodeuterio derivative **15** prepared by reaction of **2** with $NaBD_4$ are shown in Figure 1.

(8) Hackett, P.; Johnson, B. F. G.; Lewis, J.; Jaouen, G. *J. Chem. Soc., Dalton Trans.* **1982**, 1247. Jaouen, G.; Johnson, B. F. G.; Lewis, J. *J. Organomet. Chem.* **1982**, *231*, C21.

(9) The configuration of **6a** is wrongly described as (2*S*,5*R*)-(−) in ref 7.

(10) Guy, J. J.; Reichert, B. E.; Sheldrick, G. M. *Acta Crystallogr., Sect. B* **1976**, *32B*, 2504.

(11) Brown, D. A.; Chawla, S. K.; Glass, W. K.; Hussein, F. M. *Inorg. Chem.* **1982**, *21*, 2726.

Table I. Microanalytical and Spectroscopic Data

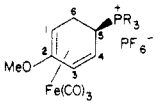
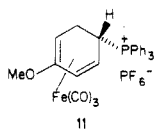
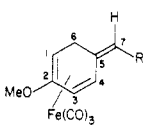
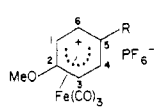
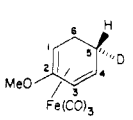
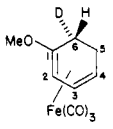
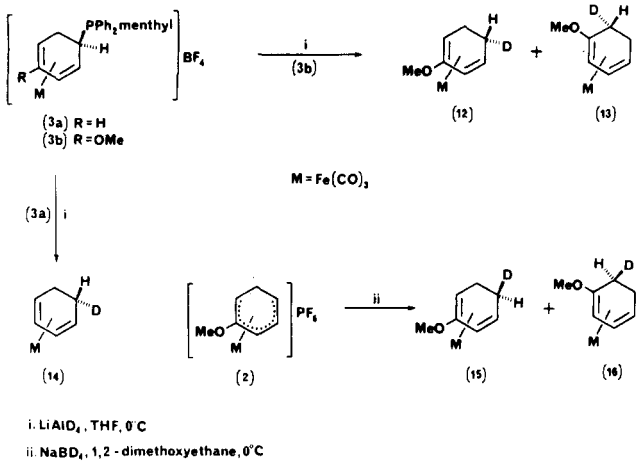
	microanal.[a]	infrared[b]	^{13}C NMR[c]		^{1}H NMR[d]		^{31}P NMR[e]
	C 46.0 (46.4)	2048	1	51.2 (6)			25.9
	H 3.61 (3.74)	1993	2	*f*			
			3	65.3 (9.7)			
			4	40.5 (9.7)			
			5	31.9 (37.8)			
			6	27.9 (3.7)			
			MeO	54.6			
			Me	6.0 (46.9)			
			Ph	117-136			
6a, $PR_3 = PPh_2Me$							
6b, $PR_3 = PPh_3$	C 51.0 (51.2)	2050	1	50.8 (6.8)			26.4
	H 3.73 (3.69)	1993	2	*f*			
			3	65.2 (3.9)			
			4	40.6 (9.8)			
			5	31.8 (35.1)			
			6	28.6 (2.0)			
			MeO	54.4			
			Ph	117-135			
6c, $PR_3 = PPhMe_2$	C 40.6 (40.6)	2051	1	51.2 (7.8)			26.8
	H 3.74 (3.80)	1993	2	*f*			
			3	65.8 (2.9)			
			4	40.9 (8.8)			
			5	33.2 (39.1)			
			6	26.8 (2.6)			
			MeO	54.8			
			Me	6.24 (53.7)			
				5.20 (53.7)			
			Ph	117-136			
	C 51.2 (51.2)	2047	1	53.9 (10.8)			25.4
	H 4.07 (3.69)	1991	2	*f*			
			3	64.3 (17.6)			
			4	43.2 (1.9)			
			5	25.4 (53.7)			
			6	32.2			
			MeO	54.8			
			Ph	116-135			
		2041	1	55.9			
		1993	2	*f*			
		1982	3	66.1			
			4	51.7			
			5	*f*			
			6	29.8			
8, R = H			7	102.9			
			MeO	54.5			
9, R = Ph	C 60.8 (60.4)	2042	1	58.7	1	3.59 (m)	
	H 3.88 (4.18)	1992	2	*f*	3	5.21 (dd)	
		1981	3	65.9	4	3.37 (d)	
				66.2[g]	6	2.66 (m)	
			4	51.7	7	6.25 (s)	
				51.1[g]		5.82 (s)[g]	
			5	*f*	MeO	3.67 (s)	
			6	29.9	Ph	7.11-7.28 (m)	
				32.4[g]			
			7	119.1			
			MeO	54.5			
			Ph	125-139			
	C 31.9 (32.4)	2099	1	41.2			
	H 2.54 (2.72)	2047	2	*f*			
			3	71.7			
			4	95.6			
			5	*f*			
			6	33.2			
			MeO	57.1			
			Me	23.2			
5, R = Me							
10, R = CH_2Ph	C 42.9 (42.2)	2100	1	41.3			
	H 3.23 (3.13)	2045	2	*f*			
			3	71.4			
			4	94.0			
			5	*f*			
			6	32.3			
			CH_2	42.5			
			MeO	57.1			
			Ph	128-133			
			1	55.1			
			2	*f*			
			3	67.6			
			4	50.9			
			5	23.3 (20.5)			
			6	24.8			
12, Y = OMe							

