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Optically active transition-metal complexes

I. Iron, cobalt and rhodium complexes of the optically active diolefin (+)-nopadiene and its derivatives. The crystal structure of C_5Me_5Rh(nopadiene)

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Abstract

The syntheses of metal complexes of the optically active diolefins nopadiene, acetylnopadiene, nopadiene acid and nopadiene aldehyde are described. All the ligands were coordinated to the $Fe(CO)_3$ group and some also to CpRh, CpCo, Cp*Rh and Cp*Co (Cp = cyclopentadienyl, Cp* = pentamethylcyclopentadienyl). The complexation was diastereoselective in most cases and optically active diolefin compounds were directly obtained. The solid state structure of one isomer of C_5Me_5Rh(nopadiene) is described. Various chemical transformations, such as reductions and nucleophilic additions at functional groups, are reported; depending on reaction type, these proceed diastereoselectively or even enantioselectively with generation of new chiral carbon centers. In these reactions, pronounced differences are observed in the reactivity and selectivity of complexed and free ligands. Efficient substitutions of carbonyl groups for phosphines and phosphites are also described for (nopadiene)$Fe(CO)_3$.

Introduction

Optically active metal complexes have received considerable attention in recent years. Their use as enantioselective catalysts in many organic transformations is well documented and a number of applications in the industrial synthesis of important organic intermediates are known [1,2].

Complexes are generally rendered optically active by the introduction of optically active ligands such as amines, phosphines and alcohols, not by chirality at the metal centre. Such ligands are commonly derived from natural products taken from the "chiral pool", but often also from racemic starting materials, thus requiring several derivatizing and resolution steps. At least two of the more important chiral catalysts fall into the class of organometallic π-complexes, namely a number of substituted ferrocene derivatives utilized by Hayashi [3] and Ugi [4] as well as the *ansa*-metallocenes developed by Brintzinger, useful for Ziegler–Natta polymerisation [5].

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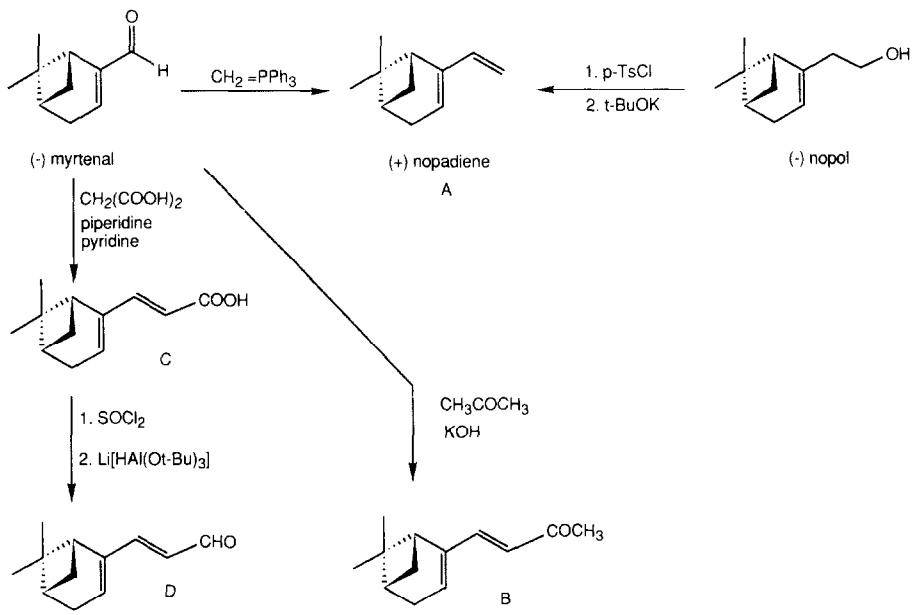
In addition to catalytic applications, stoichiometric use of optically active metal π-complexes as synthons in organic synthesis is also actively pursued, and some elegant syntheses have been developed from cyclopentadienyl iron [6] as well as cyclopentadienyl titanium complexes [7].

In extension of our previous work on the synthesis and reactivity of metal-olefin complexes [8], we became interested in the chemistry of optically active olefin complexes. As all prochiral diolefinic and aromatic ligands such as cyclopentadienyl or benzene derivatives will form chiral metal π-complexes, a vast array of optically active compounds is in principle accessible. Although these complexes are configurationally stable under ambient conditions, resolution of enantiomers has only been achieved in relatively few cases [9]. The methods employed range from classical resolution with chiral derivatizing agents to such modern methods as enantioselective chromatography [10].

The most serious obstacle hindering development of this field of chemistry is still the often laborious procedure required for resolution of enantiomers. This can be avoided by the use of optically active olefinic or aromatic ligands. If the organic ligand has C_2-symmetry, metal complexation from either side of the ligand will give an identical enantiomerically pure product. This approach has been utilized for the synthesis of several half-sandwich complexes [11,12]. Other optically active ligands will, in principle, yield two diastereomeric products due to complexation from their two non-identical "faces". Should the complexation be "face-selective", an optically active complex will again be directly obtained. This is most likely to occur when one side of the ligand is sterically crowded while the other is readily accessible. This has been observed on complexation of the optically active diolefins carvone, limonene



Scheme 1

and α-phellandrene [13] as well as the cyclopentadienyl ligands derived from the natural products (−)-nopol and (−)-verbenone [14,15].

Our primary interest was in the chemistry of the optically active diolefin ligand (+)-nopadiene, also readily available from (−)-nopol in two steps. Several other functionalized derivatives can also be made from the aldehyde (−)-myrtenal as outlined below (Scheme 1).

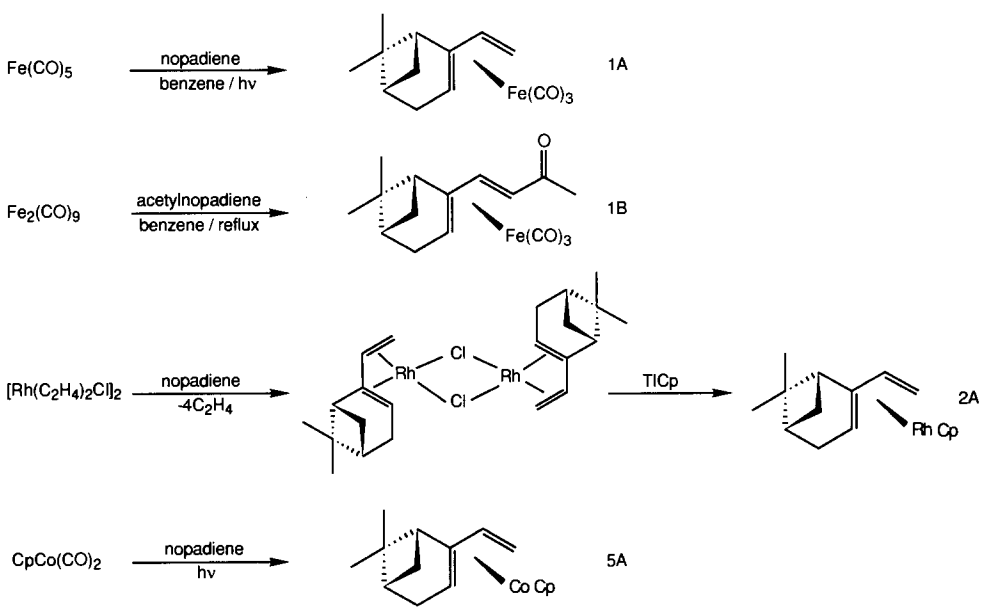
The aim of our research was to investigate whether enantiomerically pure diolefin complexes could be made from these ligands by face-selective complexation and to find out in which way new chiral centres could be generated by subsequent transformations. In addition, we hoped to gain insight into those organometallic reaction mechanisms that are not easily deducible from reactions of racemic mixtures.

Results and discussion

1. Synthesis of complexes

The organic ligands were prepared as outlined in Scheme 1. They were all obtained in good to excellent yields. For the complexation with iron carbonyl two methods were used: (a) photolysis of ligand and $Fe(CO)_5$ in benzene at 40 °C; and (b) reaction of ligand and $Fe_2(CO)_9$ in benzene under reflux.

Method (a) was preferrable for the unsubstituted diene **A** as well as the aldehyde and carboxylic acid derivatives **C** and **D**, but method (b) gave higher yields for reaction with acetylnopadiene **B**. In all cases only one single diastereomer was isolated, the NMR spectra showing no trace of any other product. We assume that in all complexes the $Fe(CO)_3$ group is coordinated opposite to the bridge carbon



Scheme 2

bearing the two methyl groups. This was later confirmed to some extent by the X-ray structural study of (phenylnopadiene)$Fe(CO)_3$ [16].

