

# Synthesis and Structure of Chiral Rhenium Allyl Complexes of the Formula $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}_2\text{C}(\text{R}')=\text{CHR})$

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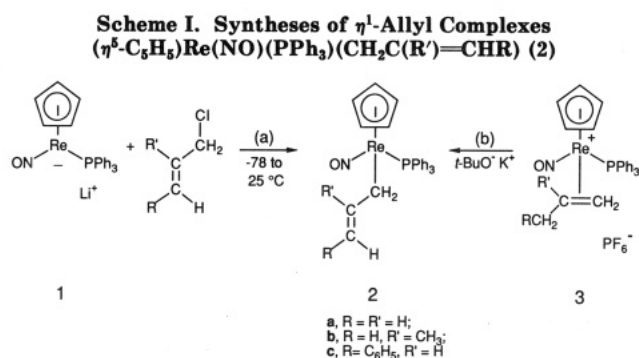
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Reaction of  $\text{Li}^+[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)]^-$  with allyl, methallyl, and cinnamyl chlorides gives  $\eta^1$ -allyl complexes  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}_2\text{C}(\text{R}')=\text{CHR})$  (**2a-c**) in 72–93% yields. Complexes **2** are also prepared (70–84%) by reaction of  $t\text{-BuO}^-\text{K}^+$  with alkene complexes  $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{H}_2\text{C}=\text{C}(\text{R}')\text{CH}_2\text{R})]^+ \text{PF}_6^-$  and are characterized by NMR, IR, and mass spectroscopy. The crystal structure of **2c** (monoclinic,  $P2_1/n$ ,  $a = 13.509$  (3) Å,  $b = 14.871$  (2) Å,  $c = 14.698$  (3) Å,  $\beta = 112.54$  (1)°,  $Z = 4$ ) shows two conformations of the cinnamyl ligand which differ primarily in orientation about the  $\text{C}_\alpha\text{-C}_\beta$  bond. Difference  $^1\text{H}$  NOE experiments on **2c** and **2a** suggest the presence of analogous conformations in solution.

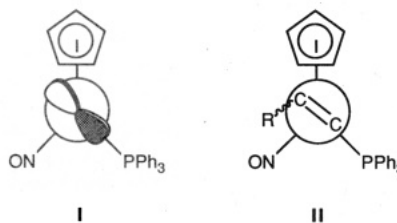
## Introduction

Numerous transition-metal  $\eta^1$ -allyl complexes have been prepared.<sup>3–5</sup> They undergo a variety of interesting transformations, many of which involve electrophilic attack at the  $\text{C}_\gamma$  allyl terminus. Rosenblum has in particular pioneered the chemistry of "FP" allyl complexes  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{CHR}'\text{C}(\text{R}')=\text{CHR})$  and developed a number of stoichiometric reactions that have utility in organic synthesis.<sup>3</sup> However, there have been surprisingly few studies of chiral-at-metal  $\eta^1$ -allyl complexes.<sup>5</sup> These would be expected to have significant potential for asymmetric organic synthesis.

Chiral rhenium complexes  $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{L})]^{n+}$  are readily available in optically active form<sup>6</sup> and undergo a number of highly stereoselective ligand-based transformations.<sup>7</sup> Furthermore, the pyramidal  $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)]^+$  fragment is a powerful  $\pi$  donor, with the high-lying rhenium-centered d orbital HOMO shown in I.<sup>8</sup> Hence, back-bonding into unsaturated ligands L is pronounced and is generally an important conformation-determining factor. In this paper, we report (1) two high-yield routes to allyl complexes  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}_2\text{C}(\text{R}')=\text{CHR})$  and (2) NMR and X-ray structural studies that reveal some interesting confor-



tional features. Reactions of these allyl complexes with electrophiles will be described in a separate paper.<sup>9</sup>



## Results

**1. Synthesis of Allyl Complexes  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}_2\text{C}(\text{R}')=\text{CHR})$ .** Iron allyl complexes  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{CH}_2\text{C}(\text{R}')=\text{CHR})$  are frequently prepared by reaction of the iron "anion"  $\text{M}^+ [(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^-$  and an allyl halide  $\text{XCH}_2\text{C}(\text{R}')=\text{CHR}$ .<sup>3</sup> Hence, the rhenium anion  $\text{Li}^+[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)]^-$  (**1**)<sup>10</sup> was generated as previously described and treated with slight excesses of (a) allyl, (b) methallyl, and (c) cinnamyl chloride at  $-78^\circ\text{C}$  (Scheme I). Workup gave  $\eta^1$ -allyl complexes  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}_2\text{C}(\text{R}')=\text{CHR})$  (**2a-c**) as orange powders or crystals in 72–93% yields. The first reaction was reported earlier as part of another study.<sup>10</sup>

Iron allyl complexes  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{CH}_2\text{C}(\text{R}')=\text{CHR})$  have also been prepared by deprotonation of cationic alkene complexes  $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{H}_2\text{C}=\text{C}(\text{R}')\text{CHR})]^+ \text{X}^-$ .<sup>3</sup> Hence, the readily available propene complex

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**Table I. Summary of Crystallographic Data for (*E*)-(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Re(NO)(PPh<sub>3</sub>)(CH<sub>2</sub>CH=CHC<sub>6</sub>H<sub>5</sub>) (2c)**

molecular formula	C <sub>32</sub> H <sub>29</sub> NORe
fw	660.8
cryst system	monoclinic
space group	P2 <sub>1</sub> /n
cell dimens (25 °C)	
<i>a</i> , Å	13.509 (3)
<i>b</i> , Å	14.871 (2)
<i>c</i> , Å	14.698 (3)
β, deg	112.54 (1)
<i>V</i> , Å <sup>3</sup>	2727 (1)
<i>Z</i>	4
<i>d</i> <sub>calcd</sub> , g/cm <sup>3</sup>	1.61
<i>d</i> <sub>obsd</sub> , g/cm <sup>3</sup> (22 °C)	1.61
cryst dimens, mm	0.30 × 0.32 × 0.36
radiatn, Å	λ(Mo Kα) = 0.71069
data collectn method	θ-2θ
scan speed, deg/min	15-60 (variable)
2θ scan range, deg	3 ≤ 2θ ≤ 60
reflectns measd	± <i>h</i> , + <i>k</i> , + <i>l</i>
scan range	Kα <sub>1</sub> - 1.0 to Kα <sub>2</sub> + 1.3
no. of reflectns between stds	97
total unique data	7999
obsd data, <i>I</i> > 3σ( <i>I</i> )	4233
abs coeff (μ), cm <sup>-1</sup>	48.0
method of refinement	full-matrix least squares
no. of variables	399
<i>R</i> = Σ(  <i>F</i> <sub>o</sub> - <i>F</i> <sub>c</sub>  )/Σ  <i>F</i> <sub>o</sub>	0.0375
<i>R</i> <sub>w</sub> = Σ(  <i>F</i> <sub>o</sub> - <i>F</i> <sub>c</sub>  ) <sup>2</sup> /Σ  <i>F</i> <sub>o</sub>   <sup>2</sup>	0.0355
goodness of fit	1.14
weighting factor, <i>w</i>	1/(σ <sup>2</sup> ( <i>F</i> <sub>o</sub> ) + 0.0003( <i>F</i> <sub>o</sub> ) <sup>2</sup> )
Δρ(max), e Å <sup>3</sup>	0.6, <1 Å from Re

