solid of 4 (0.011 mmol, 46% yield). Pure 4 of pale yellow needle crystals for microanalysis and X-ray diffraction study was obtained by recrystallization from benzene–pentane (v/v = 1/1) down to −10 °C. 4: mp 159–161 °C (under N_2). ^{1}H NMR ($CDCl_3$): δ 0.21 (s, 3 H, $SiCH_3$), 0.48 (s, 3 H, $SiCH_3$), 0.96 (td, $^3J_{HH} \approx {}^3J_{HP} \approx 14.8$ Hz, 18 H, $PCCH_3$), 1.18–1.68 (m, 12 H, PCH_2), 6.83 (d, $^4J_{HP(trans)} \approx 14.6$ Hz, $^3J_{HPt} \approx 122.9$ Hz, 2 H, CH=), 6.99–7.37 and 7.61–7.83 (each m, 10 H, C_6H_5). ^{31}P NMR ($CDCl_3$): δ −2.7 ($^1J_{PPt}$ = 1741 Hz). IR (Nujol): 1510 (m), 1232 (m), 1038 (m), 868 (m), 836 (m), 760 (s), 716 (m), 698 (m), 570 (m) cm^{-1}. Anal. Calcd for $C_{30}H_{48}P_2PtSi$: C, 51.93; H, 6.97. Found: C, 52.33; H, 7.01.

^{1}H NMR measurement before opening the NMR tube indicated the presence of Me_2SiH_2 in solution (−0.02 (t, $^3J_{HH}$ = 4.1 Hz, $Si-CH_3$) ppm, ~5%). In addition, GC analysis (OV-1701) of the solution showed at least 20 peaks arising from unreacted phenylacetylene (A, ~0.007 mmol), styrene (B, ~0.004 mmol), and other volatile products. The structures of the products except for Me_2SiH_2 and styrene were not fully confirmed yet because of the difficulty of their separation. However, some of them were tentatively assigned by GC–MS to be 1:1 adducts of Me_2SiH_2 with phenylacetylene (C1, C2) and five- and six-membered silacycles such as 1,1-dimethyl-2,4-, 1,1-dimethyl-2,5-, or 1,1-dimethyl-3,4-diphenyl-1-sila-2,4-cyclopentadiene (D), 1,1-dimethyl-2,4-, 1,1-dimethyl-2,5-, 1,1-dimethyl-3,4-, or 1,1-dimethyl-3,5-diphenyl-1-sila-2-cyclopentene (E), 1,1,4,4-tetramethyl-2,5- or 1,1,4,4-tetramethyl-2,6-diphenyl-1,4-disila-2,5-cyclohexadiene (F), 1,1,4,4-tetramethyl-2,5- or 1,1,4,4-tetramethyl-2,6-diphenyl-1,4-disila-2-cyclohexene (G), and 1,1,4,4-tetramethyl-2,5- or 1,1,4,4-tetramethyl-2,6-diphenyl-1,4-disialcyclohexene (H). The approximate GC area ratio of A:B:C1:C2:D:E:F:G:H was estimated at ~20:~10:0.5:0.5:5:3:8:14:1 (OV-1701, FID). The GC–MS spectral data (m/z (relative intensity)) of the products (C–H) are as follows. C1: 162 (M^+, 26), 147 (100), 145 (29), 121 (38), 59 (21), 58 (22), 43 (22). C2: 162 (M^+, 28), 147 (100), 145 (45), 121 (20), 59 (12), 58 (25), 43 (24). D: 262 (M^+, 100), 247 (60), 145 (15), 105 (15), 43 (22). E: 264 (M^+, 86), 249 (52), 205 (36), 204 (27), 173 (34), 161 (68), 145 (100), 135 (57), 121 (39), 59 (71), 43 (28). F: 320 (M^+, 85), 305 (100), 203 (24), 173 (20), 145 (38), 73 (41), 43 (31). G: 322 (M^+, 80), 263 (29), 218 (46), 161 (36), 135 (40), 73 (40), 43 (18). H: 324 (M^+), fragment peaks could not be confirmed to have come from H because of the partial overlapping of the GC peak with G.

Thermolysis of 4. A benzene-d_6 (0.30 mL) solution of 4 (0.0014 mmol) in a sealed NMR tube was heated at 120 °C for 40 min. The ^{1}H NMR signals for 4 disappeared, and new $Si-CH_3$ proton signals emerged at 0.24, 0.41, 0.45, and 0.55 ppm with an integral ratio of 2.9:3.1:1:3.5. GC and GC–MS analyses of the solution revealed the formation of 6 as the sole volatile product. 6 was separated by short-path silica gel chromatography using hexane as eluent. The ^{1}H NMR spectrum of 6 in $CDCl_3$ was in good agreement with the reported one[28] (in benzene-d_6, 0.40 ($Si-CH_3$) and 6.24 (=CH) ppm). The yield of 6 was estimated at 30% by means of the ^{1}H NMR of the reaction mixture. The GC–MS fragmentation pattern of 6 was the same as that of the compound D formed in the reaction of 2 with phenylacetylene.

X-ray Crystallographic Analysis for 4. A crystal was sealed in a glass capillary tube and an empirical absorption correction (ψ scan) was applied to the data. Cell constants were obtained from 25 higher angle ($30 < 2\theta < 40°$) reflections. The structure was solved by MULTAN 78,[29] and the program system UNICS III[30] was used for calculations. A total of 4211 reflections ($|F_o| \geq 3\sigma|F_o|$) was used. Six hydrogen atoms were taken from a difference Fourier map; the remainder were located with calculated positions. Refinement was by full matrix least squares, $R = 0.0817$ ($R_w = 0.102$); the position and temperature factors of hydrogen atoms were not refined. Scattering factors for atoms were taken from ref 31.

Acknowledgment. We are indebted to Dr. Andrew J. Wynd who participated in the preliminary experiments.

Supplementary Material Available: Tables of the coordinates of hydrogen atoms, thermal parameters, complete bond lengths and angles, least-squares planes with atomic deviations, and angles between the planes for 4 (19 pages). Ordering information is given on any current masthead page.