Table I (*Continued*)

	microanal.[a]	infrared[b]	^{13}C NMR[c]	^{1}H NMR[d]	^{31}P NMR[e]
			MeO 54.0		
14, Y = H			1,4 62.3		
			62.4		
			2,3 85.3		
			5,6 23.6 (20.5)		
			23.7		
			1 *f*		
			2,3 78.5		
			77.6		
			4 58.3		
			5 23.2		
13			6 24.9 (20.5)		
			MeO 56.7		

[a] Calculated figures in parentheses. [b] cm^{-1}; CH_2Cl_2 solution except **8**, **9** (hexane), and **5** (acetone). [c] Ppm from Me_4Si; $CDCl_3$ solution except **5** and **10** ($CF_3CO_2D/CDCl_3$); for **6a-c** and **11**, J(P-C) in parentheses; for **12-14**, J(C-D) in parentheses. [d] Ppm from Me_4Si; $CDCl_3$ solution; m = multiplet, d = doublet, s = singlet. [e] Ppm from 85% H_3PO_4; $CDCl_3$ solution. [f] Quaternary carbon not detected. [g] Resonances due to minor isomer **9b**. [h] The ^{13}C spectrum of the exo deuterio isomer **15** is essentially superposable.

Scheme II



Decoupling experiments allow a clear differentiation between the C-5 and C-6 protons, although an exo/endo assignment is not possible since both exhibit similar couplings to the outer diene protons. The exo/endo assignment at C-5 may be made by using the spectrum of **15**, as hydride attack is known to be almost exclusively exo.[12] In the spectrum of **15** also, the residual intensity of the exo resonance at δ 1.1 is greater than that expected on the basis of residual hydrogen in the $NaBD_4$, implying some endo deuteride attack in the reaction of **2** with $NaBD_4$. Also evident in the proton spectrum are traces (~1%) of (1-methoxycyclohexadiene)Fe(CO)$_3$ resulting from hydride attack at C-1; this is assigned structure **16** but was not isolated separately due to its low abundance.[13] In contrast, the spectrum of **12** clearly shows that elimination of phosphine from **3b** using $LiAlD_4$ proceeds with *inversion* of configuration at C-5, and the absence of any residual endo resonance implies essentially 100% stereospecificity.