[(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Re(NO)PPh<sub>3</sub>](H<sub>2</sub>C=CHCH<sub>3</sub>)<sup>+</sup>PF<sub>6</sub><sup>-</sup> (**3a**; ca. 2:1 mixture of diastereomers)<sup>9,11,12</sup> was treated with *t*-BuO<sup>-</sup>K<sup>+</sup>/*t*-BuOH in chlorobenzene at 0 °C. Workup gave the parent allyl complex **2a** in 84% yield. Isobutylene complex [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Re(NO)(PPh<sub>3</sub>)(H<sub>2</sub>C=C(CH<sub>3</sub>)<sub>2</sub>)<sup>+</sup>PF<sub>6</sub><sup>-</sup> (**3b**)<sup>9,11</sup> and allylbenzene complex [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Re(NO)(PPh<sub>3</sub>)(H<sub>2</sub>C=CHCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sup>+</sup>PF<sub>6</sub><sup>-</sup> (**3c**; ca. 2:1 mixture of diastereomers)<sup>9,12</sup> were similarly treated with *t*-BuO<sup>-</sup>K<sup>+</sup> in THF to give methallyl complex **2b** (73%) and *E*-cinnamyl complex **2c** (70%), respectively. In contrast to iron allyl complexes (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>(CH<sub>2</sub>C(R')=CHR), **3a-c** were not deprotonated by the weaker base N(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>.

Allyl complexes **2a-c** were, unlike alkyl analogues such as (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Re(NO)(PPh<sub>3</sub>)(CH<sub>3</sub>), extremely air sensitive in solution. An identical oxidation rate trend has been noted with the related cyclopentadienyl iron allyl and alkyl complexes. However, solid samples of **2a-c** did not appreciably decompose over the course of several days in air. Complexes **2a-c** were characterized by microanalysis and IR, mass, and <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy, as summarized in the Experimental Section. The IR ν<sub>NO</sub> (1623-1633 cm<sup>-1</sup>, KBr), <sup>31</sup>P NMR PPh<sub>3</sub> chemical shifts (23.8-24.2 ppm), and <sup>1</sup>H and <sup>13</sup>C NMR cyclopentadienyl ligand chemical shifts (δ 4.89-4.92, 90.0-91.6 ppm) were characteristic of neutral (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Re(NO)(PPh<sub>3</sub>)(X) complexes.

Complexes **2a-c** exhibited weak IR ν<sub>C=C</sub> at 1607-1618 cm<sup>-1</sup> and distinct <sup>1</sup>H NMR resonances for the diastereotopic H<sub>α</sub> protons. The H<sub>γ</sub> vinyl proton <sup>1</sup>H NMR resonances of **2a** and **2c** (δ 4.23-5.82) appeared upfield of the H<sub>β</sub> vinyl proton resonances (δ 6.22-6.77). Similarly, the C<sub>γ</sub> carbon <sup>13</sup>C NMR resonances (102-119 ppm; <sup>4</sup>J<sub>CP</sub> < 1 Hz) were upfield of the C<sub>β</sub> carbon resonances (147-162 ppm; <sup>3</sup>J<sub>CP</sub> = 4 Hz). This was confirmed by a proton-

**Table II. Selected Bond Lengths (Å) in 2c**

Re-P	2.337 (2)	Re-N	1.740 (6)
N-O	1.209 (8)	Re-C1	2.192 (6)
C1-C2	1.486 (11)	C2-C3	1.304 (13)
C3-C4	1.476 (13)	C4-C5	1.423 (16)
C4-C9	1.372 (13)	C5-C6	1.405 (13)
C6-C7	1.346 (14)	C7-C8	1.366 (17)
C8-C9	1.355 (13)	Re-C10	2.224 (7)
Re-C11	2.259 (7)	Re-C12	2.335 (8)
Re-C13	2.338 (9)	Re-C14	2.289 (7)
P-C21	1.824 (5)	P-C31	1.823 (6)
P-C41	1.838 (6)	C10-C11	1.428 (10)
C10-C14	1.409 (11)	C11-C12	1.409 (14)
C12-C13	1.381 (10)	C13-C14	1.358 (13)
C2'-C1	1.480 (18)	C2'-C3'	1.300 (23)
C3'-C4'	1.480 (21)		

**Table III. Selected Bond Angles (deg) in 2c**

P-Re-N	91.8 (1)	P-Re-C1	92.1 (2)
N-Re-C1	93.3 (3)	C1-C2-C3	126.3 (10)
C2-C3-C4	127.9 (11)	C3-C4-C5	125.2 (8)
C3-C4-C9	118.6 (9)	C4-C5-C6	120.6 (8)
C4-C9-C8	121.3 (10)	C5-C4-C9	116.2 (8)
C5-C6-C7	120.5 (10)	C6-C7-C8	118.2 (9)
C7-C8-C9	123.1 (9)	Re-N-O	178.7 (4)
Re-C1-C2	105.7 (5)	C10-C11-C12	106.6 (7)
C10-C14-C13	107.9 (6)	C11-C10-C14	107.3 (8)
C11-C12-C13	107.7 (7)	C12-C13-C14	110.5 (8)
Re-C1-C2'	105.3 (9)	C1-C2'-C3'	124.3 (18)
C2'-C3'-C4'	130.3 (19)	C3'-C4'-C5'	127.1 (10)
C3'-C4'-C9'	112.9 (10)		

coupled <sup>13</sup>C NMR spectrum of parent complex **2a**, which showed the upfield C=C resonance to be a triplet (102.3 ppm, <sup>1</sup>J<sub>CH</sub> = 153.7 Hz), indicative of two directly bound hydrogens. The downfield C=C resonance was a doublet (152.9 ppm, <sup>1</sup>J<sub>CH</sub> = 147.7 Hz), indicative of one directly bound hydrogen. The C<sub>α</sub> carbon resonances were upfield of TMS (-1 to -6 ppm) and exhibited <sup>2</sup>J<sub>CP</sub> of 4.4-5.2 Hz. The assignment of **2c** as an *E* C=C geometric isomer was based upon the magnitude of <sup>3</sup>J<sub>H(β)H(γ)}</sub> (15.4 Hz)<sup>13</sup> and was confirmed by an X-ray crystal structure as described below.

**2. Structural Studies of Allyl Complexes.** X-ray data were acquired on cinnamyl complex **2c** as summarized in Table I. Refinement, described in the Experimental Section, yielded the structures shown in Figure 1. The cinnamyl ligand was found to adopt two conformations, differing primarily in orientation about the C1-C2 (C<sub>α</sub>-C<sub>β</sub>) bonds and slightly in orientation about the Re-C1 (Re-C<sub>α</sub>) bonds (Figure 1, top). The occupations of these conformers refined to 78.8 (2):21.2 (2). Atoms of the minor conformer are designated by primes.

