seems likely that the intermediate is a mixture of the endo and exo isomers of Cp_2Ta(cyclopentadiene)ZnCp. The initial product could not be obtained pure because of the occurrence of a subsequent reaction, which was slow at room temperature and resulted in formation of the final product $Cp_2Ta(ZnCp)_3$. This compound was characterized by ^1H and ^{13}C NMR spectroscopy (Table II) and elemental analysis. Hydrolysis gave the expected products Cp_2TaH_3, $Zn(OH)_2$, and cyclopentadiene. The mechanism of the formation of $Cp_2Ta(ZnCp)_3$ is still unclear.

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Registry No. $(Cp'_2TaH_2)_2Zn$, 87451-31-8; Cp'_2TaH_2ZnCp, 87451-32-9; $Cp'_2TaH(ZnCp)_2$ (isomer I), 87451-33-0; $Cp'_2TaH(ZnCp)_2$ (isomer II), 87507-30-0; Cp_2Zn, 11077-31-9; Cp'_2TaH_3, 41370-94-9; $Cp_2Ta(ZnCp)_3$, 87451-34-1; $Cp_2Ta(C_3H_6)H$ (endo isomer), 68586-68-5; $Cp_2Ta(C_3H_6)H$ (exo isomer), 68680-01-3; $Cp_2Ta(C_2H_4)H$, 66786-38-7; Zn, 7440-66-6; Ta, 7440-25-7.

Supplementary Material Available: Listings of structure factor amplitudes, all positional and thermal parameters, and bond distances and angles (16 pages). Ordering information is given on any current masthead page.

Optically Active Transition-Metal Compounds. 80.[1] Synthesis, Stereochemistry, and X-ray Analysis of Allylcarbonylnitrosyl(aminophosphine)iron Complexes

Henri Brunner* and Hannelore Weber

Institut für Anorganische Chemie, Universität Regensburg, D-8400 Regensburg, Germany

Ivan Bernal and George M. Reisner

Department of Chemistry, University of Houston, Houston, Texas 77004

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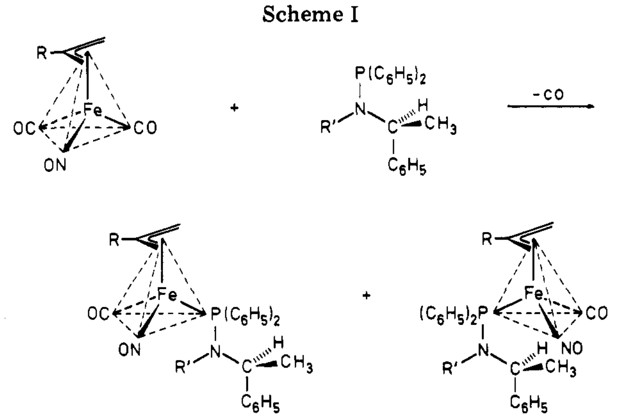
The complexes $(\eta^3\text{-}RC_3H_4)Fe(CO)(NO)(C_6H_5)_2PN(R')CH(CH_3)(C_6H_5)$ (R, R' = H, CH_3), 1-4, were synthesized by reaction of $(\eta^3\text{-}RC_3H_4)Fe(CO)_2NO$ with the corresponding (*S*)-aminophosphine. Two diastereoisomers, **b** (*RS*) and **a** (*SS*), differing only in the Fe configuration, were formed that could be separated by fractional crystallization and preparative liquid chromatography. The compounds are configurationally stable at the Fe atom up to 120 °C. The absolute configurations of diastereomers **1a** and **2b** have been determined by X-ray analysis. The conformations of a series of aminophosphine complexes are compared.

$(\eta^3\text{-}C_3H_5)Co[P(OCH_3)_3]_3$ is a homogeneous catalyst for the hydrogenation of aromatic hydrocarbons under mild reaction conditions.[2,3] $\sigma \rightleftarrows \pi$ allyl conversion and/or phosphite dissociation[4,5] is supposed to precede the activation of hydrogen at the Co center.

$(\eta^3\text{-allyl})$Fe complexes are known for a variety of ligand combinations supplementing the iron shell to rare-gas configuration. In the compounds $(\eta^3\text{-}RC_3H_4)Fe(CO)(NO)P(C_6H_5)_3$[6-8] the Fe atom is an asymmetric center.[9] With the aminophosphine ligands $(C_6H_5)_2PN(R')CH(CH_3)(C_6H_5)$[10,11] (R' = H, CH_3), derived from (*S*)-(−)-1-phenylethylamine instead of $P(C_6H_5)_3$, diastereoisomers should be formed that differ only in the Fe configuration.

Scheme I



b a

1a,b, R = H, R' = H; **2a,b**, R = H, R' = CH_3; **3a,b**, R = CH_3, R' = H; **4a,b**, R = CH_3, R' = CH_3

After separation of the diastereomer, the stability of the Fe configuration with respect to epimerization and/or

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Table I. Specific Optical Rotation (1-4 × 10^{-3} M Solutions in Benzene) and Optical Purities of Complxes 1a,b-4a,b

		fractional crystallizatn			liquid chromatography		
compd	λ, nm	$[\alpha]^{25}_{\lambda}$	optical purity, %	solubility	$[\alpha]^{25}_{\lambda}$	optical purity, %	elutn sequence
1a	578	−355	100	less soluble isomer	−350	100	first zone
	546	−290			−285		
	436	+1905			+1910		
1b	578				+345	100	second zone
	546				+260		
	436				−2215		
2a	578				−310	100	second zone
	546				−205		
	436				+2440		
2b	578	+360	86	less soluble isomer	+355	100	first zone
	546	+285			+290		
	436	−2440			−2550		
3a	578				−50	24	faster eluting
	546				−25		
	436				+100		
3b	578				+50	20	slower eluting
	546				+20		
	436				−95		
4a	578				−255	100	second zone
	546				−155		
	436				+2045		
4b	578	+245	94	less soluble isomer	+245	100	first zone
	546	+185			+185		
	436	−1510			−1575		