Similar stereochemical considerations apply to the small amount of labeled (1-methoxycyclohexadiene)Fe(CO)$_3$ formed. Assignment of the C-5 and C-6 protons (Figure 2) in the unlabeled material may be made from decoupling experiments. On the unproven assumption that the exo/endo assignment may be made on the basis of the

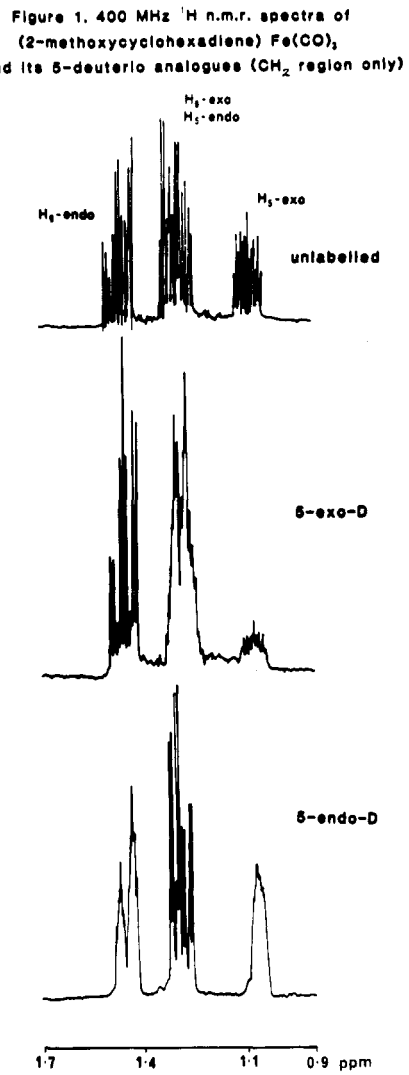


Figure 1. 400-MHz ^{1}H NMR spectra of (2-methoxycyclohexadiene)Fe(CO)$_3$ and its 5-deuterio analogues (CH_2 region only) (benzene-d_6).

order established in Figure 1, the spectrum of **13** indicates an endo stereochemistry for the deuterium at C-6. Thus, even in the product of concerted elimination, the steric bulk of the phosphine seems sufficient to direct attack at the metal-complexed face of the diene. The residual intensity of the endo resonance is, however, higher than expected, implying some small amount of exo attack in the

(12) $NaBD_4$ attack on **1** proceeds to yield exo and endo isomers in a ratio of approximately 10:1: Karel, K. J.; Brookhart, M.; Aumann, R. *J. Am. Chem. Soc.* **1981**, *103*, 2695.

(13) This reaction has been reported to yield exclusively (2-methoxycyclohexadiene)Fe(CO)$_3$: Birch, A. J.; Westerman, P. W.; Pearson, A. J. *Aust. J. Chem.* **1976**, *29*, 1671.

Figure 2. 400-MHz ^1H NMR spectra of (1-methoxycyclohexadiene)$Fe(CO)_3$ and its 6-deuterio analogue (benzene-d_6).

formation of **13**. The ^{13}C spectra of these deuterated derivatives have also been recorded and allow an unambiguous assignment of the CH_2 resonances for both (1- and 2-methoxycyclohexadiene)$Fe(CO)_3$.

The deuteride elimination may be applied to the *pure* diastereoisomer **3a** to yield, after workup, complex **14** in which chirality resides solely in the isotopic substitution at C-5. Although both (+)-5-methyl- and (+)-5-*tert*-butylcyclohexadiene are known to be *R*[14] the sign of rotation is sensitive to substituent on the diene carbons; the *R* configuration drawn in Scheme II is therefore arbitrary. One may note also that, in contrast to **3b**, any small amount of concerted phosphine elimination in the reaction of **3a** will result in a small degree of racemization. Although ^1H NMR spectra establish conclusively that the deuterium is endo[15], we have not yet established the enantiomeric purity of **14**.

Finally, we have attempted to use diastereoisomercially pure **3a** as a precursor for enantiomerically pure 5-alkyl-substituted salts using the reactions outlined in Scheme I. Although ylide formation is evident on the reaction of **3a** with a variety of strong bases [BuLi, $NaNH_2$], no methylenecyclohexadiene complexes were isolated from addition of formaldehyde or benzaldehyde. The steric bulk of the phosphine evidently reduces dramatically the reactivity of the ylide.