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Synthesis, Structure, and Reactivity of Allene Complexes of the Chiral Rhenium Fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$

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Reactions of the chlorobenzene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClC_6H_5)]^+BF_4^-$ and excess (a) allene, (b) methylallene, and (c) 1,1-dimethylallene give the π adducts $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}C{=}CRR')]^+BF_4^-$ (**1a–c**) in 90–91% yields. The crystal structure of **1a** (monoclinic, $P2_1/n$, a = 10.327 (1) Å, b = 10.401 (1) Å, c = 23.919 (2) Å, β = 99.233 (2)°, Z = 4) shows the coordinated $=CH_2$ group to be syn to the PPh_3 ligand, with a 23.7° angle between the Re—P bond and the Re—C=C plane. NMR data show that the methyl groups in **1b,c** occupy the less hindered positions on the free C=C linkages. Analogous reactions of chiral 1,3-dialkylallenes give mixtures of diastereomeric adducts with modest selectivities. Reaction of **1a** and t-BuO^-K^+ in THF (−80 to +25 °C) gives the methylacetylide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C{\equiv}CCH_3)$ (**3**, 92%). A similar reaction of **1a** and CH_3Li gives the allenyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH{=}C{=}CH_2)$ (**4**, 70%), which upon treatment with $HBF_4{\cdot}OEt_2$ gives mainly the propyne complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(HC{\equiv}CCH_3)]^+BF_4^-$ (**5**). Reaction of $Li^+[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^-$ and $HC{\equiv}CCH_2OTs$ gives the propargyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2C{\equiv}CH)$, which isomerizes to **4** at 67–80 °C. Thus, the conversion of **1a** to **3** is proposed to involve **4** and **5** as intermediates.

The physical and chemical properties of transition-metal allene complexes have been the subject of numerous investigations.[1-4] Depending upon the C=C=C substitution pattern, a diverse array of linkage isomers and ste-

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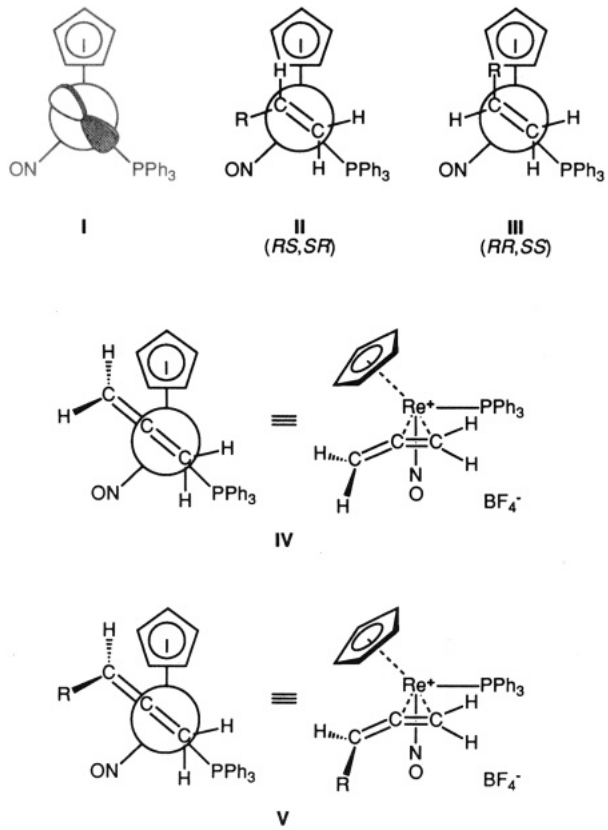
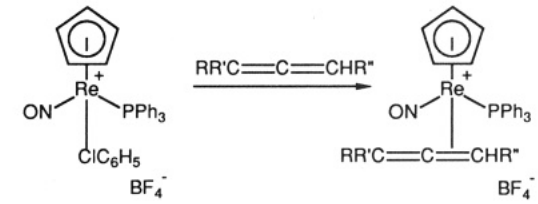
Chart I. (I) d-Orbital HOMO of the Chiral Rhenium Fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$, (II, III) Idealized Structures of Diastereomeric Monosubstituted Alkene Complexes, (IV) Idealized Structure of the Parent Allene Complex 1a, (V) Idealized Structure of the Most Stable Isomer of a Monosubstituted Derivative of 1a



reoisomers are possible. Also, fluxional processes in which the metal traverses the orthogonal C=C π moieties have been documented.[2,3]

We have had an ongoing interest in π hydrocarbon complexes of the chiral rhenium fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (I).[5-10] In many cases, one of two possible diastereomeric adducts can be obtained with high selectivity.[5] Also, a variety of highly stereoselective transformations of these and related compounds have been developed.[7,8] Importantly, 1,3-disubstituted allenes are chiral.

Scheme I. Synthesis of Allene Complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}RR'C{=}C{=}CHR'')]^+BF_4^-$ (1)



a R = R' = R" = H (90%)
b R = CH_3; R' = R" = H (90%)
c R = R' = CH_3; R" = H (91%)
d R = H; R' = R" = CH_3 (96%)
e R = H; R' = R" = C_2H_5 (91%)
f R = H; R' and R" = $-(CH_2)_6-$ (51%)

Thus, there is the possbility of chiral recognition—i.e., the selective binding of one enantiomer to a given enantiomer of I. Hence, we set out to study the synthesis, structure, and reactivity of allene complexes of the general formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}R''HC{=}C{=}CRR')]^+BF_4^-$ (1).

Some previously established properties of I provide a helpful background for this chemistry. First, I possesses the high-lying d orbital HOMO shown in Chart I.[11] Thus, alkenes adopt Re—(C=C) conformations that allow a high degree of overlap of their π^* acceptor orbitals with this orbital. With monosubstituted alkenes, the larger =CHR terminus is found anti to the bulky PPh_3 ligand.[5] For such alkenes two configurational diastereomers are also possible, as illustrated by II and III in Chart I. These differ in the alkene enantioface bound to the rhenium. Typically, K_{eq} values (II/III) are >96:4, reflecting the destabilizing interaction of the C=C substituents with the cyclopentadienyl ligands in III.[5] Thus, we expected that coordinated allenes would generally adopt the idealized Re—(C=C) conformation shown in IV and that any substituent on the uncoordinated C=C moiety would preferentially occupy the position directed away from (or trans to) the metal fragment, as in V.

Results

1. Complexes of Achiral Allenes. The chlorobenzene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClC_6H_5)]^+BF_4^-$ (2) was generated at −45 °C as previously described.[12] This compound has been shown to be a mixture of linkage and constitutional isomers and a convenient functional equivalent of the chiral rhenium Lewis acid I. An excess of allene (1,2-propadiene) was then condensed into the solution. The reaction vessel was stoppered and kept at room temperature for 20 h and then 85 °C for 21 h. Workup gave the parent allene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}C{=}CH_2)]^+BF_4^-$ (**1a**) as a pale yellow powder in 90% yield (Scheme I).