Table II. ^{1}H NMR Spectra[a,b] of Complexes 1a,b-4a,b in Benzene-d_6

compd	aromatic protons	*C(H)	allyl protons	$N(CH_3)$	*$C(CH_3)$	allyl CH_3
1a	1.44-2.99 (m)[c]	5.76 (m)[d]	6.32-7.40 (m)[c]		8.93 (2, 6.8)	
1b	1.44-2.99 (m)[c]	5.76 (m)[d]	6.32-7.40 (m)[c]		8.82 (2, 6.6)	
2a	1.46-3.03 (m)[c]	4.37 (8)[e]	6.54-7.36 (m)[c]	7.88 (2, 7.6)	8.64 (2, 6.4)	
2b	1.44-3.08 (m)[c]	4.33 (8)[e]	6.47-7.32 (m)[c]	7.89 (2, 7.8)	8.54 (2, 7.0)	
3a	1.48-3.02 (m)[c]	5.77 (m)[d]	6.48-7.34 (m)[c]		8.96 (2, 6.8)	9.15 (1)
3b	1.48-3.02 (m)[c]	5.77 (m)[d]	6.48-7.34 (m)[c]		8.83 (2, 6.6)	9.15 (1)
4a	1.45-3.02 (m)[c]	4.36 (8)[e]	6.53-7.21 (m)[c]	7.87 (2, 7.6)	8.64 (2, 7.2)	9.31 (1)
4b	1.45-3.09 (m)[c]	4.35 (8)[e]	6.48-7.12 (m)[c]	7.89 (2, 7.8)	8.59 (2, 7.0)	9.35 (1)

[a] Bruker WH 9o (90 MHz). τ values (Me_4Si internal standard) (multiplicities, coupling constants in Hz). [b] Integrals in accord with proposed structures. [c] Broad multiplets. [d] Splitting 1:3:1:3:3:1:3:1. [e] Splitting 1:3:1:1:3:3:3:3:3:3:3:1:1:3:1.

Table III. Summary of Data Collection and Processing Parameters

	2b	1a
space group	$P2_12_12_1$	$P4_1$
cell const		
a, Å	12.191 (6)	9.605 (3)
b, Å	13.747 (7)	
c, Å	13.906 (9)	25.161 (9)
V Å^3	$FePO_2N_2C_{25}H_{27}$	$FePO_2N_2C_{24}H_{25}$
mol wt	474.3	460.3
molecules/cell	4	4
D(calcd), g cm^{-3}	1.35	1.32
abs coeff, cm^{-1}	5.6	5.7
radiatn (Mo Kα) λ, Å	0.710 73	
collectn range	4° ⩽ 2θ ⩽ 64°	4° ⩽ 2θ ⩽ 60°
scan width, deg	Δθ = (1.00 + 0.35 tan θ)	Δθ = (0.80 + 0.30 tan θ)
max scan time, s	360	240
scan speed range, deg/min	0.38-5.03	0.31-5.03
total data collected	4077	4192
independent data with $I > 3\sigma(I)$	2081	1437
total variables	168	172
$R\ (\Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|)$	5.5	3.5
$R\ (\Sigma w(\|F_o\|-\|F_c\|)^2/\Sigma wF_o^2]^{1/2})$	4.7	2.6
weights	$w = [\sigma(F)]^{-2}$	
goodness-of-fit	4.0	0.8

phosphine exchange should be investigated.

Complex Synthesis and Diastereoisomer Separation. In the reaction of (η^3-allyl)$Fe(CO)_2NO$ derivatives with triphenylphosphine the monosubstitution products (η^3-RC_3H_4)Fe(CO)(NO)$P(C_6H_5)_3$ are obtained.[6-8] Aminophosphines $(C_6H_5)_2PN(R')CH(CH_3)(C_6H_5)$, very similar to triphenylphosphine,[12] can be used in the same reaction.

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For the synthesis of the deep red complexes 1–4 (η^3-C_3H_5)Fe(CO)$_2$(NO) or (η^3-2-$CH_3C_3H_4$)Fe(CO)$_2$(NO) is heated in benzene with the optically pure ligands (*S*)-(−)-$(C_6H_5)_2$PN(H)CH(CH_3)(C_6H_5)[10] or (*S*)-(+)-$(C_6H_5)_2$PN(CH_3)CH(CH_3)(C_6H_5)[11] (Scheme I). Depending on which of the two enantiotopic CO groups is replaced by the aminophosphine, two different configurations, *R* or *S* arise at the Fe atom. In combination with the *S* configuration at the ligand, two diastereoisomers, **b** (*RS*) and **a** (*SS*) are possible. In the reaction according to Scheme I the diastereoisomers **b** and **a** for complexes 1–4 are formed in about equal amounts, indicating a low optical induction of the *S* configurated asymmetric carbon atom in the aminophosphine ligand on the formation of the Fe configuration. Complexes 1–4 can be purified by chromatography. Diastereoisomer separation is achieved by fractional crystallization and by preparative liquid chromatography,[10,13] as described in the Experimental Section. The diastereoisomeric purities obtained are summarized in Table I.

For compounds 1 and 3, derived from the aminophosphine with R′ = H, the less soluble diastereoisomers **a** show $(-)_{578}$ rotation, whereas for compounds 2 and 4, derived from the aminophosphine with R′ = CH_3, the $(+)_{578}$ rotating isomers **b** are the less soluble diastereoisomers. In the petroleum ether/benzene chromatography, using silica for complexes 1 and 3, the $(-)_{578}$ diastereoisomers **a** are eluted first, whereas for complexes 2 and 4, the $(+)_{578}$ diastereoisomers **b** elute first. In agreement with these solubility and chromatography properties the absolute configurations of **1a** and **2b**, determined by X-ray crystallography to be *SS* and *RS*, are opposite at the Fe atoms (vide infra).