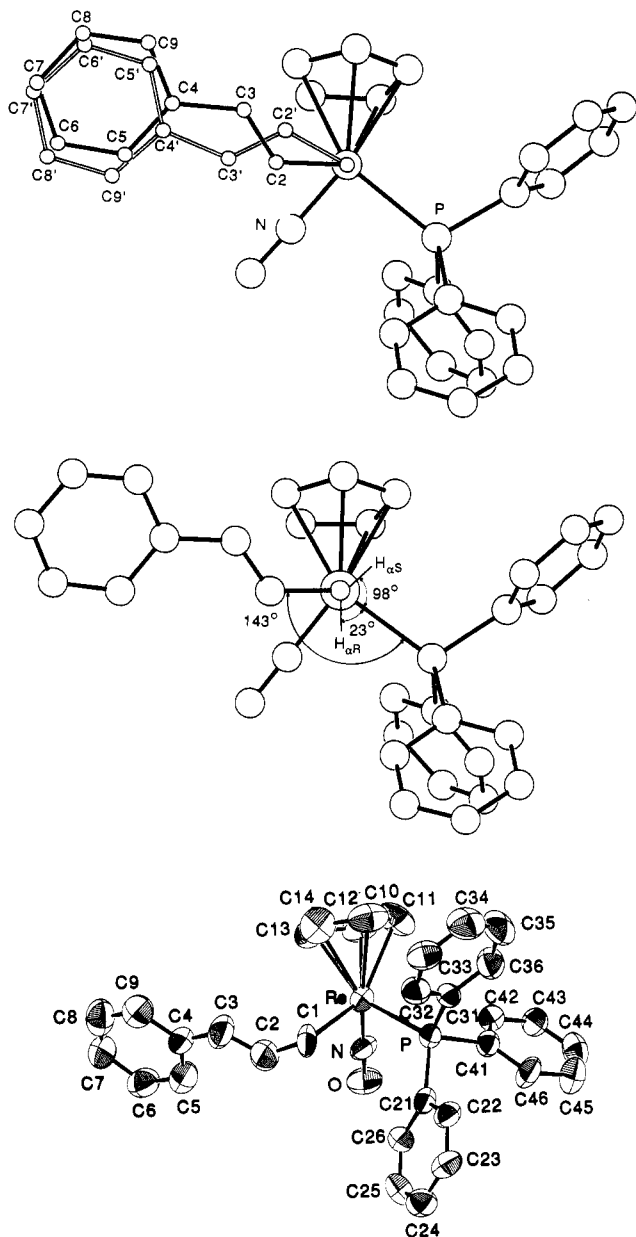
Key bond lengths and angles are given in Tables II and III, respectively. Atomic coordinates, a complete listing of bond lengths and angles, anisotropic thermal parameters, and calculated and observed structure factors are given in the supplementary material. The P-Re-C1-C2 and P-Re-C1'-C2' torsion angles in the major and minor cinnamyl ligand conformers were found to be 143° and 170°, respectively. The Re-C1-C2-C3 torsion angles of the two conformers were found to differ by 170°. Hydrogen atom positions were calculated for C1 (C<sub>α</sub>) of the major conformer and gave P-Re-C1-H<sub>αR</sub> and P-Re-C1-H<sub>αS</sub> torsion angles of 23° and 98°, respectively (Figure 1, middle).

The solution structures of cinnamyl complex **2c** and parent allyl complex **2a** were also briefly probed by NMR. First, in a difference NOE experiment,<sup>14-16</sup> the cyclo-

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**Figure 1.** Molecular structure of cinnamyl complex (*E*)-( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Re(NO)(PPh<sub>3</sub>)(CH<sub>2</sub>CH=CHC<sub>6</sub>H<sub>5</sub>) (**2c**): top, Newman projection showing major (dark) and minor (light) cinnamyl ligand conformations; middle, selected torsion angles in the major conformation; bottom, numbering diagram for major conformation.

pentadienyl ligand <sup>1</sup>H NMR resonance of **2c** was irradiated. The downfield H<sub>α</sub> proton ( $\delta$  3.04) exhibited no enhancement, the upfield H<sub>α</sub> proton ( $\delta$  2.62) exhibited a small enhancement (0.8%), and the H<sub>β</sub> and H<sub>γ</sub> protons exhibited moderate enhancements (3.2% and 3.6%). An identical experiment was conducted with **2a**. The downfield H<sub>α</sub> proton ( $\delta$  2.78) exhibited no enhancement, the upfield H<sub>α</sub> proton ( $\delta$  2.40) exhibited a small enhancement (1.0%), and the H<sub>β</sub>, H<sub>γ(Z)</sub>, and H<sub>γ(E)</sub> protons exhibited moderate to small enhancements (3.0%, 1.8% and 1.1%).

Next, variable-temperature <sup>1</sup>H NMR spectra were recorded. It has previously been shown that the <sup>3</sup>J<sub>H(α)P</sub> of

the diastereotopic H<sub>α</sub> protons in complexes of the type ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)M(L)(PPh<sub>3</sub>)(CH<sub>2</sub>R) exhibit a Karplus-type dependence upon the M-C<sub>α</sub> conformation.<sup>15-18</sup> The study of their variation with temperature can help elucidate preferred solution conformations. These couplings are easily discerned in 300–500 MHz spectra of **2c** recorded at 20–40 °C (downfield H<sub>α</sub>, 6.7 Hz; upfield H<sub>α</sub>, 2.7 Hz; CD<sub>2</sub>Cl<sub>2</sub>). However, spectra recorded at 0 °C or below exhibited broadened H<sub>α</sub> resonances from which <sup>3</sup>J<sub>H(α)P</sub> could not be dissected. The temperature dependence of the corresponding coupling constants in **2a** (downfield H<sub>α</sub>, 8.4 Hz; upfield H<sub>α</sub>, 2.2 Hz; C<sub>6</sub>D<sub>5</sub>Cl) was not examined due to the greater complexity of the spin system.

## Discussion

The two routes developed to chiral rhenium allyl complexes ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Re(NO)(PPh<sub>3</sub>)(CH<sub>2</sub>C(R')=CHR) (Scheme I) have complementary advantages. First, the allyl ligand framework can be introduced either as an allyl halide (route a) or as an alkene (route b). The precursor to the rhenium "anion" Li<sup>+</sup>[( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Re(NO)(PPh<sub>3</sub>)]<sup>-</sup> (**1**) utilized in route a, hydride complex ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Re(NO)(PPh<sub>3</sub>)(H), is available in two steps from methyl complex ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Re(NO)(PPh<sub>3</sub>)(CH<sub>3</sub>) (HCOOH, then 110 °C).<sup>10</sup> However, hydride complex ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Re(NO)(PPh<sub>3</sub>)(H) is not presently available in high optical purity, and reactions proceeding via d<sup>8</sup> "anions" such as **1** generally occur with a high degree of racemization at the metal.<sup>9,19,20</sup> The alkene complexes [( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Re(NO)(PPh<sub>3</sub>)(H<sub>2</sub>C=C(R')-CH<sub>2</sub>R)]<sup>+</sup>X<sup>-</sup> (**3**) utilized in route b can be synthesized in a single step from methyl complex ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Re(NO)(PPh<sub>3</sub>)(CH<sub>3</sub>)<sup>9,12</sup> and are easily obtained in optically pure form. Hence, route b should be the best method for synthesizing optically active allyl complexes **2**.