Complex **1a** was characterized by microanalysis (Experimental Section) and IR and NMR (^1H, ^{13}C, ^{31}P) spectroscopy (Table I). Four =CH ^1H NMR resonances were observed. Two (δ 2.16, 2.33) were upfield of that of free allene (δ 4.45, CCl_4)[13] and, by analogy to chemical shift

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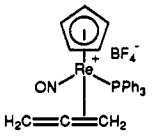
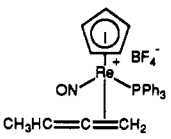
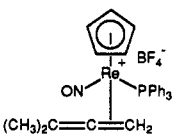
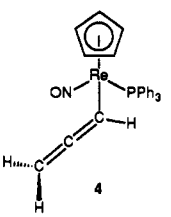
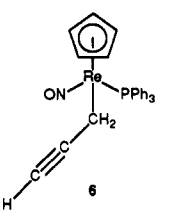
Table I. Spectroscopic Characterization of New Rhenium Complexes

compd	IR (cm^{-1}, thin film)	^1H NMR[a] (δ)	$^{13}C\{^1H\}$ NMR[b] (ppm)	$^{31}P\{^1H\}$ NMR[c] (ppm)
 1a	ν_{NO} 1737[d] (s)	7.64–7.55 (m, PPh_3) 7.17 (ddd, J_{HH} 3.3, 3.3, 3.3, =C*H*H′/free) 5.99 (dddd, J_{HH} 3.3, 3.3, 3.3, J_{HP} 1.4, =CH*H*′/free) 5.80 (s, C_5H_5) 2.33 (dddd, J_{HH} 3.3, 3.3, 10.8, J_{HP} 12.0, =C*H*H′/bound) 2.16 (dddd, J_{HH} 3.3, 3.3, 10.8, J_{HP} 5.6, =CH*H*′/bound)[e]	147.6 (s, =C=) PPh_3 at 132.9 (d, J 9.9, ortho), 132.3 (s, para), 129.8 (d, J 11.2, meta), 128.9 (s, part of ipso) 110.2 (s, $=CH_2$/free) 90.1 (s, C_5H_5) 9.0 (d, J 6.5, $=CH_2$/bound)[f]	11.9 (s)
 1b	ν_{NO} 1736[d] (s)	7.60–7.33 (m, PPh_3) 6.14 (m, =CHR) 5.78 (s, C_5H_5) 2.29 (dd, J_{HH} 10.0, J_{HP} 10.0, =C*H*H′) 2.11 (d, J_{HH} 4.8, CH_3) 1.98 (m, =CH*H*′)[e]	138.0 (s, =C=) PPh_3 at 133.2 (d, J 10.2, ortho), 132.7 (s, para), 130.0 (d, J 11.2, meta), 129.4 (s, part of ipso) 122.2 (s, =CHR) 98.3 (s, C_5H_5) 23.4 (s, CH_3) 8.6 (d, J 6.0, $=CH_2$)[e]	12.2 (s)
 1c	ν_{NO} 1735[d] (s)	7.59–7.27 (m, PPh_3) 5.84 (s, C_5H_5) 2.22 (s, CH_3) 2.01 (s, CH_3') 1.82 (m, =C*H*H′) 1.74 (m, =CH*H*′)[f]	PPh_3 at 133.9 (d, J 10.0, ortho), 132.4 (s, para), 129.8 (d, J 11.2, meta), 128.8 (s, part of ipso) 131.5 ($=CR_2$)[g] 126.7 (s, =C=) 97.5 (s, C_5H_5) 29.1 (s, CH_3) 23.8 (s, CH_3') 6.9 (s, $=CH_2$)[f]	12.2 (s)
 4	ν_{NO} 1644 (s) $\nu_{C=C=C}$ 1900 (w)	7.73–7.16 (m, PPh_3) 6.59 (ddd, J_{HH} 6.4, 6.4, J_{HP} 4.4, ReCH) 5.05 (s, C_5H_5) 4.05 (ddd, J_{HH} 7.9, 6.4, J_{HP} 3.8, =C*H*H′) 3.98 (ddd, J_{HH} 7.9, 6.4, J_{HP} 3.8, =CH*H*′)[f]	207.1 (d, J 2.5, =C=) PPh_3 at 137.2 (d, J 52.7, ipso), 134.5 (d, J 10.4, ortho), 131.0 (s, para), 129.2 (d, J 9.9, meta) 93.2 (s, C_5H_5) 64.3 (d, J 10.7, ReCH=) 60.7 (s, $=CH_2$)[f]	20.2 (s)
 6	ν_{NO} 1635 (s) $\nu_{C=C}$ 2079 (w)	7.60–6.90 (m, PPh_3) 4.73 (s, C_5H_5) 3.01 (ddd, J_{HH} 15.2, 2.7, J_{HP} 5.9, ReC*H*H′) 2.47 (ddd, J_{HH} 15.2, 2.7, J_{HP} 4.4, ReCH*H*′) 2.15 (dd, J_{HH} 2.7, 2.7, ≡CH)[h]	PPh_3 at 136.6 (d, J 51.3, ipso), 133.8 (d, J 10.7, ortho), 130.1 (s, para), 128.5 (d, J 9.6, meta) 91.2 (s, C_5H_5) 85.4 (s, CC≡) 66.5 (s, ≡CH) 1.5 (s, CH_2)[h]	24.8 (s)

[a] At 300 MHz and ambient probe temperature; couplings are in hertz. [b] At 75 MHz and at ambient probe temperature; couplings (hertz) are to phosphorus. [c] At 121 MHz and ambient probe temperature and in the solvent specified for $^{13}C\{^1H\}$ NMR; referenced to external 85% H_3PO_4 (0.00 ppm). [d] Some spectra exhibited a 5–6-cm^{-1} splitting. [e] In CD_2Cl_2 and referenced to $CHDCl_2$ (δ 5.32) or CD_2Cl_2 (53.8 ppm). [f] In $CDCl_3$ and referenced to $Si(CH_3)_4$ (δ 0.00) or $CDCl_3$ (77.0 ppm). [g] Provisional assignment of resonance. [h] In C_6D_6 and referenced to $Si(CH_3)_4$ (δ 0.00) or C_6D_6 (128.0 ppm).

trends in the corresponding alkene complexes,[5] were assigned to the coordinated C=CH_2 moiety. The geminal coupling was appreciable ($^1J_{HH}$ 11–12 Hz), and phosphorus couplings ($^3J_{HP}$) were similar to those in alkene complexes.[5] The ^1H NMR resonances of the uncoordinated C=CH_2 moiety (δ 7.17, 5.99) were downfield of those of free allene, and exhibited much smaller geminal and phosphorus ($^4J_{HP}$) couplings. Similar =CH_2 chemical shift trends have been observed in the related allene complexes (η^5-C_5Me_5)Re(CO)$_2$(H_2C=C=CH_2)[4a] and [(η^5-C_5H_5)Fe(CO)(PPh_3)(H_2C=C=CH_2)]$^+BF_4^-$.[14]