Several methods were employed for the synthesis of cyclopentadienyl derivatives of cobalt and rhodium. Treatment of bis(ethylene)rhodium chloride dimer with nopadiene immediately gave (nopadiene)rhodium chloride dimer with release of ethylene. This product was further treated with TlCp and also $TlCp^*$ [Cp = cyclopentadienyl, Cp^* = pentamethylcyclopentadienyl]. Again, the complexes CpRh(nopadiene) (2A) and Cp^*Rh(nopadiene) (3A) were isolated in enantiomerically pure form as one single diastereomer.

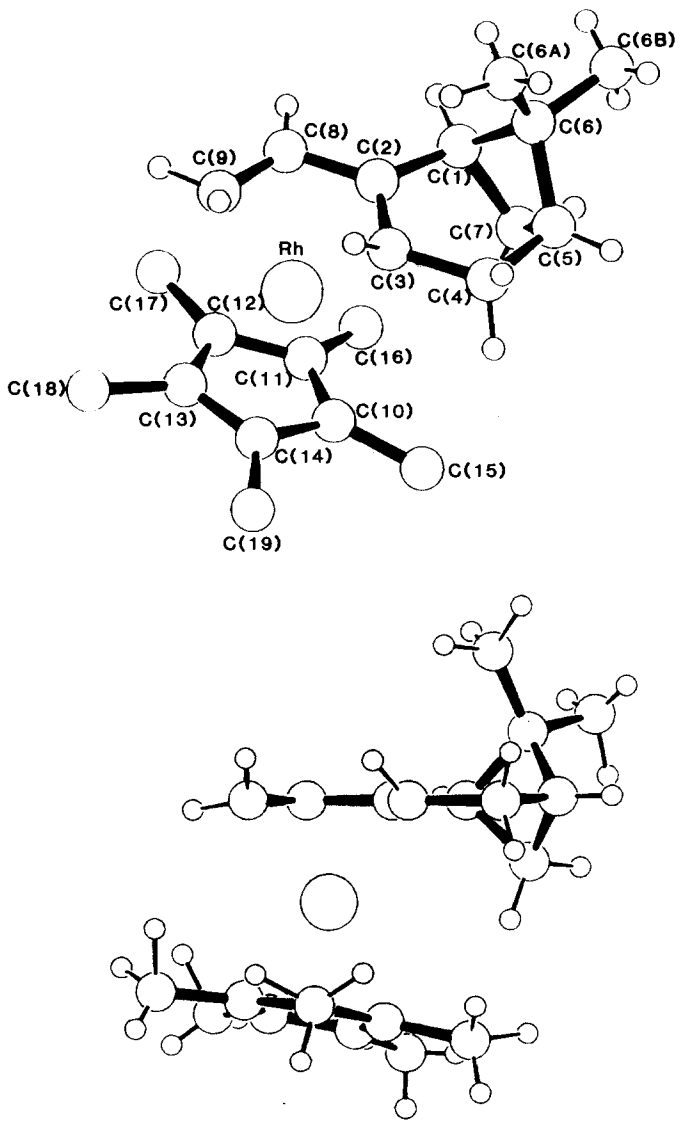


Fig. 1. Two views of C_5Me_5Rh(nopadiene) (3A) with atom numbering scheme.

Table 1

Final positional and thermal parameters for C_5Me_5Rh(nopadiene) (**3A**)

Atom	x	y	z	U_{eq} (Å^2)
Rh	0.89712(2)	0.79886(1)	0.08230(3)	0.03550(4)
C(3)	0.7673(2)	0.8233(1)	0.2253(3)	0.0407(6)
C(4)	0.7513(2)	0.7950(2)	0.3843(3)	0.0491(7)
C(5)	0.7996(2)	0.8577(2)	0.4922(3)	0.0496(8)
C(7)	0.9100(2)	0.8734(1)	0.4446(3)	0.0518(7)
C(1)	0.8680(2)	0.9430(1)	0.3419(3)	0.0435(7)
C(6)	0.7785(2)	0.9546(2)	0.4524(3)	0.0513(8)
C(6A)	0.6750(2)	0.9789(2)	0.3948(4)	0.0644(9)
C(6B)	0.8070(3)	1.0158(2)	0.5782(4)	0.078(1)
C(2)	0.8277(2)	0.8995(1)	0.2078(3)	0.0368(6)
C(8)	0.8443(2)	0.9272(1)	0.0590(3)	0.0476(7)
C(9)	0.7996(2)	0.8769(2)	−0.0504(3)	0.0560(9)
C(10)	0.9961(2)	0.6916(2)	0.1661(3)	0.0474(7)
C(11)	1.0622(2)	0.7620(2)	0.1227(3)	0.0482(8)
C(12)	1.0461(2)	0.7783(1)	−0.0271(3)	0.0462(7)
C(13)	0.9732(1)	0.7157(1)	−0.0794(3)	0.0407(6)
C(14)	0.9424(2)	0.6619(1)	0.0374(3)	0.0454(7)
C(15)	0.9947(3)	0.6486(2)	0.3111(4)	0.075(1)
C(16)	1.1379(2)	0.8070(2)	0.2181(4)	0.074(1)
C(17)	1.0970(2)	0.8450(2)	−0.1180(4)	0.069(1)
C(18)	0.9435(2)	0.7016(2)	−0.2378(3)	0.0600(8)
C(19)	0.8773(2)	0.5814(1)	0.0284(4)	0.061(1)

Surprisingly, two diastereomers were formed when Cp*Rh(nopadiene) was made by Maitlis's general route from $[Cp^*RhCl_2]_2$, nopadiene and $NaHCO_3$ [17]. This reaction probably proceeds via an intermediate allyl complex. The two isomers were separated by fractional crystallization. The major component was identical to **3A**. As this isomer readily crystallized as single crystals, it was submitted to an X-ray structural study (see later). For the synthesis of CpCo(nopadiene) and Cp*-Co(nopadiene) a photochemical route was chosen. Irradiation of $CpCo(CO)_2$ again gave only one product **5A**, whereas the same reaction with $Cp^*Co(CO)_2$ gave two diastereomers **6A** and **7A**, separable by fractional crystallization. This result was especially surprising, since we had assumed that the bulkier Cp*-ligand would preferentially induce the formation of only the less sterically crowded isomer.

2. X-ray structure of (pentamethylcyclopentadienyl)rhodium(nopadiene) (3A)

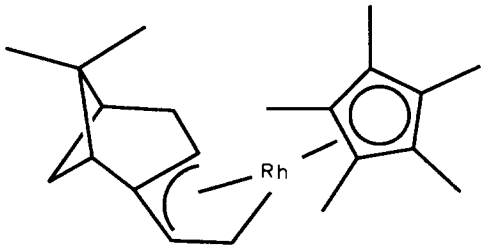
Complex **3A** has the general appearance of a normal sandwich molecule, with two planes defined by the C_5Me_5 ligand and the diolefin part of nopadiene lying not quite parallel to each other (Fig. 1). The angle between the two planes is 11.6°. The distance from the gravicenter of the ring plane to the rhodium atom is 1.870 Å and that of the diene plane is 1.679 Å. The Rh–C distances to the cyclopentadienyl ring vary significantly within the limits 2.197 and 2.276 Å. This is also the case for the Rh–C distances to the diene moiety. There seems to be connection between the tilting of the two ligand planes and the lengthening of the Rh–C bond lengths, since the longest values are found for the carbons at the "open jaw" (Fig. 1).