Spectra. Complexes 1-4 exhibit ν(N≡O) IR frequencies of 1937–1926 and 1693–1683 cm^{-1}, respectively (benzene solution).[14] There are no IR differences between diastereoisomers **b** and **a** for a given compound. In the mass spectrum of complex 1 the molecular ion *m/e* 460 and a fragmentation consistent with its proposed structure are observed.[14]

Table II contains the ^{1}H NMR data for compounds 1–4. The allyl protons give rise to complicated multiplets because the five protons in 1 and 2 and the four protons in 3 and 4 are symmetry inequivalent and are coupled to phosphorus. The proton H_a at the asymmetric center of the aminophosphine ligand $(C_6H_5)_2$PN(CH_3)CH_a(CH_3)(C_3H_5) is coupled to the adjacent CH_3 protons and to ^{31}P, giving a 1:3:1:3:3:1:3:1 signal with $J_{CH_3-H_a}$ = 7.0 Hz and $^3J_{P-H_a}$ = 10.7 Hz for each diastereoisomer of 2 and 4. In the corresponding complexes 1 and 3 with the aminophosphine ligand $(C_6H_5)_2$PN(H)CH_a(CH_3)(C_6H_5) there is an additional $^3J_{H-H_a}$ coupling leading to a 1:3:1:1:3:3:3:3:3:3:1:1:3:1 splitting, observed for the pure diastereomers **a** and **b**.[14]

The $(+)_{578}$ and $(-)_{578}$ components **b** and **a** of all the compounds 1–4 differ in their ^{1}H NMR spectra, especially in benzene-d_3. For the determination of the optical purity of the diastereoisomers **b** and **a** the CH_3 signals of the CH(CH_3)(C_6H_5) group are most suitable for compounds 1–3, whereas for complex 4 the CH_3 signal of the methallyl group shows the largest diastereotopic shift (Table II).

Different arrangements of the allyl and methallyl groups with respect to the fragment Fe(CO)(NO)L, L = P-$(C_6H_5)_2$N(R′)CH(CH_3)(C_6H_5), can be envisaged, analogous to the exo/endo isomers in C_5H_5Mo(CO)$_2$ allyl derivatives.[15] However, for a given diastereomer only one form was observed in the spectroscopic measurements and isomer separations of the present study.

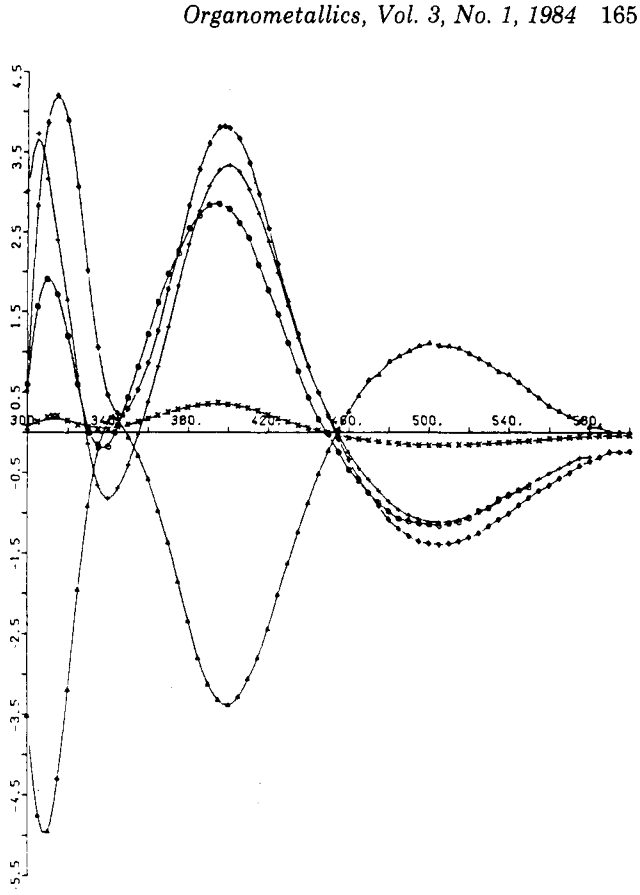

Figure 1. CD spectra of the following: ○, (−)-**1a**; △ (+)-**2b**; +, (−)-**2a**; ×, (−)-**3a**; ◇, (−)-**4a** ((2–6) × 10^{-3} M solutions in benzene; optical purity, see Table I (Jasco J-40A); Ordinate scale $[\theta]_\lambda$ [grad·L/mol·cm].

In Figure 1 the CD spectra of the $(-)_{578}$ diastereomers **1a**–**4a** are shown.[14] The CD spectra of the $(+)_{578}$ and $(-)_{578}$ diastereomers **2b** and **2a** demonstrate that the optical activity of these compounds is mainly determined by the metal chromophor leading to an almost mirror-image appearance for diastereoisomers, differing only in the Fe configuration.[9]

Configurational Stability and Ligand Exchange. Heating of a solution of optically pure **1a** in benzene-d_6 in an evacuated and sealed ^{1}H NMR tube does not lead to epimerization up to 120 °C, demonstrating a remarkable configurational stability at the Fe center. At 125 °C, the signals of diastereomer **1b** appear, in the course of hours, accompanied by some decomposition. The same observations were made with a benzene-d_6 solution of **4b**. The epimerization of **1a** is not accelerated by an equimolar addition of the aminophosphine $(C_6H_5)_2$PN(H)CH(CH_3)(C_6H_5) which is the ligand in **1a**,**b**. Furthermore there is no ligand exchange between **1a**, containing the aminophosphine $(C_6H_5)_2$PN(H)CH(CH_3)(C_6H_5), and added $(C_6H_5)_2$PN(CH_3)CH(CH_3)(C_6H_5) during the epimerization, which would be easily detectable on the basis of the different chemical shifts and coupling constants of the *N*-methyl groups of coordinated and uncoordinated $(C_6H_5)_2$PN(CH_3)CH(CH_3)(C_6H_5).[11] These observations are in accord with an intramolecular mechanism for the change in configuration at the Fe atom, although a detailed study

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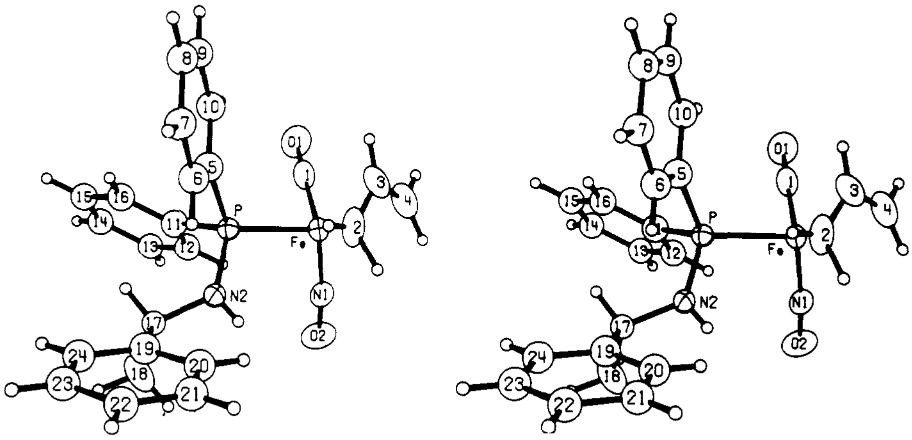

Figure 2. Stereo pair of compound 1a. The carbon atoms are labeled by their numbers only. The thermal ellipsoids are 50% equiprobability envelopes for the heavy atoms and are of arbitrary, convenient, size for the hydrogen atoms.