The $^{13}C\{^1H\}$ NMR spectrum of **1a** showed allene ligand resonances at 147.6, 110.2, and 9.0 ppm. Two of these (147.6, 9.0 ppm) were 66–67 ppm upfield from the =C= and =CH_2 resonances of free allene (213.5, 74.8 ppm, CS_2).[13] They were assigned, by analogy to chemical shift trends in the corresponding alkene complexes,[5] to the coordinated =C= and =CH_2 carbons. The remaining peak (110.2 ppm), which was ca. 35 ppm downfield from the =CH_2 resonance of allene, was attributed to the free =CH_2 moiety. These assignments were verified by a proton-coupled ^{13}C NMR spectrum, which showed $^1J_{CH}$ values of 162 and 164 Hz for the 110.2 and 9.0 ppm resonances. Free allene exhibits a similar $^1J_{CH}$ (168 Hz),[13c] and the iron allene complex [(η^5-C_5H_5)Fe(CO)(PPh_3)(H_2C=C=CH_2)]$^+BF_4^-$ shows parallel chemical shift trends (ppm: =C=, 160.8; free =CH_2, 107.3, $^1J_{CH}$ = 167 Hz; bound =CH_2, 17.0, $^1J_{CH}$ = 171 Hz).[14]

Next, **2** was treated with excess 1,2-butadiene (methylallene) and 3-methyl-1,2-butadiene (1,1-dimethylallene) for 5 days at room temperature (Scheme I). Workup gave the corresponding methylated allene complexes [(η^5-C_5H_5)Re(NO)(PPh_3)(H_2C=C=$CHCH_3$)]$^+BF_4^-$ (**1b**) and [(η^5-C_5H_5)Re(NO)(PPh_3)(H_2C=C=$C(CH_3)_2$)]$^+BF_4^-$ (**1c**) as tan powders in 90–91% yields. Both crude and purified **1b,c** generally appeared by NMR to be diastereomerically homogeneous, and data are summarized in Table I. However, a second cyclopentadienyl ^1H NMR resonance was noted in some samples of **1b** (δ 5.83, 5.78; ca. 26:74).[15]

(14) Reger, D. L.; Coleman, C. J.; McElligott, P. J. *J. Organomet. Chem.* **1979**, *9*, 1191.

Table II. Summary of Crystallographic Data for the Allene Complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}C{=}CH_2)]^+BF_4^-$ (1a)

molecular formula	$C_{26}H_{24}BF_4NOPRe$
fw	670.466
cryst syst	monoclinic
space group	$P2_1/n$
cell dimensions	
a, Å	10.327 (1)
b, Å	10.401 (1)
c, Å	23.919 (2)
β, deg	99.233 (2)
V, Å^3	2535.81
Z	4
temp of collcn, °C	16 (1)
d_{calcd}, g/cm^3	1.756
d_{obsd}, g/cm^3 (23 °C)	1.732
cryst dimens, mm	0.29 × 0.24 × 0.19
λ(Mo/Kα) radiation, Å	0.71073
data collcn method	$\theta/2\theta$
scan speed, deg/min	3.0
range/indices (h,k,l)	0,12 0,12 −28,28
scan range	$K_{\alpha 1}$ −1.0 to $K_{\alpha 2}$ +1.0
no. of reflns between stds	98
total no. of unique data	5114
no. of obsd data, $I > 3\sigma(I)$	4749
abs coeff (μ), cm^{-1}	49.66
min transm, %	62.1
max transm, %	99.9
no. of variables	328
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.0240
$R_w = [\sum w(\|F_o\| - \|F_c\|)^2/\sum w\|F_o\|^2]^{1/2}$	0.0267
goodness of fit	3.05
Δ/σ (max)	0.019
$\Delta\rho$ (max), e Å^{-3}	0.642

The $=CH_2$ ^1H NMR chemical shifts in **1b,c** (δ 2.29–1.74) were upfield of those of free allene, thus showing the C=CH_2 moieties to be bound to rhenium. The C=C=C ^{13}C NMR resonances exhibited chemical shift patterns analogous to those of free methylated allenes.[13b] The PPh_3 ligand ^{31}P NMR resonances of **1a–c** were very slightly downfield from those of analogous terminal alkene complexes, and the IR ν_{NO} values were slightly higher.[5] These trends suggest that allene ligands are somewhat stronger π acids than alkenes.

2. Structures of Achiral Allene Complexes. We sought to probe the structures of **1a–c** in the solid state and solution. First, X-ray data were collected on a crystal of **1a** as summarized in Table II. Refinement, described in the Experimental Section, gave the structures shown in Figure 1. All $=CH_2$ hydrogen atoms were located and refined. Atomic coordinates, and selected bond lengths, bond angles, and torsion angles, are given in Tables III and IV.

As is shown in Figure 1, **1a** adopts a Re—(C=CH_2) conformation close to that of the idealized structure IV (Chart I). The difference was analyzed in several ways. For example, the Re—P and Re—N bonds in IV make angles of 0 and 90°, respectively, with the Re—C=C plane. In **1a**, the corresponding angles were found to be 24 and 62°. Alternatively, the angle of the Re—C=C plane with the plane defined by the cyclopentadienyl centroid, rhenium, and C=C centroid is 45° in IV and 76° in **1a**.

Next, **1a–c** were subjected to a series of difference ^1H NOE experiments.[16] Irradiation of the cyclopentadienyl

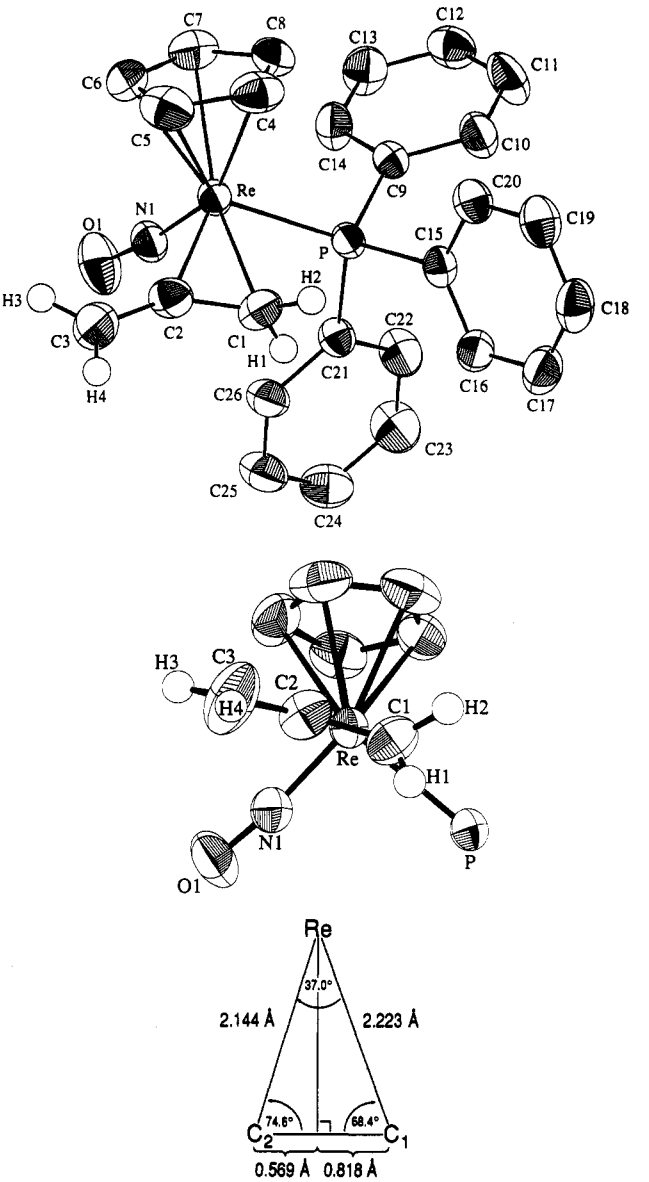
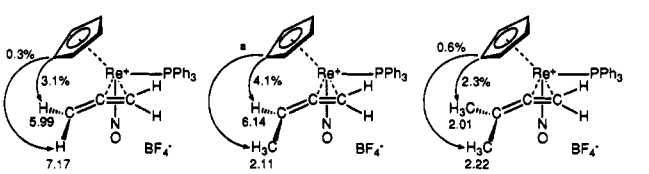