Experimental Section

NMR and infrared spectra were recorded on JEOL FX-100 and Pye Unicam SP2000 instruments. Optical rotations were measured by using an AA100 polarimeter. Tetrahydrofuran was purified by distillation over sodium and benzophenone; all other solvents were distilled and degassed before use. The concentration of BuLi was determined by titration using 2,5-dimethoxybenzyl alcohol.[16] Formaldehyde was generated externally by heating paraformaldehyde (previously dried over P_2O_5 for 24 h at 0.01 mmHg) to 160–180 °C.[17] Benzaldehyde was purified by dissolving in diethyl ether, washing with Na_2CO_3 followed by H_2O, drying with $MgSO_4$ and distillation.

(a) (2*S*,5*S*)-(−)-[(2-MeO-5-*exo*-$PPh_3C_6H_6$)$Fe(CO)_3$]PF_6 (6b). To a stirred suspension of (2*S*)-(+)-**2**[6] (0.30 g, 0.76 mmol; [α] +118°) in CH_2Cl_2 (20 mL) was added PPh_3 (0.22 g, 0.84 mmol). Immediate dissolution occurred to give a yellow solution. Removal of solvent under reduced pressure gave a yellow gum which solidfied on standing in diethyl ether (50 mL) at 0 °C. The pale yellow solid was filtered and washed with diethyl ether to give the product (0.46 g, 98%, $[\alpha]^{20}_D$ −108.8° (*c* 5.0, MeCN). The 5-*exo*-PPh_2Me **6a** ((2*S*,5*S*); $[\alpha]^{17}_D$ −92° (*c* 2.9, acetone) and 5-*exo*-$PPhMe_2$ **6c** complexes were prepared similarly, the last only in a racemic form starting from racemic **2**.

(b) (2*S*)-(+)-(2-Methoxy-5-benzylidenecyclohexadiene)-$Fe(CO)_3$ (9). A stirred suspension of (2*S*,5*S*)-(−)-**6b** (0.47 g, 0.72 mmol) in THF was cooled to −60 °C. An excess of BuLi (1.0 mmol) in hexane was added, and the mixture was stirred between −60 °C and −40 °C until all the phosphonium salt had dissolved to give a deep red solution. An excess of benzaldehyde (2.16 mmol) was added and the solution allowed to warm to room temperature over a period of 3 h. The orange solution was hydrolyzed and extracted with diethyl ether (3 × 50 mL) and the organic layer dried over $MgSO_4$. Removal of solvent, followed by chromatography on silica gel using 40–60 petroleum ether/benzene (1:1), gave **9** as yellow crystals (0.157 g, 65%; $[\alpha]^{18}_D$ +130° (*c* 4.8, $CHCl_3$). An analytical sample was obtained by sublimation (79–80 °C (0.01 mmHg)).

An analogous procedure using **6a** and **6c** gave the same product in yields of 39% and 22%, respectively.

(c) (2*S*,5*R*)-(+)-[(2-MeO-5-$(PhCH_2)C_6H_5$)$Fe(CO)_3$]PF_6 (10). (2*S*)-(+)-**9** (140 mg, 0.41 mmol) was dissolved in diethyl ether (20 mL), and an excess of HPF_6 (75% aqueous, 1.6 mmol) was added. The flask was cooled at 0 °C for 12 h, and the yellow solid was filtered, washed with diethyl ether, and recrystallized from CH_2Cl_2/Et_2O to give **10** (0.138 g, 69%; $[\alpha]^{20}_D$ +183° (*c* 4.2, MeCN)).

Complex **9** can easily be regenerated in 72% yield by treatment of a diethyl ether suspension of **10** with a twofold molar excess of EtN-*i*-Pr_2, followed by chromatography.