Table 2

Selected bond lengths (Å) and angles (°) in **3A**

Rh–C(3)	2.186(3)	C(3)–C(4)	1.535(4)
Rh–C(4)	3.368(3)	C(3)–C(2)	1.424(4)
Rh–C(1)	3.271(3)	C(4)–C(5)	1.520(4)
Rh–C(2)	2.133(3)	C(5)–C(7)	1.537(5)
Rh–C(8)	2.101(3)	C(5)–C(6)	1.556(4)
Rh–C(9)	2.136(3)	C(1)–C(7)	1.527(4)
		C(1)–C(6)	1.564(4)
Rh–H(3)	2.727(0)	C(1)–C(2)	1.495(4)
Rh–H(8)	2.801(0)	C(6)–C(6A)	1.509(5)
Rh–H(91)	2.815(0)	C(6)–C(6B)	1.534(5)
Rh–H(92)	2.767(0)	C(2)–C(8)	1.445(4)
		C(8)–C(9)	1.564(4)
Rh–C(10)	2.237(3)	C(10)–C(11)	1.444(5)
Rh–C(11)	2.276(3)	C(10)–C(14)	1.448(4)
Rh–C(12)	2.225(3)	C(10)–C(15)	1.483(4)
Rh–C(13)	2.197(3)	C(11)–C(12)	1.411(5)
Rh–C(14)	2.225(3)	C(11)–C(16)	1.495(4)
Rh–C(15)	3.371(3)	C(12)–C(13)	1.440(4)
Rh–C(16)	3.409(3)	C(12)–C(17)	1.480(4)
Rh–C(17)	3.286(3)	C(13)–C(14)	1.412(4)
Rh–C(18)	3.346(3)	C(13)–C(17)	1.517(5)
Rh–C(19)	3.387(3)	C(13)–C(19)	1.507(4)
Rh–C(3)–H(3)	108.8(2)	Rh–C(10)–C(15)	128.8(2)
Rh–C(8)–H(8)	116.5(2)	Rh–C(11)–C(16)	128.1(2)
Rh–C(9)–H(91)	115.7(2)	Rh–C(12)–C(17)	123.7(2)
Rh–C(9)–H(92)	116.1(3)	Rh–C(13)–C(18)	127.6(2)
		Rh–C(14)–C(19)	129.3(2)
C(2)–C(3)–C(4)	114.6(3)	C(2)–C(8)–C(9)	116.8(3)
C(3)–C(4)–C(5)	112.3(2)	C(11)–C(10)–C(19)	135.2(2)
C(4)–C(5)–C(7)	108.2(3)	C(11)–C(10)–C(15)	125.9(3)
C(4)–C(5)–C(6)	112.3(3)	C(15)–C(10)–C(19)	97.8(3)
C(7)–C(5)–C(6)	87.3(2)	C(10)–C(11)–C(12)	108.0(3)
C(1)–C(7)–C(5)	86.6(2)	C(10)–C(11)–C(16)	126.0(3)
C(1)–C(6)–C(5)	84.7(2)	C(12)–C(11)–C(16)	125.9(3)
C(7)–C(1)–C(6)	87.3(2)	C(11)–C(12)–C(13)	107.8(3)
C(2)–C(1)–C(6)	108.3(2)	C(11)–C(12)–C(17)	127.0(3)
C(2)–C(1)–C(7)	108.8(3)	C(13)–C(12)–C(17)	125.2(3)
C(5)–C(6)–C(6A)	118.7(3)	C(12)–C(13)–C(14)	109.3(3)
C(5)–C(6)–C(6B)	111.5(3)	C(12)–C(13)–C(18)	125.8(3)
C(6A)–C(6)–C(6B)	109.4(3)	C(14)–C(13)–C(18)	124.5(3)
C(1)–C(2)–C(3)	118.3(3)	C(10)–C(14)–C(13)	107.0(3)
C(3)–C(2)–C(8)	115.6(3)	C(10)–C(14)–C(19)	125.5(3)
C(1)–C(2)–C(8)	126.1(3)	C(13)–C(14)–C(19)	127.0(3)

The structure determination confirms that the bridge carbon with the two methyl groups is on the opposite side to the Cp^*Rh unit. It is surprising that the other isomer with the sterically demanding bridge methyls pointing towards the metal can be made at all for Cp^*Rh and Cp^*Co, since Fig. 1 suggests that there might be strong steric interaction between the methyl groups of the two ligands. Possibly the tilting of the two ligand planes is much more pronounced in this isomer.



4A

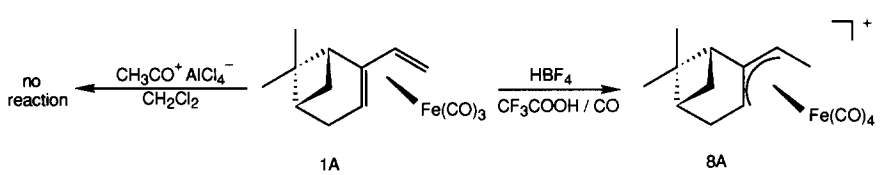
Fig. 2. Proposed structure of **4A**.

Unfortunately, we have been unable to grow single crystals of this type of complex. A severe distortion of the olefinic ligand in **4A** is, however, indicated by the $^{1}J(^{103}Rh, ^{13}C)$ coupling constants. **3A** shows the expected pattern of two larger couplings (16.5, 18.5 Hz) to the terminal carbons C-3 and C-9 of the diolefin ligand and two smaller couplings (6.5, 7.9 Hz) to the internal carbons C-2 and C-8, values quite characteristic for a CpRh(diolefin) complex [17]. **4A**, on the other hand, shows one very large coupling (26.1 Hz) to C-9, two intermediate couplings (13.9 and 15.2 Hz) for C-3 and C-8, and one small coupling of 6.4 Hz for C-2. This is consistent with a formulation of **4A** as a σ–π-allyl- rather than a diolefin complex, as a value of 26 Hz is characteristic of a rhodium-carbon σ-bond and the other values closely match those of known rhodium-π-allyl complexes [18] (Fig. 2).

3. Reactivity of complexes

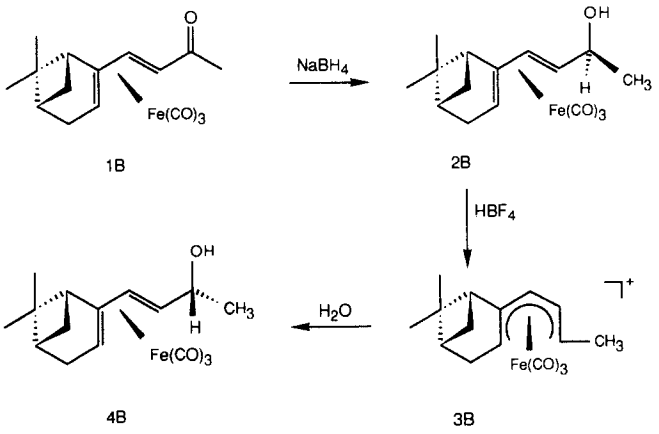
We had shown previously [19], that protonation of CpM(diene) complexes [M = Co, Rh, Ir] in the presence of CO was an elegant and efficient route for the synthesis of $[CpM(allyl)CO]^{+}$ derivatives. We therefore treated CpRh(nopadiene) (**2A**) and Cp^{*}Co(nopadiene) (**6A**) with HBF_4/CO and obtained in each case a mixture of two isomeric allyl complexes, but we were unable to separate these and did not characterize them further.

Similar protonation of (nopadiene)$Fe(CO)_3$ (**1A**) with $HBF_4/CF_3COOH/CO$ gave only one product **8A**, which was not very stable in solution, but could be characterized by its NMR spectrum in CF_3COOD. This showed that protonation had occurred at the unsubstituted end of the diolefin (Scheme 3), in agreement with the regioselectivity generally observed for electrophilic addition to (diene)$Fe(CO)_3$ complexes [20].



1A 8A

Scheme 3



Scheme 4

We were unable to effect any acetylation of **1A** with CH_3CO^+ according to Pauson's method for (butadiene)$Fe(CO)_3$ [21], and it seems that the formation of stable allyl complexes of this strained ligand is severely restricted, since acetylation is known to proceed via an intermediate allyl complex.

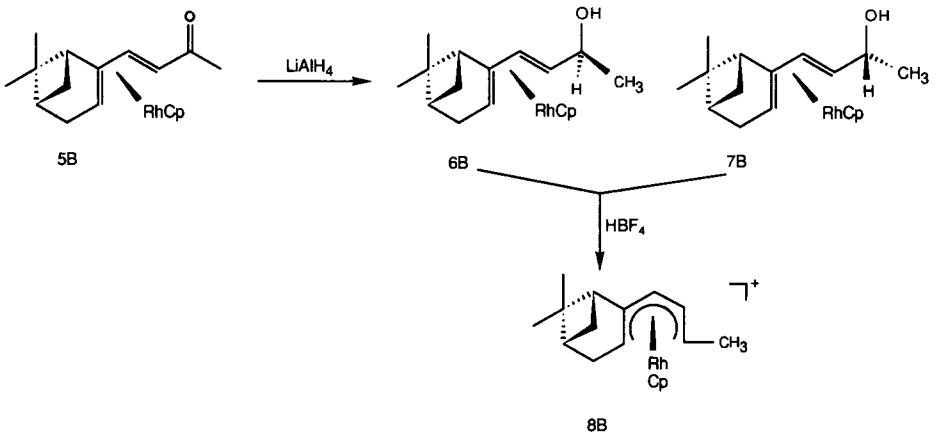
We were also unable to isolate any definite products from nucleophilic addition to **1A** with lithium reagents analogous to reactions carried out by Semmelhack with acyclic (diolefin)$Fe(CO)_3$ complexes [22]. Nucleophilic addition should occur at low temperatures at an internal position of the coordinated diene, with subsequent rearrangement at ambient temperatures to the more stable adduct in which the nucleophile had added at a terminal carbon. Repeated attempts with or without CO present failed to give a defined organometallic or organic product after quenching. Once again the formation of an allyl intermediate, crucial to the success of this reaction, appears to be hindered for this ligand, and other reaction pathways become more favourable, resulting in overall decomposition.