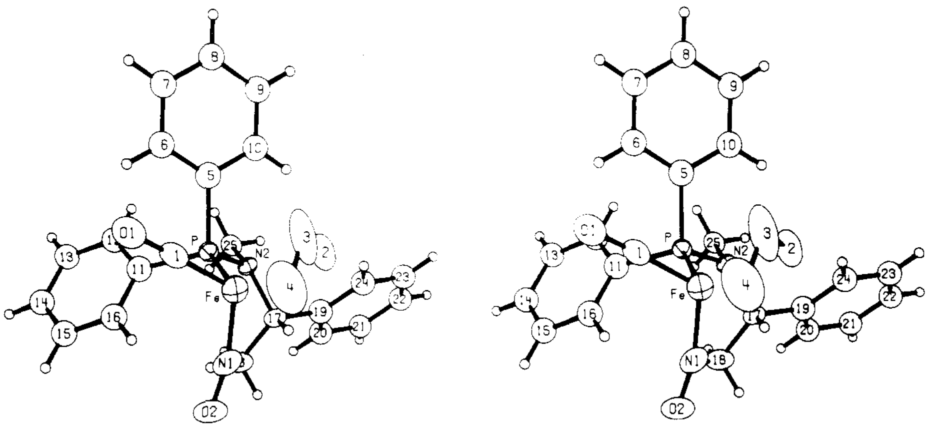

Figure 3. Stereo pair of compound **2b**

is prevented by the limited range of configurational lability before and onset of thermal decomposition. Pseudorotational processes seem most probable because compounds **1** and **2** possess approximately trigonal-bipyramidal structures, as shown by the X-ray structure analyses of **1a** and **2b**.

Crystallographic Results. Details of intensity data collection and structure refinement are described in the Experimental Section. Atomic parameters (Tables IV and V) have been deposited. Bond distances and angles are given in Tables VI and VII. Figures 2 and 3 represent stereo drawings of compounds **1a** and **2b**, respectively. The molecules of both compounds consist of a central iron atom surrounded by the phosphorus of the $(C_6H_5)_2PN(R')CH(CH_3)(C_6H_5)$ group, carbonyl, nitrosyl, and the $(\eta^3\text{-}C_3H_5)$ ligand. If allyl bonding to iron is assumed via the two terminal carbon atoms ignoring the central allyl C atom, then the coordination polyhedron may be viewed as trigonal bipyramidal. Such a geometry is common for $Fe(CO)_5$ derivatives, e.g., the recently determined $Fe(CO)_4P(C_6H_5)_3$.[16] Our compounds can be viewed as being derived from $Fe(CO)_4PR_3$ by the substitution of three CO's by one NO and the allyl. Thus, the basal plane of the pyramid is defined by CO, NO, and C2 (one of the allyl terminal carbons), the axial positions being occupied by C4 and the phosphine P atoms. The bulky aminophosphine ligand occupies the axial position as does $P(C_4H_5)_3$ in $Fe(CO)_4P(C_6H_5)_3$, and the allyl, having a small bidentate ligand bite, spans across an axial and an equatorial position for which the steric requirements are less than for a pair of equatorial ones. Another consequence of the small bite of the allyl system is that the angle C4–Fe–P is only about 150° (Table VII). The dihedral angle between the plane of the allyl carbons (C2–C4) and the basal plane (M, C1, C2) is about 50° for both compounds. A major objection to the omission of the central carbon (C3) from the above considerations is that, of the three Fe–C(allyl) distances, it is the shortest in both cases (Table VI).

Assuming with Eisenberg[17] that the allyl ligand is considered a single binding point (i.e., either use C3 or the center of mass of the allyl ligand) the coordination polyhedron around iron is an approximate tetrahedron with angles ranging from 90 to 120° for **2b** and 93 to 119° for **1a**.

These results are similar to those obtained for $(\eta^3\text{-}C_3H_5)Ru(NO)[P(C_6H_5)_3]_2$.[17] However, such values of the angles as 90° are rather extreme to be accepted as "tetrahedral" values. If we adopt the square-pyramidal model advocated by Muetterties, who reported the structure of $(\eta^3\text{-}C_8H_{13})Co[P(OCH_3)_3]_3$,[18] and by Harlow, who studied $(\eta^3\text{-}C_8H_{13})Fe[P(OCH_3)_3]_3$,[19] for our com-

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Table VI. Intramolecular Bond Distances (Å)

	2b	1a
Fe-P	2.245 (3)	2.222 (1)
Fe-C1	1.713 (11)	1.753 (5)
Fe-N1	1.677 (10)	1.646 (4)
Fe-C2	2.202 (11)	2.142 (5)
Fe-C3	2.112 (14)	2.084 (5)
Fe-C4	2.151 (12)	2.117 (6)
C1-O1	1.174 (11)	1.163 (5)
N1-O2	1.162 (10)	1.168 (4)
C2-C3	1.352 (16)	1.347 (8)
C3-C4	1.481 (20)	1.419 (9)
P-N2	1.671 (7)	1.671 (3)
P-C5	1.819 (5)	1.822 (2)
P-C11	1.840 (5)	1.837 (2)
N2-C17	1.486 (10)	1.464 (4)
N2-C25	1.473 (9)	
N2-H1		0.77 (4)
C17-C18	1.531 (11)	1.545 (6)
C17-C19	1.504 (10)	1.513 (5)
Fe-Cent[a]	1.879 (13)	1.852 (5)

[a] Cent = the geometric center of the π-allyl ligand.

in the case of compounds **2b**) is somewhat distorted. As can be seen from Figure 3 the temperature factors of the (η^3-C_3H_5) group are relatively high. In view of the low R factor attained and since the geometry of the rest of the compound is reasonable and in close agreement to values found in the literature, we relate these problems to the ability of the π-allyl group to undergo librational motion.