A number of structural features of cinnamyl complex **2c** merit analysis. First, **2c** exhibits the ca. 90° P-Re-N, P-Re-C<sub>1</sub>, and N-Re-C<sub>1</sub> bond angles noted earlier for this formally octahedral class of compounds (Table III).<sup>6,2a</sup> The Re-C<sub>1</sub> (Re-C<sub>α</sub>) bond length (2.192 (6) Å; Table II) is very close to those of benzyl complex (-)-(*R*)-( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Re(NO)(PPh<sub>3</sub>)(CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>) (**4**; 2.203 (8) Å)<sup>6</sup> and substituted benzyl complex (*SS,RR*)-( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Re(NO)(PPh<sub>3</sub>)(CH(CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)C<sub>6</sub>H<sub>5</sub>) (2.215 (4) Å).<sup>8a</sup> The C<sub>1</sub>/C<sub>2</sub>/C<sub>3</sub>/C<sub>4</sub> (C<sub>α</sub>/C<sub>β</sub>/C<sub>γ</sub>/C<sub>δ</sub>) bond lengths and angles within the cinnamyl ligand are similar to those found previously in dicinnamyl disulfide (e.g., C<sub>1</sub>-C<sub>2</sub>, C<sub>2</sub>-C<sub>3</sub>, C<sub>3</sub>-C<sub>4</sub> = 1.486, 1.318, and 1.462 Å).<sup>21</sup>

A search of the Cambridge crystallographic data base revealed 13 other structurally characterized  $\sigma$ -allyl complexes of general formula L<sub>n</sub>MCH<sub>2</sub>CH=CRR'. These exhibited mean C<sub>α</sub>-C<sub>β</sub> and C<sub>β</sub>-C<sub>γ</sub> bond lengths of 1.48 (2) and 1.30 (7) Å. The chiral ruthenium methallyl complex<sup>5c</sup> ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Ru(PMe<sub>3</sub>)(PPh<sub>3</sub>)(CH<sub>2</sub>C(CH<sub>3</sub>)=CH<sub>2</sub>) and the binuclear rhenium complex<sup>22</sup> (CO)<sub>5</sub>ReCH<sub>2</sub>CH=CHC-H<sub>2</sub>Re(CO)<sub>5</sub> seemingly bear the closest relationships to **2c**. However, the long C=C double bond in the latter (1.43

(17) Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 4292.

(18) For P-M-C<sub>α</sub>-H torsion angles of ±90°, <sup>3</sup>J<sub>H(α)P</sub> near 0 Hz are expected. For torsion angles near 0° or 180°, larger <sup>3</sup>J<sub>H(α)P</sub> are expected (≥18 Hz). Gorenstein, D. G. *Phosphorus-31 NMR, Principles and Applications*; Academic Press: Orlando, 1984; pp 43-47.

(19) Heah, P. C.; Patton, A. T.; Gladysz, J. A. *J. Am. Chem. Soc.* **1986**, *106*, 1185.

(20) Theoretical calculations predict a trigonal metal geometry for d<sup>8</sup> ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)MLL' complexes: Hofmann, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 536.

(21) Donohue, J.; Chesick, J. P. *Acta Crystallogr., Sect. B* **1975**, *B31*, 986.

(22) Beck, W.; Raab, K.; Nagel, U.; Sacher, W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 505.

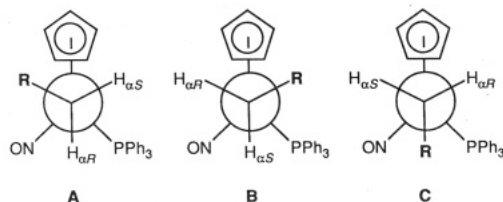
(14) Sanders, J. K. M.; Hunter, B. K. *Modern NMR Spectroscopy*; Oxford University Press: New York, 1987; Chapter 6.

(15) Hunter, B. K.; Baird, M. C. *Organometallics* **1985**, *4*, 1481.

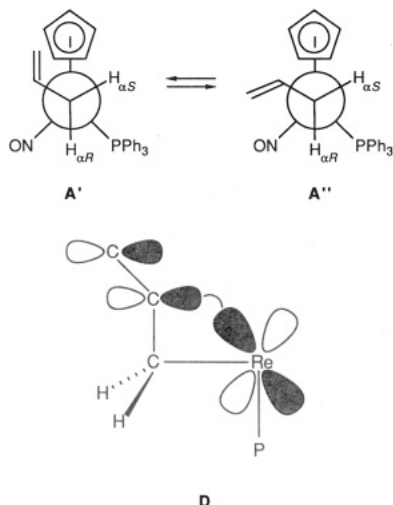
(16) (a) Davies, S. G.; Dordor-Hedgecock, I. M.; Sutton, K. H.; Whittaker, M. J. *Am. Chem. Soc.* **1987**, *109*, 5711. (b) Seeman, J. I.; Davies, S. G. *Ibid.* **1985**, *107*, 6522.

(2 Å) and other distortions suggest a somewhat different bonding description.<sup>22</sup>

Three generic types of "staggered" Re-C<sub>α</sub> rotamers A-C should in principle be possible in allyl or alkyl complexes (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Re(NO)(PPh<sub>3</sub>)(CH<sub>2</sub>R). It is intuitive from steric considerations that rotamers of the type A, in which the C<sub>α</sub> substituent residues between the small NO and medium-sized cyclopentadienyl ligands, should be the most stable.<sup>8b,15,16</sup> Benzyl complex (-)-(R)-(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Re(NO)(PPh<sub>3</sub>)(CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>) (4) adopts a solid state Re-C<sub>α</sub> conformation of the type A, with a P-Re-C<sub>α</sub>-C<sub>β</sub> torsion angle of 157°, and the plane of the phenyl ring (C<sub>α</sub>-C<sub>β</sub>-C<sub>γ</sub>) approximately perpendicular to the Re-C<sub>α</sub> bond.<sup>6</sup>



As noted above, the HOMO of the rhenium fragment [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Re(NO)(PPh<sub>3</sub>)]<sup>+</sup> is the high-lying d orbital shown in I. This orbital can overlap with the C<sub>β</sub> lobe of the allyl ligand C<sub>β</sub>=C<sub>γ</sub> π and π\* orbitals in Re-C<sub>α</sub> conformations of the type A, provided that the plane of the allyl ligand (C<sub>α</sub>-C<sub>β</sub>-C<sub>γ</sub>) is approximately perpendicular to the Re-C<sub>α</sub> bond. A representative interaction is sketched in structure D. Overlap of the Re-C<sub>α</sub> σ-bonding orbital with the C=C π and π\* orbitals can also occur whenever the C<sub>α</sub>-C<sub>β</sub>-C<sub>γ</sub> plane is perpendicular to the Re-C<sub>α</sub> bond. While these orbital interactions may constitute minor Re-C<sub>α</sub> conformation-influencing factors, they serve to impart C<sub>γ</sub> nucleophilicity.<sup>23</sup> Hence, conformation A is expected to be the most reactive toward electrophiles. Further, A leads directly to the most stable C=C conformation of the cationic alkene complex products (II).<sup>24</sup>



In contrast to benzyl complex 4, allyl complexes 2 have two subclasses of rotamer A, A' and A'', in which the C<sub>α</sub>-C<sub>β</sub>-C<sub>γ</sub> plane remains perpendicular to the Re-C<sub>α</sub> bond. Note that the C<sub>β</sub>=C<sub>γ</sub> double bond faces are diastereotopic and that A' and A'' differ in the diastereoface oriented anti to the rhenium. Iron allyl complexes (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>

(CHR'CH(R')=CHR) undergo electrophilic attack upon the C<sub>β</sub>=C<sub>γ</sub> face anti to the iron.<sup>3</sup> Hence, if one of the two conformers A' or A'' were to be more reactive toward electrophiles, efficient 1,4-asymmetric induction should be possible. Thus, the finding of *both* types of conformers in the crystal structure of 2c (Figure 1) somewhat diminished our hopes of developing highly stereoselective C<sub>γ</sub> reactions with electrophiles.