The acetylnopadiene complex **1B**, not accessible by acetylation, was, however, prepared by an independent synthesis of the free ligand and its subsequent complexation, and proved to be a completely stable species. Sodium borohydride reduction of **1B** gave only one alcohol **2B** with enantioselective generation of a new chiral carbon atom. The free ligand, on the other hand, under identical conditions, gave the two diastereomeric alcohols in approximately equal proportions.

This shows, that metal complexation allows the reducing agent to attack the keto group from one side only, possibly also restricting free rotation of the acetyl group, as required for an enantioselective addition. This is in agreement with previous observations on the reduction of racemic keto complexes [23].

The other isomeric alcohol complex can also be made by established organometallic routes [24]: protonation of the alcohol with HBF_4 generates the stable dienyl salt **3B**, which in turn produces one single alcohol **4B** on hydrolysis, this time with the opposite configuration at the alcohol carbon.

The corresponding cyclopentadienyl rhodium complex **5B** was not reduced by $NaBH_4$, so the stronger hydride donor $LiAlH_4$ was used. Surprisingly, two diastereomeric alcohols **6B** and **7B** were obtained. The reason for this may lie in the different nature of the reducing agent, since $NaBH_4$ in methanol is known to react

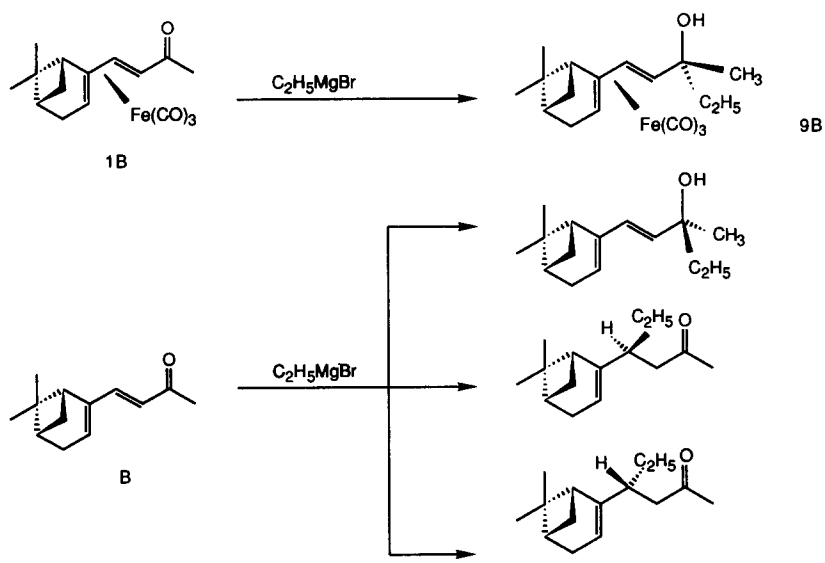


Scheme 5

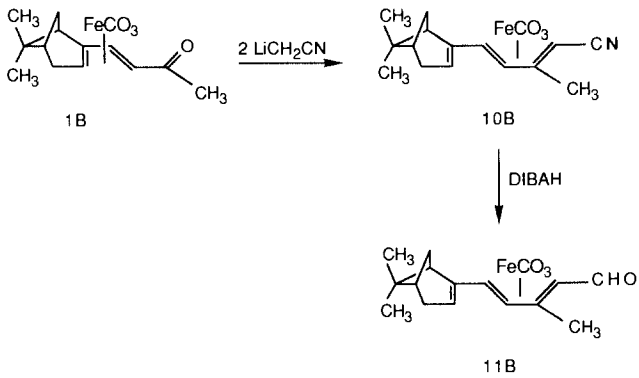
very stereoselectively [25]. Protonation of this mixture of alcohols produced one single cationic dienyl complex **8B** in good yields, showing that this general route is very suitable for preparation of optically active half-open sandwich complexes.

The reaction of **1B** with ethyl magnesium bromide proceeded slowly (48 h) but efficiently to give once again a single product **9B** with a new chiral carbon atom. The free ligand itself gave three products with the same reagent, two of which resulted from Michael addition (Scheme 6).

We previously described an unusual condensation/migration sequence on treatment of (sorbic aldehyde)$Fe(CO)_3$ with $LiCH_2CN$ [26]. On performing the same reaction with **1B**, we obtained a single product **10B** in excellent yield (Scheme 7).



Scheme 6

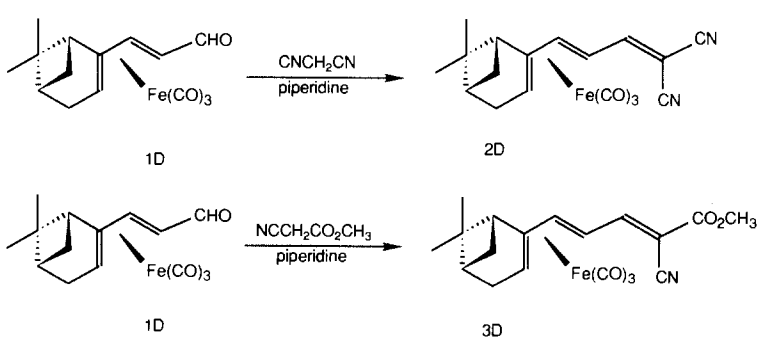


Scheme 7

The $Fe(CO)_3$ group again had migrated completely to the newly formed double bond during the condensation reaction. The fact that only one diastereomer was formed established unequivocally that the migration occurred in a concerted manner, probably via a suprafacial shift of $Fe(CO)_3$ with full retention of optical activity. This is in contrast to known thermally induced migrations of $Fe(CO)_3$ groups along an olefinic carbon chain, which lead to complete racemization [27]. The free ligand, while undergoing a similar condensation, gave only the primary alcohol adduct.

10B was reducible with DIBAH to the aldehyde complex **11B**. The organic ligand in **10B** and **11B** is an optically active sesquiterpene, although of a type that, as far as we have been able to ascertain, has not yet been found in nature.

We also investigated the reactivity of the aldehyde complex **1D** towards nucleophilic additions. We showed previously that a wide range of anionic nucleophiles react with racemic (sorbic aldehyde)$Fe(CO)_3$ [26]. **1D** reacts similarly, and condensation with malodinitrile gave product **2D** and with methylcyanoacetate produced one single diastereomer **3D** after Knoevenagel reaction (Scheme 8). The stereochemistry of **3D** at the newly formed double bond with the proton trans to the cyano group was established by analysis of the $^3J(^{13}C, ^1H)$ coupling constants, which are 12.7 Hz for $^3J(CN, H)$ and 4.3 Hz for $^3J(CO_2R, H)$. We are currently studying the reactivity of the additional double bond in this complex in enantioselective cycloadditions and catalytic hydrogenation.



Scheme 8

Table 3

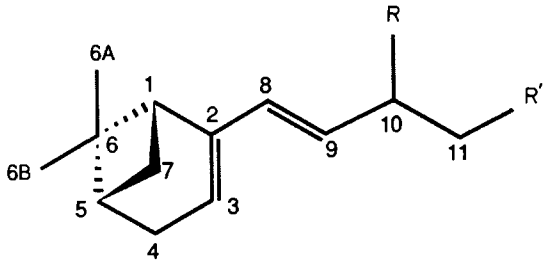
^{13}C-NMR data for the cobalt and rhodium complexes, proton-noise decoupled, 50.3 MHz, $^{1}J(^{103}Rh, ^{13}C)$ in square brackets