Figure 1. Structure of the cation of the allene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}C{=}CH_2)]^+BF_4^-$ (**1a**): (top) numbering diagram; (middle) Newman-type projection; (bottom) view of Re—C=C plane.

Chart II. Summary of ^1H Difference NOE Data for Allene Complexes 1a–c



[a] The CH_3 and $=CH_2$ ^1H NMR resonances of **1b** overlap. Thus, this enhancement could not be accurately determined.

ligand gave the enhancements summarized in Chart II. In **1a**, the proton of the uncoordinated C=CH_2 moiety that showed the larger enhancement (δ 5.99) was assigned as cis to the rhenium. A similar enhancement was found for the $=CHCH_3$ proton of methylallene complex **1b**. Hence, the proton and methyl substituents in **1b** were assigned as cis and trans to the rhenium, respectively. Finally, the methyl group that showed the larger enhancement in 1,1-dimethylallene complex **1c** (δ 2.01) was assigned as cis to the rhenium. These data fully support the bonding

(15) In view of the data on 1,3-disubstituted allene complexes below, we believe that if this resonance represented a second diastereomer of **1b**, additional CH_3 ^1H and ^{13}C NMR resonances, as well as PPh_3 ^{31}P NMR resonances, would have been detected.

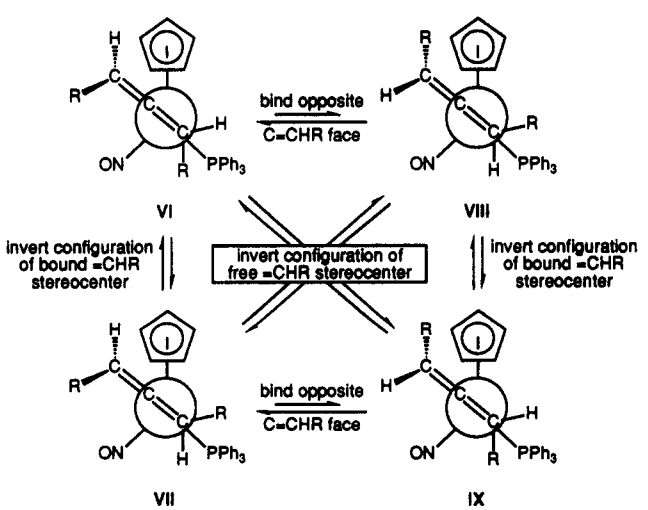
(16) Neuhaus, D.; Williamson, M. *The Nuclear Overhauser Effect in Structural and Conformational Analyses*; VCH: New York, 1989; Chapter 7.

Table III. Atomic Coordinates and Equivalent Isotropic Parameters for Refined Atoms in 1a[a]

atom	x	y	z	B (Å²)
Re	0.53095 (2)	0.34022 (2)	0.16507 (1)	3.196 (3)
B	0.4907 (6)	0.8266 (7)	0.2382 (3)	4.6 (1)
F1	0.4102 (5)	0.7556 (4)	0.1979 (2)	9.7 (1)
F2	0.5862 (4)	0.7523 (5)	0.2665 (2)	9.3 (1)
F3	0.5510 (5)	0.9230 (5)	0.2125 (2)	8.6 (1)
F4	0.4208 (4)	0.8873 (7)	0.2727 (2)	11.1 (2)
N	0.6230 (4)	0.2198 (5)	0.1383 (2)	4.1 (1)
O	0.6894 (4)	0.1350 (5)	0.1260 (2)	6.8 (1)
P	0.3436 (1)	0.3035 (1)	0.09234 (5)	3.21 (2)
C1	0.5343 (6)	0.5114 (6)	0.1097 (2)	4.6 (1)
C2	0.6577 (5)	0.4851 (6)	0.1400 (2)	4.6 (1)
C3	0.7835 (6)	0.5110 (8)	0.1497 (3)	7.1 (2)
C4	0.4504 (7)	0.4538 (6)	0.2350 (2)	5.6 (1)
C5	0.5867 (6)	0.4394 (7)	0.2505 (3)	5.8 (2)
C6	0.6123 (6)	0.3059 (8)	0.2581 (2)	5.9 (2)
C7	0.4917 (6)	0.2403 (6)	0.2454 (2)	5.1 (1)
C8	0.3920 (5)	0.3319 (7)	0.2317 (2)	4.9 (1)
C9	0.2302 (4)	0.1819 (5)	0.1095 (2)	3.4 (1)
C10	0.0952 (5)	0.2004 (6)	0.1012 (3)	4.9 (1)
C11	0.0136 (5)	0.0986 (7)	0.1100 (3)	6.0 (2)
C12	0.0646 (6)	−0.0199 (6)	0.1266 (3)	5.1 (1)
C13	0.1972 (6)	−0.0380 (6)	0.1357 (3)	5.2 (1)
C14	0.2804 (5)	0.0633 (6)	0.1280 (3)	4.5 (1)
C15	0.2431 (5)	0.4457 (5)	0.0716 (2)	3.5 (1)
C16	0.2303 (5)	0.4951 (6)	0.0173 (2)	4.2 (1)
C17	0.1586 (6)	0.6058 (6)	0.0033 (3)	5.4 (1)
C18	0.0985 (6)	0.6678 (6)	0.0432 (3)	5.5 (1)
C19	0.1101 (6)	0.6187 (6)	0.0972 (3)	5.2 (1)
C20	0.1820 (5)	0.5084 (6)	0.1120 (2)	4.6 (1)
C21	0.3841 (5)	0.2407 (5)	0.0260 (2)	3.6 (1)
C22	0.2857 (6)	0.1818 (6)	−0.0119 (2)	5.0 (1)
C23	0.3119 (6)	0.1361 (7)	−0.0631 (3)	6.0 (2)
C24	0.4358 (6)	0.1456 (7)	−0.0769 (2)	5.6 (1)
C25	0.5336 (6)	0.2037 (7)	−0.0399 (2)	5.3 (1)
C26	0.5090 (5)	0.2522 (6)	0.0114 (2)	4.3 (1)
H1	0.514 (6)	0.510 (6)	0.079 (2)	5.0
H2	0.468 (6)	0.584 (6)	0.112 (2)	5.0
H3	0.845 (6)	0.457 (6)	0.175 (2)	5.0
H4	0.808 (6)	0.565 (6)	0.130 (2)	5.0

[a] Atoms refined anisotropically are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

Chart III. Possible Diastereomeric Adducts of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (I) and 1,3-Disubstituted Allenes RHC═C═CHR



model in Chart I and establish that the ^1H NMR chemical shifts of the ═CR_2 groups that are cis to the rhenium in **1a,c** are upfield from those that are trans.