Interestingly, the P-Re-C<sub>α</sub>-C<sub>β</sub> torsion angles in the major (A') and minor (A'') Re-C<sub>α</sub> conformations of 2c (143° and 170°) are symmetrically arrayed about that of benzyl complex 4 (157°).<sup>6</sup> Note that steric interactions between C<sub>γ</sub> substituents and the cyclopentadienyl ligand in A' are relieved by decreasing the P-Re-C<sub>α</sub>-C<sub>β</sub> torsion angle. Steric interactions between a C<sub>β</sub> hydrogen substituent and the cyclopentadienyl ligand in A'' would be less than those between the C<sub>γ</sub> ortho carbon and the cyclopentadienyl ligand in benzyl complex 4, leading to a larger torsion angle.

In conformer A', the <sup>1</sup>H NMR difference NOE enhancement upon cyclopentadienyl ligand irradiation would be expected to be much larger for H<sub>γ(z)</sub> than H<sub>β</sub>. However, with conformer A'', the enhancement should be much larger for H<sub>β</sub> than H<sub>γ</sub>. The fact that H<sub>γ</sub> and H<sub>β</sub> in 2c (and 2a) exhibit nearly equal enhancements suggests that there are appreciable (and rapidly interconverting) populations of both A' and A'' in solution. Indeed, as will be detailed in our subsequent paper,<sup>9</sup> the *minor* solid-state conformer of 2c (A'') proves to be the more reactive toward electrophiles. Contributing factors may include the better overlap of the donor orbital shown in I with the C=C π and π\* orbitals in the minor conformer (P-Re-C<sub>α</sub>-C<sub>β</sub> torsion angle closer to 180°) and the formation of the more stable alkene complex diastereomers (i.e., R syn to the nitrosyl ligand in II).

Since the major and minor C<sub>α</sub>-C<sub>β</sub> conformers of 2c differ significantly in their P-Re-C<sub>α</sub>-H<sub>α</sub> torsion angles (Figure 1), they should exhibit different <sup>3</sup>J<sub>H(α)P</sub>.<sup>18</sup> Thus, as the relative conformer populations should vary with temperature, <sup>3</sup>J<sub>H(α)P</sub> should likewise vary, irrespective of any change in the relative populations of Re-C<sub>α</sub> rotamers A-C.<sup>25</sup> Unfortunately, experimental limitations precluded a detailed study of the temperature dependence of the <sup>3</sup>J<sub>H(α)P</sub> in 2c and 2a.

Interestingly, Davies has observed a considerable variation of <sup>3</sup>J<sub>H(α)P</sub> with temperature in the iron allyl complex (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Fe(CO)(PPh<sub>3</sub>)(CH<sub>2</sub>CH=CH<sub>2</sub>).<sup>16a</sup> Although a scenario involving C<sub>α</sub>-C<sub>β</sub> conformers of the types A' and A'' was not considered, the data could be satisfactorily modeled by the equilibration of two Fe-C<sub>α</sub> conformers (one being an eclipsed rotamer intermediate between A and B). The Fe-C<sub>α</sub> conformations of a variety of other iron alkyl complexes were also analyzed in detail.

While the present data do not allow a comparably detailed analysis of our rhenium complexes, several features suggest significant differences and/or additional complicating features. For example, the upfield H<sub>α</sub> protons in iron complexes (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Fe(CO)(PPh<sub>3</sub>)(CH<sub>2</sub>R) (R = CH=CH<sub>2</sub>, Ph, alkyl) exhibit the *larger* <sup>3</sup>J<sub>H(α)P</sub> and have been reasonably assigned from chemical shift and Karplus arguments to the proton corresponding to H<sub>R</sub> in A. However, with 2a and 2c (but not 2b), the upfield H<sub>α</sub>

(25) The Karplus relationship suggests that <sup>3</sup>J<sub>H(α)P</sub> might be similar in the two C<sub>α</sub>-C<sub>β</sub> rotamers of 2c, as the P-Re-C<sub>α</sub>-H<sub>α</sub>S torsion angles (ca. 98° and 81°) straddle the value where <sup>3</sup>J<sub>H(α)P</sub> should be zero (ca. 90°).<sup>18</sup> Hence, this coupling constant might not vary significantly with temperature. However, the difference in the P-Re-C<sub>α</sub>-H<sub>α</sub>R torsion angles in the two C<sub>α</sub>-C<sub>β</sub> rotamers of 2c (ca. 23° and 50°) should lead to an appreciable difference in <sup>3</sup>J<sub>H(α)P</sub>.

(23) Hosomi, A.; Traylor, T. G. *J. Am. Chem. Soc.* 1975, 97, 3682.

(24) The donor orbital in I will also overlap with the allyl ligand C=C π and π\* orbitals in a Re-C<sub>α</sub> rotamer with a 0° P-Re-C<sub>α</sub>-C<sub>β</sub> torsion angle. However, such a rotamer is clearly an energy maximum from steric considerations.



proton exhibits the smaller  $^3J_{\text{H}(\alpha)\text{P}}$  (2.2 vs. 8.4 Hz; 2.5 vs. 6.7 Hz). Furthermore, deuterium-labeling experiments have shown that the upfield  $\text{H}_\alpha$  proton resonance in benzyl complex **4** and ethyl complex  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}_2\text{CH}_3)$  corresponds to  $\text{H}_\beta$  in **A**.<sup>8a,11</sup> On the basis of the greater NOE enhancement of the upfield  $\text{H}_\alpha$  protons in **2a** and **2c** and their smaller  $^3J_{\text{H}(\alpha)\text{P}}$ , we likewise assign them as the proton corresponding to  $\text{H}_\beta$  in **A**.

In summary, we have demonstrated the ready availability of a variety of rhenium allyl complexes of the formula  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}_2\text{C}(\text{R}')=\text{CHR})$  (**2**) and defined their basic spectroscopic and structural features. In particular, the conformational disorder found in crystalline **2c** appears to be mirrored in solution with this class of compounds. The chemical properties of allyl complexes **2** will be detailed in our subsequent publication.<sup>9</sup>

### Experimental Section

**General Data.** All reactions were carried out under a dry  $\text{N}_2$  atmosphere. IR spectra were recorded on a Perkin-Elmer Model 1500 (FT) spectrometer. NMR spectra were recorded on Varian SC-300, XL-300 ( $^1\text{H}$ ,  $^{13}\text{C}$ ), and FT-80A ( $^{31}\text{P}$ ) spectrometers unless noted. Mass spectra were obtained on a VG Analytical 7050-E double-focusing instrument. Microanalyses were conducted by Galbraith and Schwarzkopf Laboratories. Melting points were determined in evacuated capillaries and were not corrected.