Compound	C-3	C-9	C-2	C-8	C-4, C-7	C-1, C-5	C-6	C-6A, B	C-10	C-11	Cp	Cp*
2A [a]	46.0	29.3	111.6	75.1	40.6	45.4	29.3	26.3			83.8	
	[16.3]	[17.8]	[6.3]	[8.4]	32.1	42.6		22.0			[5.5]	
3A [a]	42.0	37.0	110.1	76.9	37.8	45.4	38.9	26.3				94.2
	[16.5]	[18.5]	[6.5]	[7.9]	28.0	42.9		21.9				[5.9]
												10.6
4A [a]	63.3	41.0	94.5	75.9	34.2	51.9	39.4	27.1				96.0
	[13.9]	[26.1]	[6.4]	[15.2]	32.5	27.9		18.6				[5.6]
5A [a]	46.3	29.9	110.5	73.9	36.9	42.4	39.1	26.0			80.2	
					31.6	41.0		21.6				
6A [a]	59.6	31.2	110.8	96.6	32.5	43.8	37.7	26.5				94.4
					31.9	40.9		21.0				10.0
7A [a]	61.4	29.5	112.3	96.5	31.2	41.5	38.0	25.8				94.3
					29.9	32.1		20.3				9.0
5B [b]	47.9	49.4	112.5	75.5	39.8	45.0	38.3	25.9	206.8	28.3	84.6	
	[16.7]	[15.0]	[6.3]	[8.9]	31.7	41.9		21.8			[5.6]	
6B/7B [b]	46.9	60.7	109.6	74.3	40.0	44.9	30.4	26.0	69.8	24.7	84.2	
	[16.5]	[18.4]	[7.2]	[8.0]	39.8	41.9		21.8		23.7	[5.1]	
	46.8	58.6	109.4	74.0	31.7						83.9	
	[16.5]	[18.3]	[7.1]	[8.1]	31.0						[5.1]	
8B [b]	84.6	91.2*	131.2	93.7*	39.3	48.6	37.5	25.3	73.9	22.7	91.4	
	[10.5]	[6.4]	[5.1]	[6.1]	32.8	41.0		21.9	[11.5]		[6.0]	

[a] In C_6D_6. [b] In $CDCl_3$. * The assignment of these resonances may be reversed.

Table 4

^{13}C-NMR data for the organic ligands and the iron complexes, proton-noise decoupled, 50.3 MHz



Compound	C-3	C-9	C-2	C-8	C-4, C-7	C-1, C-5	C-6	C-6A, B	C-10	C-11	R	R′	CO
A [a]	124.3	109.8	147.3	138.3	31.9	41.2	37.7	26.3					
					31.3	40.5		20.7					
B [a]	124.3	143.3	146.1	134.3	32.5	41.0	37.5	25.8	197.0	27.0			
					31.0	40.6		20.5					
C [b]	147.6	113.6	145.7	135.7	32.5	40.8	37.5	25.8	173.5				
					30.8	40.3		20.4					
D [b]	152.9	125.2	145.9	136.6	32.3	40.8	37.2	25.2	193.9				
					30.5	39.9		20.2					
1A [a]	55.1	37.0	121.0	80.6	32.3	47.4	39.9	25.8					213.2
					29.7	42.5		21.7					
8A [c]	64.2	16.8	122.4	92.5	30.0	47.2	37.1	21.3					197.4
					27.9	39.0		18.1					195.3
													194.9
													194.4

1B [b]	55.4	47.4	120.6	80.9	36.4 29.7	47.3 42.0	39.9	25.7 21.8	204.1	29.6			211.1
2B [b]	53.9	62.4	117.2	81.0	36.9 29.5	47.2 42.2	39.9	25.8* 21.8	69.8	25.6*			213.1
3B [b]	89.1	98.7*	132.3	100.3*	36.0 31.2	49.2 39.7	38.3	25.0 21.6*	86.9	20.8*			202.7
4B [b]	54.5*	58.3*	118.6	82.7	36.9 29.6	47.3 42.3	39.9	25.8* 21.9	70.9	24.7*			212.9
9B [a]	53.6	63.1	116.9	81.2	37.1 29.4	47.3 42.4	39.8	25.7* 2.16	69.0	27.3	25.9*	18.8	213.7
10B [b,d]	123.1	81.9	145.0	66.1	31.3 30.5	41.5 39.8	37.6	25.8 20.1	95.6	25.7	20.0	121.1	212.6 208.5 206.7
11B [b,d]	123.9	83.1	145.3	66.8	31.8 31.0	41.7 39.8	37.8	24.9 20.1	97.7	57.0	19.3	197.4	212.3 209.2 207.5
1C [b]	72.0	30.8	142.8	114.0	32.7 26.9	47.5 39.5	41.6	25.0 21.2	171.2				
1D [b]	56.2*	48.1*	121.1	80.6	36.2 29.4	46.9 41.9		25.4 21.5	195.7				211.0
2D [b]	57.5*	46.8*	121.9	81.7	35.8 29.4	45.5 41.6	39.7	25.3 21.7	168.1	79.5		113.5 (CN) 111.8 (CN)	209.5
3D [b]	56.7*	46.8*	121.3	82.8	39.6 29.3	45.7 41.6	35.9	25.3 21.6	163.4	101.3		162.4 (CO_2R) 114.5 (CN) 46.2 (CH_3)	210.0

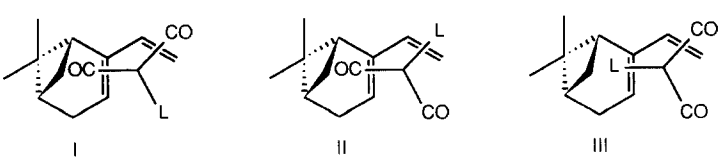
[a] In C_6D_6. [b] In $CDCl_3$. [c] In CF_3COOH. [d] At $-40°$ * The assignment of these resonances may be reversed.

All this confirms that the reactivity of a functionalized diolefin is considerably altered by metal complexation as far as regio- as well as stereoselectivity of reactions at functional groups is concerned. The $Fe(CO)_3$ group, in particular, functions as an efficient protecting and directing group, surpressing undesirable side reactions and promoting enantioselectivity.

Our final synthetic effort was directed at modification of the tricarbonyl group in **1A** by a selective displacement of one or more carbon monoxide groups by phosphine or phosphite ligands. This is known to affect the electron density at the metal and so influence the reactivity of the organic ligand [28]. In addition, replacement of two CO groups by two different ligands L^1 and L^2 generates a new chirality center at the metal, which, in conjunction with the chirality of the optically active ligand and the planar chirality of the diolefin complex itself should give rise to diastereomeric complexes (nopadiene)$Fe(CO)L^1L^2$. These could possibly be formed in unequal ratio due to optical induction.

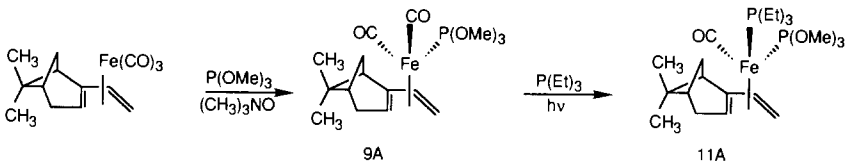
A well tested method for the displacement of one carbon monoxide group in (diene)$Fe(CO)_3$ complexes involves treatment with Me_3NO in the presence of the new ligand and the solvent MeCN [29]. We were, indeed, able to prepare the monosubstituted complexes (nopadiene)$Fe(CO)_2L$ with L = PPh_3, $P(OMe)_3$ in very good yields in this manner. Diolefin-dicarbonyl complexes of iron are known to be dynamic in solution on the NMR time scale by either ligand rotation or ψ rotation at the metal center ("turnstile mechanism") [29]. As our diolefin ligand is chiral, the CO groups of the dicarbonyl compounds are diastereotopic and two ^{13}C resonances are therefore to be expected even in the fast exchange limit. At low temperatures, three conformational isomers I–III have to be considered, and these have in fact been observed in similar racemic complexes, although isomer III is often unfavourable for steric reasons (Fig. 3) [29].

The ^{13}C-NMR spectra of (nopadiene)$Fe(CO)_2P(OMe)_3$ (**9A**) and (nopadiene)$Fe(CO)_2PPh_3$ (**10A**) at room temperature show two carbonyl signals with very different $^2J(P, C)$ coupling constants. **10A** also shows one signal at 74 ppm in the ^{31}P-NMR spectrum, which remains unchanged even on cooling to $-90\,°C$, and two IR resonances in the carbonyl region at 1973 and 1916 cm^{-1}. We conclude from these data that ligand rotation in **10A** is sufficiently hindered to allow observation of the slow exchange even at ambient temperatures and that effectively only the sterically most favourable rotamer II is present. In II, one carbonyl group is in the basal and one in the apical position of the square-pyramidal conformation of (diene)$Fe(CO)_2L$ complexes, giving rise to the two very different $^2J(P, C)$ coupling constants (2.6 and 22.1 Hz, respectively). The properties of **10A** are in contrast to those of other diene$Fe(CO)_2L$ species so far investigated, which are normally still fluxional at room temperature and on moderate cooling show at least two observable rotamers (generally I and II) in more or less equal ratio [29].