The differentiation between the carbonyl and nitrosyl ligands was arrived at by the details of the refinement (in terms of temperature factors and R values). Thus, two identical least-squares refinements differing only in the mutual assignment of the nitrosyl and carbonyl groups were performed for both compounds. In the case of compound **2b**, for instance, the assignment, hereafter considered to be the correct one, gave a lower R factor (6.6% vs. 6.8%). Also, the isotropic temperature factors (U_{iso}) of carbon and nitrogen when incorrectly assigned were 0.05 and 0.10 A°^{2}, respectively, whereas the correct assignment resulted in both temperature factors being almost equal (close to 0.07 Å^2). Similar differences between the two assignments were found also in the case of compound **1a**. The proper choice of NO and CO ligands lead to Fe–N distances of 1.646 (4) and 1.677 (10) Å and Fe–Co bond lengths of 1.753 (5) and 1.713 (11) Å which are all in excellent agreement with the values reported in the literature.[41-43] Therefore, the differentiation between CO and NO is sound, and this implies that there is no crystallographic disorder or diastereoisomer mixture at the central atom.

Table VII. Intramolecular Bond Angles (deg)

	2b	1a
P-Fe-C1	90.0 (4)	93.3 (2)
P-Fe-N1	105.0 (3)	101.1 (1)
C1-Fe-N1	114.2 (5)	116.8 (2)
P-Fe-C2	89.6 (3)	87.9 (2)
P-Fe-C4	152.3 (5)	149.3 (2)
N1-Fe-C2	117.2 (5)	111.2 (2)
N1-Fe-C4	100.3 (6)	104.7 (3)
C1-Fe-C2	126.7 (5)	130.6 (3)
C1-Fe-C4	89.9 (6)	89.7 (3)
C2-Fe-C4	68.5 (5)	67.4 (2)
Fe-C1-O1	177 (1)	177.5 (5)
Fe-N1-O2	166 (1)	170.4 (4)
C2-C3-C4	120 (2)	117.5 (7)
Fe-P-C5	112.2 (2)	116.0 (1)
Fe-P-C11	113.4 (2)	115.2 (1)
Fe-P-N2	117.2 (2)	109.1 (1)
C5-P-C11	102.5 (3)	104.2 (1)
C5-P-N2	102.8 (3)	105.5 (2)
C11-P-N2	107.2 (3)	106.1 (2)
P-N2-C17	120.3 (5)	127.1 (3)
P-N2-C25	117.8 (5)	
C17-N2-C25	113.7 (5)	
N2-C17-C18	112.8 (8)	111.2 (4)
N2-C17-C19	110.2 (7)	112.4 (3)
C18-C17-C19	114.4 (8)	111.3 (3)
Cent[a]-Fe-P	118.4 (3)	116.3 (2)
Cent-Fe-C1	106.0 (3)	107.7 (2)
Cent-Fe-N1	119.6 (3)	118.9 (2)

[a] Cent = center for the π-allyl ligand.

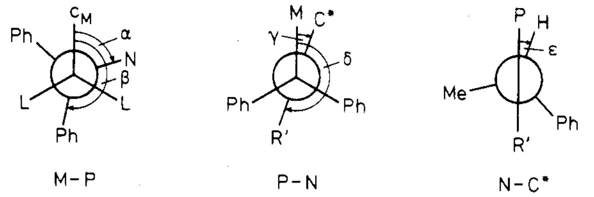

Figure 4. Newman projections and conformational parameters α–ε for the aminophosphine complexes **1a**, **2b**, and **5–8** in Table VIII.

pounds, then the square base would be defined by the two terminal alkyl carbons C2 and C4, by the carbonyl carbon C1, and P. The unique axial ligand would be the nitrosyl N1. In both cases **2b** and **1a**, the Fe atom is above the basal plane by 0.65 and 0.63 Å, respectively, displaced toward the nitrosyl N1. However, the atoms defining the "best least-squares planes" for the square base have deviations as large as 0.21 and 0.16 Å in **2b** and **1a**, respectively.

The π-allyl ligand is coordinated in an η^3 fashion to the Fe atom. The central carbon atom of the π-allyl fragment in **1a** and **2b** is somewhat closer to the iron atom (2.084 (5) and 2.112 (14) Å) than the terminal atoms (2.142 (5), 2.117 (6) and 2.202 (11), 2.151 (12) Å). In previously studied π-allyl iron complexes the corresponding distances range from 2.03 to 2.09 Å and 2.09 to 2.20 Å, respectively.[34-40] The geometry of the π-allyl fragment (especially

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Table VIII. Conformational Parameters α–ε (deg) for Aminophosphine Complexes 1a, 2b, and 5–8 As Defined in Figure 4

compound	α	α′	β	γ	δ	ε
$C_3H_5Fe(CO)(NO)P(Ph)_2N(H)CH(Me)(Ph)$ (1a)	−86.0	32.8	−205.1	−5.2[a]	−164.5[a]	−12.4
$C_3H_5Fe(CO)(NO)P(Ph)_2N(Me)CH(Me)(Ph)$ (2b)	+70.7	−47.9	+196.4	+32.7	+179.2	−36.6
$C_5H_5Mo(CO)(NO)P(Ph)_2N(Me)CH(Me)(Ph)$ (5)[23]	+64.7	−51.0	+193.2	+36.0	+181.7	−45.0
$C_7H_7Mo(CO)(I)P(Ph)_2N(Me)CH(Me)(Ph)$ (6)[24]	+69.6	−50.3	+193.2	+28.7	+185.2	−24.8
$C_6H_6Ru(Me)(SnCl_3)P(Ph)_2N(H)CH(Me)(Ph)$ (7)[25]	+68.6[b]	−48.0	+189.6[b]	+5.7[a]	+174.8[a]	+12.1
$C_5H_5Fe(CO)(COMe)P(Ph)_2N(H)CH(Me)(Ph)$ (8)[26]	+70.7[b]	−49.7	+192.1[b]	−27.5[a]	+172.6[a]	+31.9

[a] γ/δ interchange with respect to Figure 4 (P–N): N–R′, R′ = H, eclipses M–P; N–C* staggers the two P–Ph bonds. [b] α/β (gauche/trans) interchange with respect to Figure 4 (M–P) because of strong intramolecular H bonds.