Solvents and reagents were purified as follows: benzene, ether, and THF, distilled from Na/benzophenone; heptane, hexanes, and toluene, distilled from Na;  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , and chlorobenzene, distilled from  $\text{P}_2\text{O}_5$ ;  $\text{CD}_2\text{Cl}_2$ , vacuum transferred from  $\text{CaH}_2$ ; allyl chloride and 2-methylallyl chloride (Aldrich), refluxed over and distilled from  $\text{P}_2\text{O}_5$ ; cinnamyl chloride (Aldrich), distilled under vacuum; TMEDA (Aldrich), distilled from  $\text{CaH}_2$ ; *n*-BuLi (Aldrich) was standardized before use.<sup>26</sup>

**Preparation of  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}_2\text{C}(\text{CH}_3)=\text{CH}_2)$  (**2b**).** A Schlenk flask was charged with  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{H})$  (0.200 g, 0.367 mmol),<sup>10</sup> THF (20 mL), and a stir bar and was cooled to  $-15^\circ\text{C}$  (ethylene glycol/ $\text{CO}_2$  bath). Then TMEDA (60  $\mu\text{L}$ , 0.398 mmol) and *n*-BuLi (170  $\mu\text{L}$ , 2.5 M in hexanes, 0.425 mmol) were added sequentially with stirring to give a deep red solution of  $\text{Li}^+[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)]^-$  (**1**).<sup>10</sup> After 0.5 h, the solution was cooled to  $-78^\circ\text{C}$  and 2-methylallyl chloride (70  $\mu\text{L}$ , 0.717 mmol) was added. The reaction immediately turned orange and after 0.25 h was warmed to  $-15^\circ\text{C}$  and stirred for an additional 0.25 h. Solvent was then removed under oil pump vacuum as the orange solution was allowed to warm to room temperature. The resulting foam was transferred to a glovebox and was extracted with ether. The extract was filtered, and ether was removed from the filtrate by high vacuum rotary evaporation. The resulting oil was dissolved in toluene, layered with three volumes of heptane, and kept at  $-20^\circ\text{C}$  for 3 days. Small orange crystals formed, which were collected by filtration, washed with cold ether, and dried in vacuo to give **2b** (0.187 g, 0.312 mmol, 85%), mp  $175\text{--}177^\circ\text{C}$  dec. Anal. Calcd for  $\text{C}_{27}\text{H}_{27}\text{NOPRe}$ : C, 54.07; H, 4.51. Found: C, 54.37; H, 4.54. B. A Schlenk flask was charged with  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{H}_2\text{C}=\text{C}(\text{CH}_3)_2)^+\text{PF}_6^-$  (**3b**,<sup>11</sup> 0.077 g, 0.103 mmol), THF (5 mL), and a stir bar. Then *t*-BuO $^-$ K $^+$  (150  $\mu\text{L}$ , 0.75 M in *t*-BuOH, 1.1 equiv) was added with stirring. The reaction immediately turned orange and was stirred for 3 h. Solvent was then removed under oil pump vacuum. The resulting foam was transferred to a glovebox and extracted with ether. The extract was filtered, and hexanes was added to the filtrate. Complex **2b** precipitated as an orange powder, which was collected by filtration and dried in vacuo (0.045 g, 0.075 mmol, 73%). C. Spectroscopic data: IR ( $\text{cm}^{-1}$ , KBr)  $\nu_{\text{NO}}$  1623 s,  $\nu_{\text{C}=\text{C}}$  1611 w;  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CD}_2\text{Cl}_2$ ) 7.42 (m, PPh $_3$ ), 4.86 (s,  $\text{C}_5\text{H}_5$ ), 4.26 (s,  $=\text{CH}_2$ ), 2.68 (dd,  $J_{\text{H}(\alpha)\text{H}(\alpha')} = 11.0$  Hz,  $^3J_{\text{H}(\alpha)\text{P}} = 2.8$  Hz,  $\text{H}_\alpha$ ), 2.57 (dd,  $J_{\text{H}(\alpha')\text{H}(\alpha)} = 11.0$  Hz,  $^3J_{\text{H}(\alpha')\text{P}} = 8.1$  Hz,  $\text{H}_{\alpha'}$ ), 1.78 (s,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (ppm,  $\text{CD}_2\text{Cl}_2$ ) 161.7 (d,  $J_{\text{PC}} = 3.8$  Hz,  $\text{C}_\beta$ ), PPh $_3$  at 136.8 (d,  $J_{\text{CP}} = 51.4$  Hz, *ipso*), 134.2

(d,  $J_{\text{CP}} = 10.3$  Hz), 130.6 (d,  $J_{\text{CP}} = 1.8$  Hz, *p*), 128.9 (d,  $J_{\text{CP}} = 10.1$  Hz); 101.4 (s,  $=\text{CH}_2$ ), 91.6 (s,  $\text{C}_5\text{H}_5$ ), 24.3 (s,  $\text{CH}_3$ ),  $-0.7$  (d,  $J_{\text{CP}} = 4.5$  Hz,  $\text{C}_\alpha$ );  $^{31}\text{P}\{^1\text{H}\}$  NMR (ppm,  $\text{CH}_2\text{Cl}_2$ ) 23.8 (s); mass spectrum (18 eV, *m/e*,  $^{187}\text{Re}$ ) 599 ( $\text{M}^+$ , 29%), 544 ( $\text{M}^+ - \text{C}_4\text{H}_7$ , 9%), 467 ( $\text{M}^+ - \text{C}_4\text{H}_7 - \text{C}_6\text{H}_5$ , 5%), 337 ( $\text{M}^+ - \text{PPh}_3$ , 33%), 262 ( $\text{PPh}_3^+$ , 100%).