(d) (2*S*,5*R*)-(+)-[(2-MeO-5-MeC_6H_5)$Fe(CO)_3$]PF_6 (5). (2*S*,5*S*)-(−)-**6a** (0.48 g, 0.8 mmol) was suspended in THF and cooled to −60 °C. BuLi (1.12 mmol) in hexane was added, and the suspension was stirred between −60 to −40 °C until the salt had completely dissolved to give a deep red solution (1.5 h). Externally generated formaldehyde was bubbled through a wide bore tube into the solution, which was stirred vigorously and allowed to warm gradually to room temperature to give a yellow solution. After hydrolysis, the product was extracted with diethyl ether (3 × 50 ml), the organic layer dried over $MgSO_4$, and the solvent evaporated. Chromatography on silica gel using petroleum ether (40–60)/diethyl ether (80:20) gave 0.108 g of product 8. Dissolution in diethyl ether (20 mL) and addition of excess HPF_6 (75% aqueous, 0.82 mmol) precipitated a yellow solid. After the solution was cooled at 0 °C for 12 h the precipitate was filtered,

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(15) The 400-MHz ^1H NMR spectrum of (cyclohexadiene)$Fe(CO)_3$ (C_6D_6) exhibits two-proton multiplets at δ 1.1 and 1.4 assignable to exo and endo CH_2 protons; the endo resonance is reduced in intensity by one in the spectrum of **14**.

(16) Winkle, M. R.; Losinger, J. M.; Roland, R. C. *J. Chem. Soc., Chem. Commun.* **1980**, 87.

(17) Gilman, H.; Catlin, W. E. "Organic Synthesis"; Wiley: New York, 1964; Coll. Vol. 1, p 188.

washed with diethyl ether, and recrystallized from acetone/diethyl ether to give **5** (0.084 g, 26%, $[\alpha]^{20}_D$ +134° (*c* 3.4, MeCN).

(e) [(2-MeO-5-*endo*-$PPh_3C_6H_6$)$Fe(CO)_3$]PF_6 (11). A stirred suspension of racemic **6b** (0.86 g, 1.31 mmol) in THF (30 mL) was cooled to −60 °C and an excess of BuLi in hexane (2.0 mmol) was added over 1 h to give a deep red solution. A small excess of HPF_6 (5% aqueous, 1.7 mmol) was added dropwise to give a yellow solution which was allowed to warm to room tempearture. After removal of solvent, the yellow gum was dissolved in CH_2Cl_2 (10 mL), filtered, and precipitated by addition of diethyl ether. The small amount of less soluble **6b** was removed by redissolving this crude product in acetone (10 mL). Addition of petroleum ether (10 mL) resulted in separation of **6b** as a brown oil from which the more soluble isomer **11** was readily decanted. Further additions of 40–60 petroleum ether (50 mL) followed by filtration gave **11** (0.61 g, 71%).

(f) Reduction of [(5-*exo*-(PPh_2(Me-(Me_2CH)C_6H_9))C_6H_7)$Fe(CO)_3$]BF_4. Finely powdered diastereoisomerically pure **3a**[6] (0.80 g, 1.27 mmol) was suspended in THF (40 mL) at 0 °C, and $LiAlD_4$ (0.092 g, 2.2 mmol) was added in three portions. The reaction mixture was stirred at 0 °C until the infrared spectrum indicated complete consumption of starting material (2 h). The reaction mixture was treated cautiously with 20% sodium potassium tartrate solution (50 mL) and extracted with diethyl ether (3 × 30 mL). Drying over $MgSO_4$ followed by removal of solvent and chromatography of the residue on grade II alumina using petroleum ether (40–60) gave **14** (0.135 g, 48%; $[\alpha]^{20}_D$ +4.3 ● 1.5° (*c* 3.3, $CHCl_3$) of a sample which was analytically and spectroscopically pure).