I II III

Fig. 3. Three rotamers for (diene)$Fe(CO)_2L$ complexes.



Scheme 9

9A, on the other hand, while also having only two detectable ^{13}C-NMR signals of low intensity in the carbonyl region, exhibits three resonances in the ^{31}P-NMR spectrum in an approximate ratio of 14 : 2 : 1 (188.2, 188.7 and 190 ppm) and two strong (1982, 1921 cm^{-1}) and two weak resonances (2043 and 1964 cm^{-1}) in the carbonyl region of the IR spectrum. The major component is again probably rotamer II (based on the very different ^2J(P, C) coupling constants), the other rotamers also being present at the slow exchange limit in low concentrations. This is probably due to the fact that the ligand $P(OMe)_3$ is less sterically demanding than PPh_3, while the high barrier for ligand rotation in 9A and 10A is also caused by the bulk of the bicyclic ligand.

The displacement of the second carbonyl group requires more drastic conditions, and it was known that UV irradiation of a benzene solution of a dicarbonyl complex in the presence of the second ligand L^2 gave chiral monocarbonyl complexes [29]. We utilized this method for the conversion of **9A** into (nopadiene)Fe(CO)($P(Et)_3$)($P(OMe)_3$) (**11A**). From the ^{13}C- as well as the ^{31}P-NMR spectra this complex is shown to be present as a mixture of the two possible diastereomers in an approximate ratio of 2 : 1, so that some optical induction in respect of the new chirality at the iron atom has occurred. As yet, we have been unable to separate these diastereomers, although it had been demonstrated recently that this is in principle possible by sophisticated chromatographic techniques [30].

Unfortunately, phosphine substitution in **10A** does not lead to higher nucleophilic reactivity, since this complex also does not undergo acetylation, as we had hoped it might.

We are continuing our research on the reactivity of optically active diolefin complexes in respect of their use in organic synthesis, especially in enantioselective functional group conversions.

Experimental

All experiments were carried out under nitrogen using solvents purified under nitrogen by standard procedures. $CpCo(CO)_2$ [31], $Cp^*Co(CO)_2$ [32], $[(C_2H_4)_2RhCl]_2$ [33], $[Cp^*RhCl_2]_2$ [34], TlCp [35], $TlCp^*$ [36] were prepared by published methods, (−)-myrtenal and (−)-nopol were obtained from Aldrich and Fluka, respectively. Photochemical reactions were conducted in a 300 ml vessel with a quartz finger using a 125W Philips quartz Hg-vapour lamp. ^{13}C NMR spectra were recorded on a Varian Gemini 200 spectrometer at 50.3 MHz, ^{31}P NMR on a Varian XL-200 at 81.0 MHz. Microanalysis and measurement of $[\alpha]_{589}$ values were carried out by the analytical department of the organic laboratory of the University of Zurich. IR spectra were recorded on a Biorad FST-45 spectrometer. The X-ray diffraction study of **3A** was performed on an Enraf Nonius CAD-4 diffractometer

Table 5

Details of crystal data and intensity collection

Empirical formula	$C_{21}H_{31}Rh$
Molecular weight	386.38 g mol^{-1}
Color, habit	orange needles
Crystal size	(0.35 × 0.55 × 0.58) mm^3
Space group	orthorhombic, $P2_12_12$
Unit cell dimensions	$a = 13.170(2)$, $b = 15.359(4)$, $c = 9.158(2)$ Å
(from 25 refl. with $10 < \theta < 20°$)	$\alpha = \beta = \gamma = 90.00°$
Volume	$V = 1852.5$ Å^3, $Z = 4$
Density	$d_{obs} = 1.38$ g cm^{-3}
	$d_{calc} = 1.385$ g cm^{-3}
F(000)	808 e
Absorption coefficient	$\mu = 8.21$ cm^{-1}
Radiation	Mo-K_α ($\lambda = 0.7107$ Å)
Max. transmission coefficient	0.7734
Min. Transmission coefficient	0.6538
Scan range	$2\theta_{max} = 60°$, with $-18 \leqslant h \leqslant 18$, $0 \leqslant k \leqslant 21$, $0 \leqslant l \leqslant 12$
Reflections collected	6000 (incl. standards)
Number of unique reflections	5391
Number of reflections with $I \geqslant 3\sigma(I)$	4930
Weighting scheme	$w = k/\sigma^2(F_o)$, $k = 1.2655$
Final residuals	$R = 0.0264$, $R_w = 0.0280$
Residual electron density	$(\Delta/\sigma)_{max} = 0.054$ e/Å^3
	max.: 0.75 e·Å^{-3} (0.95 Å from Rh)
	min.: −0.60 e·Å^{-3} (1.11 Å from C(6A))

with graphite monochromatized Mo-K_α radiation. ω–2θ scan data were collected at room temperature and were corrected for Lorentz and polarization effects. The details of crystal data and intensity collection are summarized in Table 5.

Crystals were grown by slow cooling of a hexane solution of **3A**. The structure was solved using the Patterson interpretation routine SHELXS86 [37] for the orthorhombic space group $P2_12_12$ chosen on the basis of data statistics, and refined by full-matrix least squares calculations minimizing $\Sigma w(\| F_o \| - \| F_c \|)^2$ with SHELX76 [38]. Atom scattering factors were from SHELX76 [38] (C, H) and from International Tables for X-Ray Crystallography [39] for the rhodium atom. All hydrogen atoms were located from the difference map. In the final refinement all hydrogen positions and their thermal parameters were kept fixed and all other atoms were refined anisotropically. Atomic coordinates and equivalent isotropic displacement parameters are listed in Table 1, and relevant bond lengths and angles in Table 2.

Synthesis of nopadiene (A)

This synthesis is an improved version of that described by Cupas and Roach [40]. A solution of 500 g *p*-tosyl chloride (2.6 mol) and 522.7 g nopol (3.14 mol) in 650 ml of $CHCl_3$ was stirred at 0 °C and 414 g pyridine were added dropwise during 30 min. The mixture was stirred for 3 h at room temperature then added to a mixture of 1600 g of ice water and 500 ml of conc. HCl. The chloroform layer was separated and the aqueous layer extracted twice with chloroform. The combined chloroform

solutions were washed with water, dried over magnesium sulfate, and evaporated first on a rotary evaporator, then under high vacuum. The thick oily residue was treated with 600 ml hexane and upon cooling to 5 °C white crystals separated. These were filtered off and washed with hexane. Further batches of crystals were obtained by cooling to −30 °C, to give a total yield of 550 g (65%) nopyl tosylate.

300 g (0.93 mol) nopyl tosylate was dissolved in 1800 ml of DMSO. 103.5 g (0.91 mol) KO^{t}Bu were added slowly.The solution was stirred for 3 h at 75 °C and then poured into 2 l H_2O. After extraction with several portions of hexane the extracts were washed with water and dried over $MgSO_4$. The solvent was evaporated and the residue distilled at 53–54 °C/10 mmHg to yield 102 g (69%) nopadiene. Anal. Found: C, 88.90; H, 10.89. $C_{11}H_{16}$ calcd.: C, 89.12; H, 10.88%. $[\alpha]_{589} = +4.9°$ (CH_2Cl_2).

*Synthesis of acetylnopadiene (**B**) [41]*

In a 500 ml round-bottom flask a mixture 25 ml acetone, 10 ml of myrtenal and 120 ml of H_2O was treated with 25 ml 10% aqueous NaOH solution with vigorous stirring. The mixture was stirred for 48 h. After two extractions with 50 ml portions of diethyl ether the organic phases were combined, dried over $MgSO_4$, and evaporated, to leave a pale yellow liquid. Yield 12 g (96%). Anal. Found: C, 81.93; H, 9.30. $C_{13}H_{18}O$ calcd.: C, 82.06; H, 9.30%. $[\alpha]_{589} = +22.3°$ (CH_2Cl_2).

*Synthesis of nopadiene acid (**C**)*

A mixture of 16.4 g malonic acid (158 mmol), 31.8 g (131 mmol) of myrtenal, 26 ml of pyridine and 1.13 g piperidine was refluxed for 1.5 h. The solution was then poured into a mixture of 80 g ice, 40 ml conc. HCl, and 130 ml H_2O. The organic phase was separated with ether, dried over $MgSO_4$ and evaporated, to leave a brown oil (36.6 g, 90%).