**Preparation of  $(E)-(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}_2\text{CH}=\text{CHC}_6\text{H}_5)$  (**2c**).** A. Complex  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{H})$  (0.200 g, 0.367 mmol), TMEDA (60  $\mu\text{L}$ , 0.398 mmol), *n*-BuLi (170  $\mu\text{L}$ , 0.425 mmol), and cinnamyl chloride (60  $\mu\text{L}$ , 0.400 mmol) were reacted in a procedure analogous to preparation A of **2b**. An identical workup gave an orange foam, which was dissolved in  $\text{CH}_2\text{Cl}_2$ . Addition of hexanes precipitated an orange powder, which was collected by filtration, washed with cold hexanes, and dried in vacuo to give **2c** (0.175 g, 0.265 mmol, 72%), mp  $148\text{--}150^\circ\text{C}$  dec. Anal. Calcd for  $\text{C}_{32}\text{H}_{29}\text{NOPRe}$ : C, 58.16; H, 4.39. Found: C, 58.01; H, 4.45. B. A Schlenk flask was charged with  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{H}_2\text{C}=\text{CHCH}_2\text{C}_6\text{H}_5)^+\text{PF}_6^-$  (**3c**, ca. 2:1 mixture of diastereomers,<sup>9,12</sup> 0.135 g, 0.167 mmol), THF (10 mL), and a stir bar. Then *t*-BuO $^-$ K $^+$  (245  $\mu\text{L}$ , 0.75 M in *t*-BuOH, 1.1 equiv) was added with stirring. After 2 h, solvent was removed under oil pump vacuum. Workup as in preparation B of **2b** gave **2c** as an orange powder (0.077 g, 0.117 mmol, 70%). C. Spectroscopic data: IR ( $\text{cm}^{-1}$ , KBr)  $\nu_{\text{NO}}$  1633 s,  $\nu_{\text{C}=\text{C}}$  1618 w;  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CD}_2\text{Cl}_2$ ) 7.45 (m, PPh $_3$ ), 7.38 (m,  $\text{C}_6\text{H}_5$ ), 6.77 (ddd,  $J_{\text{H}(\beta)\text{H}(\gamma)} = 15.4$  Hz,  $J_{\text{H}(\beta)\text{H}(\alpha)} = 7.2$  Hz,  $J_{\text{H}(\beta)\text{H}(\alpha')} = 9.7$  Hz,  $\text{H}_\beta$ ), 5.82 (d,  $J_{\text{H}(\gamma)\text{H}(\beta)} = 15.4$  Hz,  $\text{H}_\gamma$ ), 4.96 (s,  $\text{C}_5\text{H}_5$ ), 3.04 (ddd,  $J_{\text{H}(\alpha)\text{H}(\alpha')} = 10.2$  Hz,  $J_{\text{H}(\alpha)\text{H}(\beta)} = 7.2$  Hz,  $^3J_{\text{H}(\alpha)\text{P}} = 6.7$  Hz,  $\text{H}_{\alpha\beta}$ ), 2.62 (ddd,  $J_{\text{H}(\alpha')\text{H}(\alpha)} = 10.2$  Hz,  $J_{\text{H}(\alpha')\text{H}(\beta)} = 9.7$  Hz,  $^3J_{\text{H}(\alpha')\text{P}} = 2.5$  Hz,  $\text{H}_{\alpha\beta}$ );  $^{13}\text{C}$  NMR (ppm,  $\text{CD}_2\text{Cl}_2$ ) 146.8 (d,  $J_{\text{CP}} = 4.2$  Hz,  $\text{C}_\beta$ ), PPh $_3$  at 137.0 (d,  $J_{\text{CP}} = 53.1$  Hz, *ipso*), 134.3 (d,  $J_{\text{CP}} = 11.4$  Hz), 130.8 (s, *p*), 129.0 (d,  $J_{\text{CP}} = 9.4$  Hz),  $\text{C}_6\text{H}_5$  at 129.2 (s), 128.9 (s), 125.7 (s), 125.5 (s); 119.2 (s,  $\text{C}_\alpha$ ), 90.9 (s,  $\text{C}_5\text{H}_5$ ),  $-6.4$  (d,  $J_{\text{CP}} = 4.4$  Hz,  $\text{C}_\alpha$ );  $^{31}\text{P}\{^1\text{H}\}$  NMR (ppm,  $\text{CH}_2\text{Cl}_2$ ) 23.9 (s); mass spectrum (18 eV, *m/e*,  $^{187}\text{Re}$ ) 661 ( $\text{M}^+$ , 3%), 544 ( $\text{M}^+ - \text{C}_6\text{H}_5$ , 13%), 467 ( $\text{M}^+ - \text{C}_5\text{H}_5 - \text{C}_6\text{H}_5$ , 5%), 399 ( $\text{M}^+ - \text{PPh}_3$ , 34%), 262 ( $\text{PPh}_3^+$ , 100%).

**Preparation of  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}_2\text{CH}=\text{CH}_2)$  (**2a**).** A. Complex  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{H})$  (0.200 g, 0.367 mmol), TMEDA (60  $\mu\text{L}$ , 0.398 mmol), *n*-BuLi (170  $\mu\text{L}$ , 0.425 mmol), and allyl chloride (35  $\mu\text{L}$ , 0.429 mmol) were reacted in a procedure analogous to preparation A of **2b**. The resulting foam was transferred to a glovebox and extracted with ether. The extract was filtered, and ether was removed from the filtrate by high vacuum rotary evaporation. The resulting oil was dissolved in toluene, layered with heptane, and kept at  $-20^\circ\text{C}$  for 4 days. Small orange crystals formed, which were collected by filtration, washed with cold hexanes, and dried in vacuo to give **2a** (0.200 g, 0.342 mmol, 93%), mp  $141\text{--}144^\circ\text{C}$  dec. B. A Schlenk flask was charged with  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{H}_2\text{C}=\text{CHCH}_3)^+\text{PF}_6^-$  (**3a**, ca. 2:1 mixture of diastereomers,<sup>9,11,12</sup> 0.110 g, 0.151 mmol),  $\text{C}_6\text{H}_5\text{Cl}$  (10 mL), and a stir bar and was cooled to  $0^\circ\text{C}$ . Then *t*-BuO $^-$ K $^+$  (240  $\mu\text{L}$ , 0.75 M in *t*-BuOH, 1.2 equiv) was added with stirring. The reaction immediately turned orange and after 0.5 h was allowed to warm to room temperature. Solvent was removed via oil pump vacuum, and workup as in preparation B of **2b** gave **2a** as an orange powder (0.074 g, 0.127 mmol, 84%). C. Spectroscopic properties were identical with those reported previously;<sup>10</sup> additional data:  $^1\text{H}$  NMR ( $\delta$ ,  $\text{C}_6\text{D}_5\text{Cl}$ ,  $19^\circ\text{C}$ , 400 MHz) 7.40 (m, PPh $_3$ ), 6.61 (dddd,  $J_{\text{H}(\beta)\text{H}(\alpha)} = 9.7$  Hz,  $J_{\text{H}(\beta)\text{H}(\alpha')} = 7.2$  Hz,  $J_{\text{H}(\beta)\text{H}(\gamma)} = 9.9$  Hz,  $J_{\text{H}(\beta)\text{H}(\gamma')} = 17.2$  Hz,  $\text{H}_\beta$ ), 4.90 (s,  $\text{C}_5\text{H}_5$ ), 4.73 (dd,  $J_{\text{H}(\gamma)\text{H}(\beta)} = 2.7$  Hz,  $J_{\text{H}(\gamma)\text{H}(\beta')} = 17.2$  Hz,  $\text{H}_\gamma$ ), 4.61 (dd,  $J_{\text{H}(\gamma)\text{H}(\gamma')} = 2.2$  Hz,  $J_{\text{H}(\gamma)\text{H}(\beta)} = 9.9$  Hz,  $\text{H}_{\gamma\beta}$ ), 3.25 (ddd,  $J_{\text{H}(\alpha)\text{H}(\alpha')} = 10.1$  Hz,  $J_{\text{H}(\alpha)\text{H}(\beta)} = 7.2$  Hz,  $^3J_{\text{H}(\alpha)\text{P}} = 8.4$  Hz,  $\text{H}_{\alpha\beta}$ ), 2.68 (ddd,  $J_{\text{H}(\alpha')\text{H}(\alpha)} = 10.1$  Hz,  $J_{\text{H}(\alpha')\text{H}(\beta)} = 9.7$  Hz,  $^3J_{\text{H}(\alpha')\text{P}} = 2.2$  Hz,  $\text{H}_{\alpha\beta}$ ); the preceding assignments were confirmed by decoupling  $\text{H}_\beta$ ;  $^{13}\text{C}$  NMR (ppm,  $\text{CD}_2\text{Cl}_2$ ; no proton decoupling) 152.9 (d,  $^1J_{\text{CH}} = 147.7$  Hz,  $\text{C}_\beta$ ), 102.3 (t,  $^1J_{\text{CH}} = 153.7$  Hz,  $\text{C}_\gamma$ ), 90.9 (d,  $^1J_{\text{CH}} = 179.3$  Hz,  $\text{C}_5\text{H}_5$ ),  $-5.6$  (t,  $^1J_{\text{CH}} = 127.4$  Hz,  $\text{C}_\alpha$ ), and phenyl resonances.