Table IX. Yields, Properties, and Analytical Data for Complexes 1–4

compd	yield, %	mp, °C	color	formula (mol wt)		anal. C	anal. H	anal. N
1a,b	77	133–135 dec	dark red	$C_{24}H_{25}FeN_2O_2P$ (460.3)	calcd	62.63	5.47	6.09
					found	63.00	5.30	6.17
2a,b	91	150–153 dec	dark red	$C_{25}H_{27}FeN_2O_2P$ (474.3)	calcd	63.31	5.74	5.91
					found	63.31	5.65	5.80
3a,b	93	oil	dark red	$C_{25}H_{27}FeN_2O_2P$ (474.4)				
4a,b	87	168–171 dec	dark red	$C_{26}H_{29}FeN_2O_2P$ (488.4)	calcd	64.02	5.99	5.74
					found	63.87	5.87	5.85

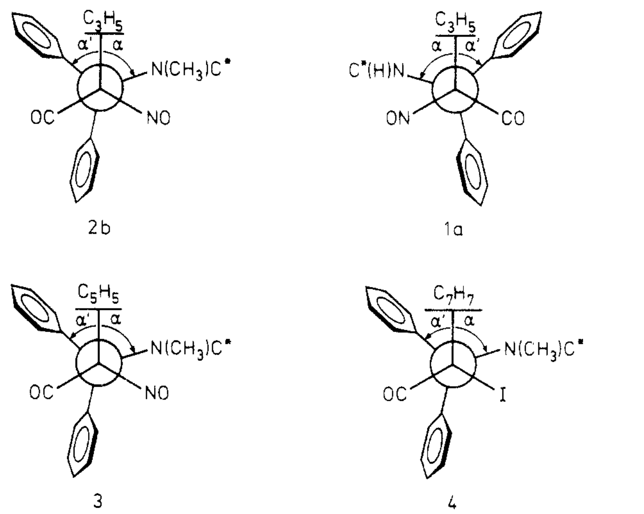

Figure 5. Newman projections and phenyl chirality in the $P(C_6H_5)_2$ groups for the aminophosphine complexes 1a, 2b, 5, and 6.

The Fe–P distances observed for compounds **2b** and **1a** are 2.245 (3) and 2.222 (1) Å. The variations in the Fe–P distances are usually small[44] and are a result of changes in the substituents at the phosphorus as was demonstrated by Sim and co-workers.[45] The values obtained by us are close to the mean value of 2.229 Å calculated for various Fe–P distances.[44] The P–C distances average 1.830 Å, which compares well with the value found in the free $P(Ph)_3$.[46] The P–N distance of 1.671 (7) Å is close to that found in tetrametaphosphimic acid.[47] The average N–C distance of 1.479 Å is that expected for a pure single bond.[48]

Determination of the Absolute Configuration. The absolute configuration of compounds **1a** and **2b** was determined by the Bijvoet method.[20] For compound **1a**, 16 reflections showed marked differences between $F_c(hkl)$ and $F_c(\bar{h}\bar{k}\bar{l})$ (Table XA), whereas for compound **2b** 24 such reflections were found (Table XB). These reflections were measured, and the results show that the coordinates initially chosen for both compounds correspond to the wrong enantiomer. *The two structures were then further refined in their correct absolute configuration to the final agreement factors given in Table I.* The coordinates listed in Tables IV and V are those of the correct enantiomer, and Figures 2 and 3 depict the compounds in their correct absolute configuration.

When the extension of the *R*, *S* system is applied to organometallic complexes, the ranking order of ligands is (η^3-C_3H_5) > P > N1 > C1[9,21,22] and consequently the configuration around the Fe atom is *S* for **1a** and *R* for **2b**. An internal check on this result is that the Bijvoet test correctly predicts that the chiral carbon of the aminophosphine in **1a** and **2b** is *S*, a fact unknown to the crystallographers before the determination of the absolute configuration.

Conformations. The conformations in **1a** and **2b** will be discussed with respect to the three Newman projections Fe–P, P–N, and N–C* shown in Figure 4. Looking down the Fe–P bond (iron part front, phosphorus part back, allyl centroid C_M up, with C_M = allyl center of mass), it is obvious that molecules **1a** and **2b** adopt a staggered conformation. Such a staggered conformation is typical for triphenylphosphine derivatives of the type C_MLLM–$P(C_6H_5)_3$. With an aminophosphine ligand, $P(C_6H_5)_2N(R')CH(CH_3)(C_6H_5)$, R′ = H, CH_3, instead of triphenylphosphine the additional question arises, whether the nitrogen substituent occupies a gauche or the trans position with respect to C_M. Previously we had examined four other structures of $C_MLL'M$ aminophosphine complexes in which C_M = C_7H_7, C_6H_6, and C_5H_5, M = Mo, Ru, and Fe, and L, L′ = CO, I, CH_3, $SnCl_3$, NO, and $COCH_3$.[23-26] For comparison with **1** and **2** the formulas and the relevant conformational parameters α–ε for compounds **5–8**, as defined in Figure 4, are given in Table VIII. It is remarkable how similar the conformations in these molecules are, although C_M comprises seven-membered, six-membered, and five-membered rings and the allyl moiety.

In compound **2b** the methylated nitrogen substituent occupies the gauche position between C_M and NO with α = 70.7°. Very similar gauche angles are observed for the

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$N(CH_3)$ aminophosphine complexes **5** and **6**, in which $N(CH_3)C^*$, with $C^* = CH(CH_3)(C_6H_5)$, staggers C_5H_5/NO and C_7H_7/I, respectively (Table VIII). Compound **1a**, though H substituted at the aminophosphine nitrogen, is related to the $N(CH_3)$ derivatives **2b**, **5**, and **6** having a gauche angle, $\alpha = -86.0°$, NHC* lying between C_3H_5 and NO. The NH derivatives **7** and **8**, however, have the NHC* substituent in the position trans to C_M.[25,26] The reason is that in **7** and **8** strong intramolecular hydrogen bonds from the NH group to the acetyl oxygen and to a $SnCl_3$ chlorine are formed, which are conformation determining and override the normal gauche conformation for aminophosphine complexes with the fragment $C_MLL'M$.