3. Complexes of Chiral Allenes. Based upon the bonding model in Chart I, symmetrically 1,3-disubstituted allenes RCH═C═CHR—which are chiral but have C_2

Table IV. Key Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) in 1a

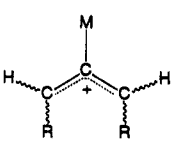
Re–P	2.4155 (7)	Re–N	1.754 (3)
Re–C1	2.223 (4)	Re–C2	2.144 (3)
Re–C4	2.308 (3)	Re–C5	2.278 (3)
Re–C6	2.277 (3)	Re–C7	2.278 (3)
Re–C8	2.310 (3)	P–C9	1.816 (3)
P–C15	1.830 (3)	P–C21	1.824 (3)
N–O	1.182 (3)	C1–C2	1.388 (5)
C2–C3	1.311 (5)	C4–C5	1.404 (5)
C4–C8	1.400 (5)	C5–C6	1.420 (6)
C6–C7	1.410 (5)	C7–C8	1.403 (5)
C1–H1	0.74 (4)	C1–H2	1.03 (4)
C3–H3	0.98 (4)	C3–H4	0.79 (4)
P–Re–N	92.43 (8)	P–Re–C1	77.58 (9)
P–Re–C2	111.34 (9)	N–Re–C1	107.0 (1)
N–Re–C2	90.5 (1)	C1–Re–C2	37.0 (1)
C1–C2–C3	148.5 (4)	C5–C4–C8	108.9 (3)
C4–C5–C6	107.2 (3)	C5–C6–C7	107.8 (3)
C6–C7–C8	108.2 (3)	C4–C8–C7	107.9 (3)
Re–P–C9	114.7 (1)	Re–P–C15	114.9 (1)
Re–P–C21	114.5 (1)	Re–N–O	173.0 (3)
Re–C1–C2	68.4 (2)	Re–C2–C1	74.6 (2)
Re–C2–C3	136.6 (3)	C2–C1–H1	128 (3)
C2–C1–H2	133 (2)	H1–C1–H2	89 (4)
C2–C3–H3	121 (2)	C2–C3–H4	116 (3)
H3–C3–H4	122 (4)		
P–Re–C1–C2	−156 (1)	N–Re–C1–C2	−67 (1)
Re–C1–C2–C3	174 (1)	H1–C1–C2–Re	−116 (6)
H1–C1–C2–C3	58 (6)	H2–C1–C2–Re	110 (5)
H2–C1–C2–C3	−76 (5)	Re–C2–C3–H3	−1 (4)
Re–C2–C3–H4	169 (5)	C1–C2–C3–H3	−172 (4)
C1–C2–C3–H4	−2 (5)		

symmetry—can in principle form at least four diastereomeric adducts with I. These are summarized in Chart III (VI–IX). The rhenium and each ═CHR moiety constitute independent stereocenters and can be defined by conventional *R/S* descriptors.[5]

Many types of relationships exist among VI–IX. For example, VI and VIII (and VII and IX) involve an *identical* allene ligand enantiomer, but differ in the C═CHR *diastereo*face bound to the rhenium. In theory, VI and VIII can equilibrate in the absence of a free allene. However, the isomerization of VI or VIII to VII or IX requires either (1) ligand exchange into a pool of free racemic allene or (2) a process that can invert the configuration of one of the ═CHR stereocenters.[17] Based upon the data with methylallene complex **1b**, we anticipated that VIII and IX, in which the larger alkyl substituent of the free ═CHR moiety is cis to the rhenium, would be the least stable—especially for cyclic allene ligands.

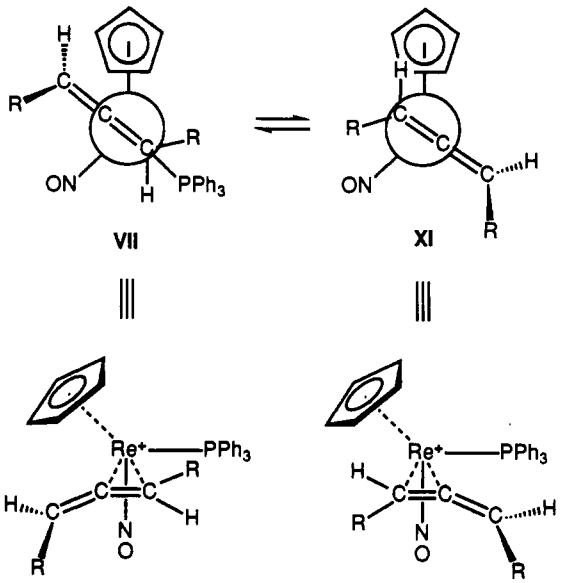
Thus, **2** and excess 2,3-pentadiene (1,3-dimethylallene) were reacted for 5 days at room temperature. Workup gave the crude 1,3-dimethylallene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3CH{=}C{=}CHCH_3)]^+BF_4^-$ (**1d**) in 94% yield. Integration of the cyclopentadienyl ^1H NMR resonances suggested a ca. 40:11:38:12 mixture of diastereomers

(17) (a) Note that exchange of the free and bound C═CHR moieties, coupled with rotation about the Re—(C═CHR) axis, also interconverts VI and VIII. (b) Alkene complexes of I are configurationally stable at rhenium at 100 °C.[5] Hence, we do not consider diastereomer interconversion mechanisms that involve inversion of configuration at rhenium. (c) As carefully analyzed by Rosenblum and Jones,[2,3] isomerization to a metal-substituted allyl cation of the type X can effect epimerization of the ═CHR stereocenters.