**$^1\text{H}$  NOED Experiments.**<sup>14</sup> The following experiment is representative. A 5-mm NMR tube was charged with **2c** (0.09 M in  $\text{CD}_2\text{Cl}_2$ ), sealed under vacuum, and inserted into a broadband Varian XL-300 probe. The NOED experiment was performed as an array consisting of two spectra in which the first was obtained with 75% irradiation of the  $\eta^5\text{-C}_5\text{H}_5$  resonance (100% irradiation was avoided to minimize complications of decoupler spillover) and the second (off-resonance) with the decoupler

frequency set  $>2$  ppm from all resonances. Spectra were obtained at 21 °C in interleaved blocks of 32 transients with four steady states per block for a total of at least 1216 transients. The acquisition time was 2.0 s, and the pulse delay was 6 s (selected to be at least three times the largest  $T_1$  of interest: 1.7 s for  $H_\gamma$ ; 1.4 s for  $H_\beta$ ; 0.5–0.6 s for  $H_{\alpha,\alpha'}$ ). Difference NOEs were calculated by subtraction of the off-resonance spectrum from the  $\eta^5$ - $C_5H_5$ -irradiated spectrum. Data were similarly acquired for **2a** with a pulse delay of 10 s;  $T_1$  values: 1.1–1.3 s for  $H_{\gamma,\gamma'}$ ; 3.2 s for  $H_\beta$ ; 0.8 s for  $H_{\alpha,\alpha'}$ .

**X-ray Crystal Structure of 2c.** A sample of **2c** (0.078 g) was dissolved in toluene (2 mL), layered with heptane (7 mL), and kept at -20 °C for 7 days. Red prisms of **2c** formed, and the mother liquor was decanted. A crystal was mounted on a glass fiber, and axial photographs showed monoclinic symmetry. Unit-cell dimensions were obtained by least-squares refinement using 15 centered reflections for which  $25^\circ < 2\theta < 36^\circ$ . Data collection was carried out on a Nicolet R3m/E four-circle diffractometer as outlined in Table I.

Data reduction<sup>27</sup> included corrections for Lorentz and polarization effects. Systematic extinctions indicated the space group  $P2_1/n$ . A Patterson synthesis gave the rhenium position, and the remaining non-hydrogen atoms were located by difference maps. These were refined with anisotropic thermal parameters by blocked-cascade least squares, minimizing  $\sum w\Delta^2$ , with 101 parameters refined in each full-matrix block. Scattering factors were taken from the literature.<sup>28</sup> Empirical absorption corrections were based on the azimuthal scan data. Calculated hydrogen

positions were used during refinement with a common refined isotropic thermal parameter.

Refinement behavior and difference maps indicated disorder of the allyl ligand. The subordinate orientation was related to the predominant orientation by rotations of ca. 27° and 170° about the Re–C1 and C1–C2 bonds, respectively, with some distortions from C1–C4 planarity to make the phenyl rings of the two orientations nearly coplanar. A disorder model giving approximate fit to the positions of difference map peaks was calculated from idealized geometry. The disorder model was introduced into the refinement with some constraints imposed on the subordinate orientation: isotropic refinement of carbon atoms; rigid group constraints for the phenyl ring; bond distances for C1–C2', C2'–C3', and C3'–C4' set at the corresponding refined distances in the predominant orientation. The occupation factor for the subordinate orientation refined to 0.212 (2). Previously refined isotropic thermal parameters for the carbons of the subordinate orientation were fixed in the final cycles of refinement to facilitate convergence.

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**Registry No.** **2a**, 97396-45-7; **2b**, 122295-31-2; **2c**, 122295-30-1; **3a** (isomer 1), 85955-92-6; **3a** (isomer 2), 85926-81-4; **3b**, 85926-83-6; **3c** (isomer 1), 115074-77-6; **3c** (isomer 2), 122442-00-6; ( $\eta^5$ - $C_5H_5$ )Re(NO)(PPh<sub>3</sub>)(H), 79919-58-7; 2-methylallyl chloride, 107-05-1; cinnamyl chloride, 2687-12-9; allyl chloride, 107-05-1.

**Supplementary Material Available:** Tables of atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **2c** (3 pages); a listing of calculated and observed structure factors for **2c** (25 pages). Ordering information is given on any current masthead page.

(27) All crystallographic calculations were performed on a Data General Eclipse computer using the SHELXTL program package by G. M. Sheldrick, Nicolet Analytical Instruments, Madison, WI, 1983.

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## Metalladiboranes of the Iron Subgroup: $K[M(CO)_4(\eta^2-B_2H_5)]$ ( $M = Fe, Ru, Os$ ) and $M'(\eta^5-C_5H_5)(CO)_2(\eta^2-B_2H_5)$ ( $M' = Fe, Ru$ ). Analogues of Metal–Olefin Complexes

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The metal carbonylates  $[M(CO)_4]^{2-}$  ( $M = Fe, Ru, Os$ ) and  $[(\eta^5-C_5H_5)M'(CO)_2]^-$  ( $M' = Fe, Ru$ ) react with  $L-BH_3$  ( $L = THF, Me_2O$ ) to yield the metalladiborane complexes  $[M(CO)_4(\eta^2-B_2H_5)]^-$  and  $(\eta^5-C_5H_5)M'(CO)_2(\eta^2-B_2H_5)$ . The molecular structure of  $(\eta^5-C_5H_5)Fe(CO)_2(\eta^2-B_2H_5)$  was determined from single-crystal X-ray data. This structure can be described as that of a diborane(6) molecule with a  $(\eta^5-C_5H_5)Fe(CO)_2$  unit replacing a bridge hydrogen. Distances and angles within the  $B_2H_5$  unit are consistent with those observed for  $B_2H_6$ . Crystal data for  $(\eta^5-C_5H_5)Fe(CO)_2(\eta^2-B_2H_5)$ : space group  $Pnam$ , orthorhombic,  $a = 11.955$  (3) Å,  $b = 6.425$  (1) Å,  $c = 11.552$  (3) Å,  $V = 887.44$  Å<sup>3</sup>, mol wt 204.04,  $\rho_{\text{calcd}} = 1.524$  g/cm<sup>3</sup>, for  $Z = 4$ . For Mo  $K\alpha$  1355 unique reflections were collected at -174 °C over the range  $5^\circ < 2\theta < 55^\circ$  with 1100 reflections greater than  $2.33\sigma(I)$  used in the final refinement.  $R_F = 0.0254$  and  $R_{wF} = 0.0303$ . Boron-11 and proton NMR spectra also indicate diborane-like structures for  $[M(CO)_4(\eta^2-B_2H_5)]^-$  ( $M = Fe, Ru, Os$ ) and  $(\eta^5-C_5H_5)M'(CO)_2(\eta^2-B_2H_5)$ . Mössbauer spectra as well as the X-ray diffraction data support a three-center, two-electron bond representation between the metal center and the two borons of the  $B_2H_5$  moiety.

### Introduction

The nucleophilic nature of transition-metal carbonylates is well established. Dessy and King<sup>1</sup> and later Pearson<sup>2</sup>

determined relative nucleophilicities of selected transition-metal carbonylates through reactions with alkyl halides. Such carbonylates are expected to form addition

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