The conformations about the P–N bond are determined by the fact that the substituents at the nitrogen atom are almost in a plane. Measures for the degree of planarity/pyramidality at N2 are the three bond angles at N2 (Table VII) and the difference $\delta-\gamma$ (Table VIII, Figure 4). In structures **2b**, **5**, and **6** N–CH_3 staggers the two phenyls at phosphorus, whereas N–C* eclipses P–M as shown by the small angles γ, allowing for good π overlap in the system N–P–Fe.[16,27,28] Compound $Co(CO)_3[Sn(CH_3)_2C(C_3H_5)_3](C_6H_5)_2PN(CH_3)CH(CH_3)(C_6H_5)$,[29] trigonal bipyramidal at the Co atom, is completely analogous to **2b**, **5**, and **6** with respect to the conformation about the P–N bond. The same π overlap is possible in **1a**, in which the orientations of N–H and N–C* are reversed compared to Figure 4. In **1a** N–H eclipses P–M and N–C* staggers the two P–$C(C_6H_5)$ bonds.

The conformations with respect to the N–C* bond are similar for compounds **1a**, **2b**, and **5–8**. The nitrogen substituent CH_3 or H is between the CH_3/C_6H_5 substituents at C*, and the P–N and C*–H bonds are almost eclipsed as evident from the torsional angles, at P–N–C*–H, ϵ in table VIII. This arrangement orients the C*–H bond in the $N(CH_3)$ compounds **2b**, **5**, and **6** in the direction of C_M/L (C_3H_5/NO in **2b**, C_5H_5/NO in **5**, and C_7H_7/I in **6**), avoiding steric hindrance.

The angle $\alpha = 70.7°$ between C_M–Fe and P–N of compound **2b** is much larger than the angle $\alpha' = -47.9°$ between C_M–Fe and P–$C(C_6H_5)$ of the gauche phenyl. So, the substituent seems to be repelled by the π-bonded allyl and the gauche phenyl comes quite close to it (Figure 5). To expose its face toward the π-bonded allyl is the best orientation of this gauche phenyl. In an edge exposed orientation its ortho hydrogens would come too close to the allyl H atoms. Since in the Newman projection of **2b**, in Figure 5, the π-bonded hydrocarbon is in front and the phenyl substituent in the back, the consequence of this face exposure is that the front half of the gauche phenyl points down and the rear part up.

The two phenyl planes of a $P(C_6H_5)_2$ group frequently are nearly perpendicular to each other.[30] In compound **2b** this angle is 62.5° thus, the gauche phenyl seems to control the orientation of the phenyl trans to the allyl moiety in bending its front half to the right and its rear half to the left.

The same geometrical situation is found for compounds **5** and **6** containing C_5H_5 and C_7H_7 in place of allyl (Figure 5). In the allyl complex **1a** and Fe atom has the opposite absolute configuration with respect to **2b**. Therefore in the Newman projection the NO and CO ligands are reversed, the NHC* substituent is on the left side, and the opposite chirality is imposed on the two phenyl groups (Figure 5). Summarizing, the chiral arrangement of the *P*-phenyls in aminophosphine complexes of type **1a**, **2b**, **5**, and 6 seems to be controlled by the repulsion between the π-bonded hydrocarbon and the gauche N substituent, the face exposure of the gauche phenyl, and the consequent response of the trans phenyl which is acquiring an approximately perpendicular orientation to the gauge phenyl. Instead of a repulsion between π-bonded hydrocarbon and N substituent, an attraction between π-bonded ligand and a face exposed gauche phenyl, observed in other system,[31,32] would also account for the observations and conclusions drawn.

Table X. Determination of Absolute Configuration for Compounds 1a and 2b

indices	$F_c(hkl)$	$F_c(\bar{h}\bar{k}\bar{l})$	$F_c(hkl)/F_c(\bar{h}\bar{k}\bar{l})$	$F_o(hkl)/F_o(\bar{h}\bar{k}\bar{l})$
		A. Compound 1a		
1,3,1	44	47	0.94	1.07
2,3,1	42	39	1.08	0.94
5,6,1	32	30	1.07	0.97
6,6,1	17	19	0.89	1.16
2,4,2	23	21	1.09	0.92
2,6,3	12	14	0.86	1.14
5,6,3	9	12	0.75	1.33
1,7,4	11	9	1.22	0.88
2,8,4	25	27	0.92	1.08
2,5,5	40	37	1.08	0.95
3,3,6	24	28	0.86	1.17
5,5,6	28	31	0.90	1.14
4,7,6	32	30	1.07	0.95
$\bar{1}$,5,1	24	26	0.92	1.09
$\bar{3}$,6,1	32	35	0.91	1.09
$\bar{1}$,6,1	23	21	1.09	0.95
		B. Compound 2b		
4,5,1	24	27	0.89	1.09
5,5,1	19	22	0.86	1.13
1,4,1	35	31	1.13	0.90
3,3,1	38	41	0.93	1.08
6,3,1	37	35	1.06	0.93
3,2,2	29	31	0.93	1.08
2,3,2	61	57	1.07	0.95
6,4,2	26	28	0.93	1.07
2,5,2	33	31	1.06	0.95
1,6,2	29	25	1.16	0.89
5,7,2	20	23	0.87	1.15
3,4,3	20	18	1.11	0.91
6,2,3	27	25	1.08	0.93
4,2,3	17	15	1.13	0.85
3,2,3	20	18	1.11	0.94
3,1,3	27	29	0.93	1.08
4,1,3	28	26	1.08	0.92
6,1,4	34	36	0.94	1.06
2,1,4	31	29	1.07	0.94
1,2,4	23	25	0.92	1.06
4,2,4	18	20	0.90	1.06
1,3,4	35	33	1.06	0.93
2,7,4	32	30	1.07	0.95
3,8,5	25	23	1.09	0.95

Experimental Section

All operations were carried out in N_2 atmosphere by using dry solvents.