X

Chart IV. Possible Rotameric Equilibria in 1,3-Disubstituted Allene Complexes



(δ, $CDCl_3$: 5.88, 5.84, 5.80, 5.75). The sample was dissolved in chlorobenzene and kept at 100 °C for 24 h. Under similar conditions, analogous terminal alkene complexes undergo an *intramolecular* equilibration of the $H_2C{=}CHR$ face bound to rhenium (e.g., VI ⇄ VIII).[5c] Workup gave **1d** in 76% yield as a ca. 18:14:61:7 mixture of the same diastereomers. Comparable results were obtained when **2** and excess 2,3-pentadiene were directly reacted at 100 °C for periods of 0.5–30 h, and in ^1H NMR-monitored reactions analyzed prior to workup. Hence, there appears to be at least a moderate thermodynamic preference for one diastereomer.[18] NMR data for the two major diastereomers are summarized in the Experimental Section.[19]

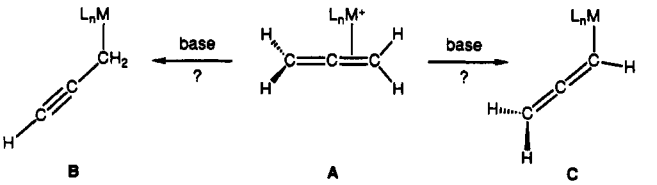
Similar experiments were conducted with other chiral allenes. For example, **2** and excess 3,4-heptadiene (1,3-diethylallene) were reacted for 4 days at room temperature and then 24 h at 90 °C. Workup gave the corresponding allene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C_2H_5CH{=}C{=}CHC_2H_5)]^+BF_4^-$ (**1e**) in 91% yield. The sample appeared to be a ca. 6:11:15:62:6 mixture of *five* diastereomers (^1H NMR (δ, $CDCl_3$) 5.97, 5.90, 5.85, 5.80, 5.76),[19] and a possible rationale is offered below. An analogous reaction of **2** and 1,2-cyclononadiene at room temperature gave $(\eta^5\text{-}C_5H_5)$-$Re(NO)(PPh_3)(\overline{CH{=}C{=}CH(CH_2)_6})]^+BF_4^-$ (**1f**) as a ca. 18:14:31:27 mixture of *four* diastereomers (δ 5.99, 5.83, 5.81, 5.76; 99%). A comparable experiment that included a 13-h period at 85 °C gave **1f** as a ca. 21:66:13 mixture of three diastereomers (δ 5.83, 5.80, 5.76; 51%).[19]

The NMR data for the most stable diastereomers of **1d–f** (Experimental Section) showed two conspicuous trends. First, the PPh_3 ^{31}P NMR resonances (16.3–17.1 ppm) were downfield from those of **1a–c** (Table I; 11.9–12.2 ppm) and the other isomers of **1d–f**. Second, the =C= ^{13}C NMR resonances of **1d,f** were strongly coupled to phosphorus ($^2J_{CP}$ 8.8–11.0 Hz). We have previously shown that in alkene and alkyne complexes of I, the C=C or C≡C carbon that is syn to the PPh_3 ligand (see II, III) exhibits—when resolved—the greater $^2J_{CP}$ value.[5a,9a] In accord with this generalization and the structures in Charts I and II, the bound $=CH_2$ carbons of **1a,b** exhibit greater $^2J_{CP}$ values (6.0–6.5 Hz) than the =C= carbons (Table I). However, the high =C= carbon $^2J_{CP}$ values in the most stable diastereomers of **1d,f** suggest that the allene ligands adopt Re—(C=CHR) conformations that differ from those in Chart III by 180°. This could in turn account for the greater than anticipated number of diastereomers for **1e,f**.

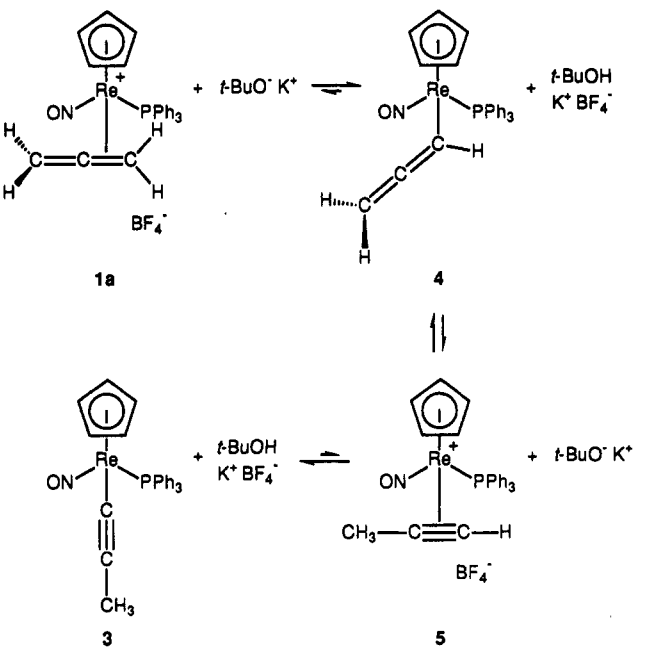
This possible equilbrium, which can be effected either by rotation about the Re—(C=CHR) axis *or* interchange of the free and bound C=CHR moieties,[17a] is illustrated for VII in Chart IV. The analogous rotational barrier in the ethylene complex of I is 16.4 kcal/mol (96 °C), while those in alkyne complexes of I are ≥22 kcal/mol (180 °C). The resulting rotamer XI is a plausible candidate for the most stable diastereomer of **1d–f**. In particular, the alkyl group of the bound C=CHR moiety occupies what would be the least hindered position in the corresponding monosubstituted alkene complexes (see II). Also, the free C=CHR moiety is bent away from the bulky PPh_3 ligand, such that only the small hydrogen substituent projects toward the phenyl rings. The steric interactions are reminiscent of these found in the analogous alkyne complexes.[9]

4. Reactivity of Allene Complexes. Cationic metal allene complexes have previously been observed to undergo deprotonation at the *free* $=CH_2$ terminus to give neutral propargyl complexes, as sketched for A → B in Scheme II.[20] However, we have found that many alkene complexes

Scheme II. Possible Deprotonation Modes of Cationic Allene Complexes A



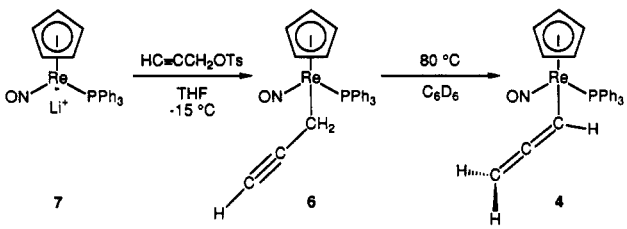
Scheme III. Proposed Pathway for the Conversion of Allene Complex 1a to Methylacetylide Complex 3



(18) The styrene complex of I does not exchange with free styrene-d_8 in $CDCl_2CDCl_2$ at 150 °C (6 h).[5c] Thus, unless an intermediate of the type X is accessible,[17c] it is doubtful that true thermodynamic equilibrium is achieved for all isomers of **1d**. However, the δ 5.88 and 5.80 isomers appear to interconvert, as well as the δ 5.84 and 5.75 isomers. Analogous pairs of diastereomers of **1f** also appear to equilibrate.