*Synthesis of nopadiene aldehyde (**D**)*

A mixture of 4 g of nopadiene acid (0.02 mol) and 3.7 g of $SOCl_2$ (2.3 ml, 0.03 mol) was refluxed until gas evolution ceased. The excess of thionyl chloride was removed under vacuum. To a suspension of 0.8 g $LiAlH_4$ (0.021 mol) in 100 ml of ether 4.8 g (0.064 mmol) t-butanol was added dropwise during 30 min at such a rate that the ether refluxed gently. The precipitate was allowed to settle, the ether was decanted and the residue taken up in 100 ml dry diglyme, and the solution was added at −78 °C during 1 h to a solution of 4 g of nopadiene acid chloride (obtained as above) in 100 ml diglyme. The mixture was allowed to warm to room temperature and added to 100 g of ice. After 15 h the solid was filtered off and the filtrate extracted with hexane, dried over $MgSO_4$, and passed through an Alox column, activity Grade IV. Hexane and diglyme were removed under reduced pressure at 50 °C/10 mmHg to leave a pale yellow oil. Overall yield from the acid 2.2 g (60%).

Synthesis of complexes

1A. A solution of 3.7 g of nopadiene (25 mmol) and 4.7 g of $Fe(CO)_5$ (24 mmol) in 350 ml of benzene was irradiated at 48 °C for 20 h, after which no further CO-evolution was observed. After removal of the solvent, the residue was taken up in hexane and the extract filtered through Alox (Grade II–III), then chromato-

graphed on silica gel. Removal of the solvent left a yellow oil (6 g, 84%). IR: 2044, 1979, 1964 (hexane), $[\alpha]_{589} = -457°$ (CH_2Cl_2). Anal. Found: C, 59.28; H, 5.92. $C_{14}H_{16}FeO_3$ calcd.: C, 59.30; H, 5.90%.

2A, 3A, 5B. To a suspension of 0.7 g (1.78 mmol) of $[Rh(C_2H_4)_2Cl]_2$ in 30 ml of hexane, at −50 °C was added 1.3 g of nopadiene (8.9 mmol). The solution was allowed to warm to room temperature, then refluxed for 15 min. After cooling TlCp (0.42 g, 1.78 mmol) was added, and the suspension was stirred overnight then filtered to remove thallium chloride. The solvent was removed from the filtrate under vacuum and the residue chromatographed on Alox (Grade IV) with hexane as eluant, and the product recrystallised from hexane at −78 °C. Yield 1.9 g (70%).

A similar procedure was used for **5B** starting from acetylnopadiene and for **3A** starting from TlC_5Me_5. Yields: **5B** 46%; **3A** 69%.

3A, 4A. A solution of 0.9 g $[C_5Me_5RhCl_2]_2$ (1.44 mmol) in 30 ml ethanol was treated with a five-fold excess (1.1 g, 7.10 mmol) of nopadiene and 0.7 g of Na_2CO_3. The solution was refluxed for 3 h, during which the colour changed from dark-red to yellow. The solvent was removed under reduced pressure and the residue chromatographed on Alox (Grade IV) with hexane as eluant. The hexane eluate contained both isomers in an approximate ratio of 1 : 1, yield 1.8 g (69%). These were separated by fractional crystallization from hexane, giving **3a** as orange-yellow crystals and **4A** as an orange oil. Anal. Found: C, 65.3; H, 8.1. $C_{21}H_{31}Rh$ calcd.: C, 65.3; H, 8.0%.

5A, 6A, 7A. $CpCo(CO)_2$ (1.5 g) and nopadiene (6 g) were dissolved in 100 ml hexane with stirring and the solution was irradiated at 5 °C for 3–4 h until CO-evolution ceased. The solvent and excess of the ligand were removed under vacuum and the residue chromatographed on Alox (Grade IV) with hexane as eluant. The product crystallized from hexane at −30 to −78 °C. Yield 1.3 g (58%).

A similar procedure starting from $C_5Me_5Co(CO)_2$ (1.5 g) and nopadiene (4.4 g) gave **6A/7A** (1.2 g, 60%) in an approximate ratio of 1 : 1. The isomers were separated by fractional recrystallisation.

8A. Carbon monoxide was bubbled for 15 min through a solution of 2.8 g of **1A** in 3 ml of trifluoroacetic acid at 0 °C. An equimolar amount of HBF_4 [1.1 ml of 50% aqueous solution in 3 ml $(CF_3CO)_2O$ at 0 °C] was added dropwise with vigorous stirring. CO bubbling was continued for 45 min then 100 ml was added, to produce a yellow precipitate. This was filtered off, washed with ether, and dried. Yield 2.4 g (80%). IR: 2083, 2044, 2007, 1979 (CH_2Cl_2).

9A. A mixture of 2.2 g of $(CH_3)_3NO \cdot 2H_2O$, 3.1 g of $P(OMe)_3$ and 3.6 g of **1A** in 30 ml of acetonitrile was stirred at 80 °C for 50 h, the mixture gradually turning red. The product was extracted with 5 portions of 20 ml hexane/ether (10 : 1), the extract was evaporated, and the residue purified by chromatograph on short Alox (Grade IV) with hexane as eluant. Yield 3 g (63%) of a yellow oil. IR (hexane): 2043w, 1982s, 1964w, 1922s cm^{-1}. ^{31}P NMR (C_6D_6): 188.2, 188.7, 190 ppm. ^{13}C NMR (C_6D_6, J(P, C) in square brackets): 220.5 [7.7], 215.6 [25.0] (CO); 118.0 (C-2); 80.4 (C-8); 51.4 [8.6] (C-3); 51.3 [6.6] ($P(OMe)_3$); 48.0, 43.0 (C-1, C-5); 40.5 (C-6); 33.2 [9.7] (C-9); 37.1, 30.5 (C-4, C-7); 26.4, 22.2 (C-6A, B). Anal. Found: C, 50.9; H, 6.1. $C_{16}H_{25}FeO_2P$ calcd.: C, 50.0; H, 6.5%.

10A was prepared similarly from 1.35 g $(CH_3)_3NO \cdot 2H_2O$, 4 g of PPh_3 and 1.35 g of **1A**. Yield 2.2 g (60%). IR (hexane): 1973, 1916 cm^{-1}. ^{31}P NMR (C_6D_6): 74.0 ppm. ^{13}C NMR (C_6D_6, J(P, C) in square brackets): 223.2 [2.6], 217.9 [22.1] (CO);

136.6 [38.1], 133.5 [10.9] 129.7, 128.3 [9.3] (PPh_3); 116.1 (C-2); 82.3 (C-8); 49.3 [7.3] (C-3) 47.4, 42.7 (C-1, C-5); 40.1 (C-6) 36.7 [5.2] (C-9); 36.3, 29.9 (C-4, C-7); 26.2, 21.9 (C-6A, B). Anal. Found: C, 71.2; H, 7.3. $C_{31}H_{31}FeO_2P$ calcd.: C, 71.3; H, 6.9%.

11A. A solution of 1 g (2.6 mmol) of **9A** in 350 ml of benzene was treated with 0.61 g (5.2 mmol) of PEt_3 and the mixture irradiated for 3 h. The progress of substitution was monitored by TLC. Yield 0.22 g (18%) of a mixture of two diastereomers (a) and (b) in an approximate ratio of 3 : 2. IR (hexane): 1880, 1882 cm^{-1}. ^{31}P NMR (C_6D_6, J(P, P) in square brackets): (a) 194.3 ($P(OMe)_3$, 53.0 (PEt_3), (b) 182.8 [10.4] ($P(OMe)_3$, 52.4 [9.6] (PEt_3). ^{13}C NMR (C_6D_6, J(P, C) in square brackets): (a) 219.8 [30.7, 16.2] (CO); 112.8 (C-2); 80.3 (C-8); 51.4 [7.1] ($P(OMe)_3$); 48.5 (C-3; 48.4, 43.3 (C-1, C-5); 40.9 (C-6); 36.5 (C-9); 36.1, 31.4 (C-4, C-7); 26.8, 22.4 (C-6A, B); 20.5 [20.3] (PCH_2CH_3); 8.0 (PCH_2CH_3). (b) 218.7 [40.3, 12.4] (CO); 112.1 (C-2); 78.8 (C-8), 51.3 [5.3] ($P(OCH_3)_3$); 46.1 (C-3), 46.2, 43.3 (C-1, C-5); 40.9 (C-6); 36.6 (C-9); 36.1, 31.3 (C-4, C-7); 26.7, 22.3 (C-6A, B); 21.0 [23.5] (PCH_2CH_3); 7.9 (PCH_2CH_3).