Synthesis of (η^3-RC_3H_4)Fe(CO)(NO)$(C_3H_5)_2$PN(R')CH(CH_3)(C_6H_5) (1–4). A 20-mmol sample of (η^3-RC_3H_4)$Fe(CO)_2NO$[7] and the equivalent amount of the aminophosphine $(C_6H_5)_2PN(R')CH(CH_3)(C_6H_5)$[10,11] were heated in 100 mL of benzene for 25 h at 50 °C. The solvent was evaporated, and the dark red oil was purified by chromatography at SiO_2. With petroleum ether, unreacted (η^3-RC_3H_4)$Fe(CO_2NO$ and $(C_6H_5)_2PN(R')CH(CH_3)(C_6H_5)$ were eluted as a broad dark red band. A mixture of petroleum ether/benzene (2:1 for complexes **1** and **2**; 4:1 for complexes **3** and **4**) gave a broad dark red band containing complexes **1–4**, respectively.

Complex **3** (yield 93%) was a dark red oil. Yields, melting points, and analytical data for complexes 1, 2, and 4 are summarized in Table IX.

Separation of the Diastereoisomers a and b of the Complexes $(\eta^3\text{-}RC_3H_4)Fe(CO)(NO)(C_6H_5)_2PN(R')CH(CH_3)(C_6H_5)$(1–4). Fractional Crystallization. A 4-g (8.7-mmol) sample of **1a,b** was dissolved in a mixture of 45 mL of petroleum ether and 15 mL of ether. The red solution, cooled to −30 °C for 3 days, gave a crystalline precipitate. This procedure, repeated 10 times with the crystalline fraction using reduced solvent quantities, yielded the less soluble diastereomer **1a** in 100% optical purity.

The more soluble diastereomer was obtained from the mother liquor of the first crystallization. The mother liquor was concentrated and cooled to −30 °C, whereby part of the remaining less soluble diastereomer crystallized. After five repetitions of this operation followed by evaporation of the resulting mother liquor, the solution gave an oil in which the more soluble diastereomer **1b** was enriched to 80% optical purity.

The diastereomer mixtures of **2a,b** were separated similarly; the optical purities obtained are given in Table I.

The diastereoisomers of **3a,b** cannot be separated in the same way because the less soluble did not crystalline at −30 °C. When the mixture was cooled to −60 °C, an oil precipitated that cannot be solidified. This operation led only to an enrichment of 20% for **3a** in the oil and **3b** in the resulting solution (Table I).

Diastereomer Separation by Preparative Liquid Chromatography. The chromatography was carried out with Merck Lobar columns type B filled with LiChroprep Si 60 (40–63 μm): eluent petroleum ether/benzene (8:1), pressure 1–2 bar, substrate between 500 mg and 1 g, dissolved in 5 mL eluent (if necessary with some additional benzene). For the complexes **2a,b** and **4a,b** twofold passage through the two-column setup, described previously,[10,13] gave two completely separated zones in approximately 6 h, containing the diastereomers **a** (second zone) and **b** (first zone), respectively, in optically pure form. For complexes **1a,b** the bands overlapped appreciably after the same passage through four columns. Diastereomer **1a** can be obtained optically pure from the front part and diastereomer **1b** from the back part of the zone. The overlap area was discarded.

Compounds **3a,b** were passed three times through the two-column system which resulted only in a broadening of the red zone. Four equal fractions were collected. The first, enriched in **3a**, and the last, enriched in **3b**, were chromatographed through another two columns, the bands being cut into three fractions, respectively. The best enrichments obtained are given in Table I.

X-ray Intensity Data Collection and Structure Solution. Intensity measurements were carried out with an Enraf-Nonius CAD-4 computer-controlled diffractometer. A summary of the crystallographically important parameters for data collection and processing are given in table III.

All data processing and calculations were carried out by using the SHELX-76 system of programs.[33] The structure were both solved by the Patterson method. Since there was no reason to expect any distortions of the phenyl rings, these were refined as rigid bodies (with the carbon–carbon bonds being 1.395 Å) with idealized hydrogens (C–H = 0.97 Å). The methyl groups were also treated as rigid bodies. The remaining non-hydrogen atoms were refined anisotropically.

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Registry No. **1a**, 87555-33-7; **1b**, 87585-10-2; **2a**, 87555-34-8; **2b**, 87585-11-3; **3a**, 87555-35-9; **3b**, 87585-12-4; **4a**, 87555-36-0; **4b**, 87585-13-5; $(\eta^3\text{-}C_3H_5)Fe(CO)_2NO$, 12071-54-4; $(\eta^3\text{-}CH_3C_3H_5)Fe(CO)_2NO$, 34664-02-3.

Supplementary Material Available: Tables of observed and calculated structure factor amplitudes and atomic coordinates and temperature factors for compounds **1a** and **2b** (Tables IV and V) (24 pages). Ordering information is given on any current masthead page.

Formate Formation during $Co_2(CO)_8/PR_3$-Catalyzed Hydroformylation

Clayton D. Wood and Philip E. Garrou*

Central Research—New England Laboratory, Dow Chemical U.S.A., Wayland, Massachusetts 01778

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Careful examination of phosphine-modified cobalt hydroformylation (2000 psig, CO/H_2 = 1:2, 190 °C, Co/P = 1:1) as a function of PR_3 reveals that moderate selectivity to formates can be achieved depending on the cone angle of the PR_3 ligand chosen. These results are rationalized in terms of a stabilization or destabilization of a carboalkoxycobalt intermediate. Formate yields as high as 46% have been achieved with PEt_3 at 4000 psig. The organometallic species present in the reaction are examined in detail for $Co_2(CO)_8/PR_3$ (PR_3 = PCy_3, PEt_3, and PPh_3) by ^{31}P NMR and IR spectroscopy.

Introduction

Recent observations concerning synthesis gas reactions in general and the hydroformylation reaction in particular[1–3] have led us to examine the formation of formates during $Co_2(CO)_8/PR_3$-catalyzed hydroformylation reactions. Hydroformylation has been the topic of scores of research publications and review articles.[4–7] The reaction is known to proceed via aldehydes to alcoholic products

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