Reduction of a 1:1 diastereoisomeric mixture of [(2-MeO-5-*exo*-(PPh_2(Me(Me_2CH)C_6H_9))C_6H_6)$Fe(CO)_3$]BF_4 (**3b**) with $LiAlD_4$ was complete in 1.5 h. Chromatography on preparative silica gel plates using petroleum ether (40–60) gave (2-$MeOC_6H_6D$)$Fe(CO)_3$ (**12**) (72%) and (1-MeO-C_6H_6D)$Fe(CO)_3$ (**13**) (8%).

The 5-*exo*-deuterio complex **15** was prepared by a literature method.[13]

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Registry No. **2**, 51508-59-9; (2*S*)-(+)-**2**, 76704-83-1; **3a**, 95463-17-5; (2*S*5*S*)-**3b**, 84525-82-6; **5**, 95406-37-4; (2*S*5*S*)**6a**, 86664-10-0; **6b**, 95463-20-0; (2*S*5*S*)-**6a**, 95463-18-6; **6c**, 95387-14-7; **8**, 86664-11-1; **9a**, 86664-12-2; **9b**, 86708-26-1; **10**, 86768-26-5; **11**, 95463-22-2; **12**, 95387-15-8; **13**, 95387-16-9; **14**, 95387-17-0; **15**, 95387-18-1; **16**, 95463-23-3; (2-methoxycyclohexadiene)$Fe(CO)_3$, 12318-19-3; (1-methoxycyclohexadine)$Fe(CO)_3$, 12318-18-2; PPh_3, 603-35-0; $PPhMe_2$, 672-66-2; PPh_2Me, 1486-28-8; benzaldehyde, 100-52-7; formaldehyde, 50-00-0.

(18) Enantiomerically pure (2*R*) (5*S*) isomer obtained by fractional crystallization has a rotation of −138°: Stephenson, G. R. *Aust. J. Chem.* **1981**, *34*, 2339. The enantiomeric purity of **5** was additionally confirmed by the presence of only two methyl resonances in the ^1H NMR spectrum of the dimethyl malonate adduct in the presence of optically active shift reagent.

Reactivity of Bis(cyclopentadienyl)niobium and -tantalum Hydrides toward Iron Penta-, Nona-, and Dodecacarbonyl. Interaction of a Bridging Carbonyl with an Early Transition Metal and Formation of an O-Metalated Carbyne

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The monohydrides $Cp_2M(CO)H$ (Cp = η^5-C_5H_5) and $Cp'_2M(CO)H$ (Cp' = η^5-$C_5H_4CMe_3$) (M = Nb or Ta) react with $Fe_2(CO)_9$ in equimolar ratio to give the Lewis acid–base adducts $Cp_2M(CO)(\mu$-H)$Fe(CO)_4$ and $Cp'_2M(CO)(\mu$-H)$Fe(CO)_4$. With $Fe_3(CO)_{12}$ or with an excess of $Fe_2(CO)_9$, the polynuclear systems $Cp_2M(CO)[(\mu$-CO)(μ-H)$Fe_3(CO)_{10}]$ and $Cp'_2M(CO)[(\mu$-CO)(μ-H)$Fe_3(CO)_{10}]$ which contain a bridging O-metalated carbyne ligand are obtained. When the trihydrides Cp_2MH_3 or Cp'_2MH_3 are treated with $Fe(CO)_5$, $Fe_2(CO)_9$, or $Fe_3(CO)_{12}$, the initial formation of the monohydrides is observed by an "in situ" carbonylation reaction.

Introduction

The research and the improvement of novel systems for the homogeneous reduction of carbon monoxide continue to be an active area of organometallic chemistry.[1] The design of catalysts affording both high selectivity and mild reaction conditions is of considerable economic interest. Of course, this goal needs the knowledge and the understanding of the elementary steps involved in the carbon monoxide hydrogenation. A key step in the reduction pathway is the formation of the first C–H bond; an alternative to insertion of CO into a M–H bond which appears as a highly unfavorable process is the nucleophilic attack by H^- upon a coordinated CO. Stoichiometric reductions of complexed carbon monoxide leading to formyl,[2] hydroxymethyl,[3] or methyl[4] complexes can be performed

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