1B. A mixture of 5 g of $Fe_2(CO)_9$ (15 mmol) and 3.8 g of acetylnopadiene (**B**) in 50 ml of benzene was refluxed overnight. After removal of the solvent, the product was passed through a short column of Alox (Grade IV) then through one of silica gel with CH_2Cl_2 as eluent in both cases. Recrystallisation from hexane at −80 °C gave a yellow solid, yield 4.6 g (70%). IR (hexane): 2055, 1994, 1976 cm^{-1}. $[\alpha]_{589} = -405.6°$ (CH_2Cl_2). Anal. Found: C, 58.46; H, 5.51. $C_{16}H_{18}O_4Fe$ calcd.: 58.20; H, 5.50%.

2B. A solution of 1 g of 1B (3.3 mmol) in 25 ml of MeOH at 0 °C was treated with 1 g of $NaBH_4$ in 10 ml of H_2O, then stirred for 20 min at 0 °C and 3 h at room temperature. Methanol was partially removed under reduced pressure and the solution diluted with 40 ml of H_2O. After extraction with ether and drying and evaporation of the extract, recrystallisation of the residue from hexane gave **2B**. Yield 0.32 g (32%). $[\alpha]_{589} = -239.4°$. Anal. Found: C, 58.1 H, 5.9. $C_{16}H_{20}O_4Fe$ calcd.: C, 58.0, H, 5.8%.

3B. A solution of 1.5 g of complex **2B** in 10 ml of propionic anhydride at 0 °C was treated dropwise at 0 °C with a solution of 0.28 ml of 50% HBF_4 in 2 ml of propionic anhydride some yellow precipitate formed, and precipitation was completed by addition of 100 ml of ether. The yellow powder was filtered off, washed with ether, and dried. IR (CH_2Cl_2): 2103, 2055, 2037, 1968 cm^{-1}. $[\alpha]_{589} = -385.3°$ (CH_2Cl_2). Anal. Found: C, 47.81; H, 4.92. $C_{16}H_{18}BF_4FeO_3$ calcd.: C, 47.8; H, 4.7%.

4B. 3B (1 g, 2.49 mmol) was treated with 30 ml of H_2O. A fine precipitate formed, but redissolved after neutralisation with 10% NaOH solution. **4B** was extracted with hexane. After drying of the extract and removal of the solid a pale yellow powder remained. Yield 1 g (95%). IR (hexane): 2041, 1977, 1964 cm^{-1} $[\alpha]_{589} = -302.4°$. Anal. Found: C, 59.4 H, 6.8. $C_{16}H_{20}FeO_4$ calcd.: C, 58.0 H, 5.8%.

6B/7B. A solution of 0.28 g of **5B** in 30 ml of ether/toluene (1 : 1) was cooled to 0 °C and treated with 0.06 g $LiAlH_4$. The mixture was stirred for 10 min then further 0.04 g of $LiAlH_4$ was added, and stirring was continued for another 10 min. The excess of $LiAlH_4$ was destroyed with 2 ml of ethyl acetate and 2 ml of MeOH. The solution was dried (K_2CO_3) and the solvent evaporated. The product was dissolved in ether and the solution passed through Alox. Removal of the ether and recrystallization of the residue from pentane/ether (3 : 2) gave yellow crystals of low

melting point. Yield 0.16 g (57%). The ^{13}C-NMR spectrum showed the presence of 2 isomers in an approximate ratio of 3:2 (Table 3). Anal. Found: C, 60.8; H, 7.0. $C_{18}H_{25}ORh$ calcd.: 60.0; H, 7.0%.

8B. To a solution of 0.12 g (0.27 mmol) of **6B/7B** in 2 ml of propionic anhydride of 0°C was added dropwise a solution of 0.02 ml of 50% HBF_4 (dissolved at 0°C) in 1 ml propionic anhydride. The product was precipitated with ether, then recrystallized from CH_2Cl_2/ether to yield 0.10 g (87%) of a yellow powder. Anal. Found: C, 62.8; H, 6.7. $C_{18}H_{23}BF_4Rh$ calcd.: C, 63.1; H, 6.7%.

9B. A Grignard-reagent was prepared from 0.2 g Mg and 0.6 ml ethyl bromide in dry ether, and a solution of 1.6 g **1B** (4.8 mmol) in THF was added. The mixture was refluxed for 48 h. After hydrolytic workup, a yellow oil was isolated from the ether phase. Yield 1.0 g (57%).

10B. A solution of 1.6 ml of (30 mmol) CH_3CN in 30 ml of THF was cooled to −78°C and treated with 18.7 ml of 1.6 *M* butyllithium in hexane. Stirring was continued for 2 h at −78°C, then a solution of 3 g of **1B** in 20 ml of THF was added. The solution was stirred for another 5 h at −78°C then allowed to warm to room temperature overnight, neutralised with 10% HCl, and evaporated under reduced pressure. The residue was extracted with $CHCl_3$, and the extract filtered through Alox and finally chromatographed on LiChroprep Si-60, 15–25 μm with $CH_2Cl;_2$ as eluant. Yield 2.6 g (84%). IR (hexane): 2061, 2004, 1984 cm^{-1}. $[\alpha]_{589} = +2.1°$ (CH_2Cl_2). Anal. Found: C, 76.8; H, 9.2; N, 6.1. $C_{15}H_{19}FeNO_3$ calcd.: C, 77.8; H, 9.2, N, 6.1%.

11B. A 1 *M* solution (20 ml) of DIBAH in hexane was added dropwise at −70°C to a solution of **10B** (4.88 mmol) in 25 ml of ether. Stirring was continued for 60 min at −70°C, then for 70 h at room temperature. Excess of DIBAH was destroyed with 1 ml of MeOH and the mixture added to 50 ml of a saturated NH_4Cl solution. The mixture was stirred for 20 min then 20 ml of 10% H_2SO_4 were added. The phases were separated and the aqueous phase extracted with several portions of ether. The combined organic phases were dried then evaporated, and a solution off the residue in hexane/ether (1/1) was filtered through Alox. The solvent was removed under reduced pressure, leaving a yellow oil. IR (hexane): 2056, 2045, 1981 cm^{-1}. $[\alpha]_{589} = -50.1°$ (CH_2Cl_2). Anal. Found: C, 60.1; H, 5.2. $C_{10}H_{20}FeO_4$ calcd.: C, 60.6; H, 5.6%.

1C. A solution of 2 g of nopadiene acid (**C**) and 2 g of $Fe(CO)_5$ in benzene was irradiated at 40°C overnight. Workup as for **1A** gave, after evaporation of the hexane, yellow-brown needles, yield 2.1 g (61%). IR (hexane): 2046, 1989, 1964 cm^{-1}. $[\alpha]_{589} = -222.88°$ (CH_2Cl_2). Anal. Found: C, 55.2; H, 5.2. $C_{15}H_{16}FeO_5$ calcd.: C, 54.2; H, 4.8%.

1D. A solution of 1 g of nopadiene aldehyde (**D**) and 1.1. g of $Fe(CO)_5$ in benzene was irradiated at 40°C overnight. Workup as for **1A** gave a reddish-brown oil, yield 1.3 g (72%). IR (hexane): 2056, 1997, 1977, 1701, 1688 cm^{-1}. $[\alpha]_{589} = -262.1°$ (CH_2Cl_2). Anal. Found: C, 57.8; H, 6.1. $C_{15}H_{16}FeO_4$ calcd.: C, 56.9; H, 5.1%.

2D, 3D. Malodinitrile (0.23 g, 3.5 mmol) and 1 g (3.1 mmol) of **1D** were dissolved in 30 ml of benzene and a catalytic amount of piperidine was added. The mixture was stirred for 50 h, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was chromatographed on Alox (Grade IV) with hexane/ether (1:1) as eluant. Yield: 0.92 g (80%). IR (hexane): 2226, 2056, 1999, 1980 cm^{-1}. $[\alpha]_{589} = 0°$

(CH_2Cl_2). Anal. Found: C, 60.1; H, 3.8, N, 7.5. $C_{18}H_{16}FeO_3N_2$ calcd.: C, 59.3; H, 4.4, N, 7.7%.

A similar procedure starting from 0.35 g (3.5 mmol) of methylcyanoacetate and 1 g (3.1 mmol) of **1D** gave 0.9 g (72%) of **3D**. IR (hexane): 2054, 1997, 1976 cm^{-1}. $[\alpha]_{589} = 106.5°$ (CH_2Cl_2). Anal. Found: C, 57.8; H, 5.2, N, 3.5. $C_{19}H_{19}FeO_5N$ calcd.: C, 57.5; H, 4.8, N, 3.5%.

Supplementary material available. Tables of hydrogen atom coordinates and isotropic temperature factors, and a list of observed and calculated structure factors are available from the authors.

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