(19) Due to the small kinetic and equilibrium concentrations involved, additional NMR resonances could not be paired with the cyclopentadienyl resonances of the minor diastereomers. Hence, these structural assignments should be regarded as provisional. However, additional PPh_3 ^{31}P NMR resonances (and for **1d**, CH_3 ^1H NMR resonances), with chemical shifts close to those of the major diastereomers, were in all cases evident.

Scheme IV. Synthesis and Isomerization of Propargyl Complex 6



of I undergo ready *vinylic* deprotonation to give neutral vinyl complexes.[6,7] If cationic allene complexes were to react similarly, neutral allenyl complexes would form, as shown for A → C.

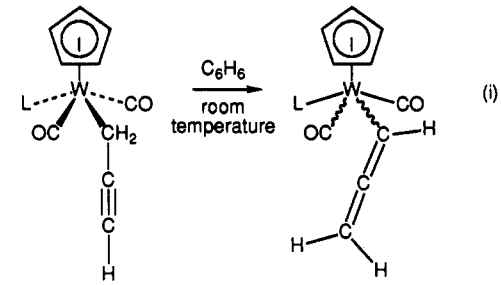
Hence, a THF solution of **1a** was cooled to −80 °C, and a THF solution of *t*-BuO⁻K⁺ (1.25 equiv) was added. The mixture was warmed to room temperature over the course of 3 h. Surprisingly, workup gave neither of the types of products anticipated in Scheme II. Rather, the previously characterized methylacetylide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C{\equiv}CCH_3)$ (**3**)[21] was isolated in 92% yield (Scheme III).

Experiments were conducted to probe the origin of **3**. First, the preceding reaction was repeated in a NMR tube in THF-d_8. After 1.5 h at −80 °C, a ^{31}P NMR spectrum was recorded (−75 °C). The resonance of **1a** had been replaced by new peaks at 21.8 and 20.5 ppm (ca. 13:87 area ratio). The sample was then kept at −10 °C for 2 h. The ratio of the two resonances subsequently increased to ca. 75:25. A ^1H NMR spectrum showed the major product to be **3**.

We suspected, on the basis of chemical intuition and the available NMR data, that the intermediate observed in the preceding reaction was the allenyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH{=}C{=}CH_2)$ (**4**). We thought that the deprotonation of **1a** by a stronger base, which would in turn generate a weaker conjugate acid, might prevent subsequent isomerization. Accordingly, reaction of **1a** and methyl lithium gave **4** as a spectroscopically pure, air-sensitive oily solid in 70% yield after workup. Complex **4** was characterized by IR and NMR spectroscopy as summarized in Table I. It exhibited IR ν_{C-C-C} (1900 cm^{-1}) and ^{13}C NMR chemical shfit values similar to those of other allenyl complexes.[21] The latter assignments were confirmed by a single-frequency proton-decoupled ^{13}C NMR spectrum, which showed the 60.7 ppm $=CH_2$ resonance to be a triplet ($^1J_{CH}$), and the 64.3 ppm ReCH= resonance to be a doublet of doublets ($^1J_{CH}$, $^2J_{CP}$).

Allenyl complexes have previously been shown to react with electrophiles at C_γ, thus generating cationic π alkyne complexes.[20] We sought to verify that **4** could behave similarly toward protic acids. Hence, **4** and $HBF_4{\cdot}OEt_2$ were reacted in chlorobenzene at −45 °C. Workup gave the previously characterized π propyne complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(HC{\equiv}CCH_3)]^+BF_4^-$ (**5**)[9b,21b] as a crude powder in 67% yield. The ^1H NMR spectrum showed minor impurities with chemical shifts characteristic of alkylidene complexes (δ, $CDCl_3$: C_5H_5 at 6.01, 5.95; Re=CH at 15.49, 15.27).[11b] These presumably arise from competing protonation at the =C= carbon. Importantly, *t*-BuO⁻K⁺ has been shown earlier to readily deprotonate **5** to the methylacetylide complex **3**.[21b]

The above data suggest that **1a** is deprotonated directly to **4** by both *t*-BuO⁻K⁺ and methyllithium. However, we considered the possibility that the propargyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2C{\equiv}CH)$ (**6**) might be the kinetic product (A → B, Scheme II). As is illustrated in eq i, others have observed the facile isomerization of



L = CO, $P(OCH_3)_3$

propargyl complexes to allenyl complexes.[22b,c] Hence, an authentic sample of **6** was sought so that its stability could be tested.

Accordingly, the anionic complex $Li^+[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^-$ (**7**) was generated, as previously described,[23] and treated with propargyl tosylate at −15 °C (Scheme IV). Workup gave crude **6** in 87% yield that was contaminated with 2% of **4** and a small amount of another byproduct. Analogous reactions with propargyl bromide and chloride gave much greater amounts of **4**. Crystallization gave pure **6** (46%), which exhibited IR $\nu_{C\equiv C}$ and C≡C ^{13}C NMR chemical shift values similar to those of other propargyl complexes (Table I).[24]

Next, a benzene-d_6 solution of **6** was kept at 67 °C and monitored by ^{31}P NMR. Over the course of 14 h, a ca. 80:20 mixture of **6** and allenyl complex **4** formed. The sample was then kept at 80 °C for 48 h. A ca. 7:78:15 mixture of **6**, **4**, and **3** formed, along with minor amounts of decomposition products (18.3, −4.8 ppm). Thus, **4** is more stable than **6**, but thermal equilibration is slow on the time scales of the deprotonations of **1a**.

As a further check, a THF solution of **6** was treated with *t*-BuOH/*t*-BuO⁻K⁺ (1 equiv each) at −80 °C. These conditions model the environment that would be experienced by any neutral intermediate in Scheme III. The sample was brought to 0 °C over the course of 1 h. A ^{31}P NMR spectrum showed that no reaction had occurred. The probe was warmed to 25 °C, and a very small amount of **3** was detected (21.6 ppm). The sample was then heated to 66.8 °C, and **6** cleanly isomerized to **3** over the course of 3.5 h. The disappearance of **6** followed a first-order rate law, with $k_{obs} = (2.82 \pm 0.11) \times 10^{-4}$ s^{-1}. A similar experiment in which no *t*-BuOH was added gave virtually identical results, with $k_{obs} = (3.17 \pm 0.13) \times 10^{-4}$ s^{-1}. Although these experiments show that the isomerization of **6** can be catalyzed, the rates are sufficiently slow that any intermediacy of **6** in Scheme III can be excluded.

Discussion

The preceding data establish that mono- and disubstituted allene complexes of the rhenium fragment I can be readily prepared in high yields. However, the lengthy

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reaction times required at room temperature show that allenes are among the weakest nucleophiles capable of displacing chlorobenzene from the precursor **2**. Only alkynes react at comparably slow rates.[9] However, elevated temperatures allow syntheses to be completed on convenient time scales.

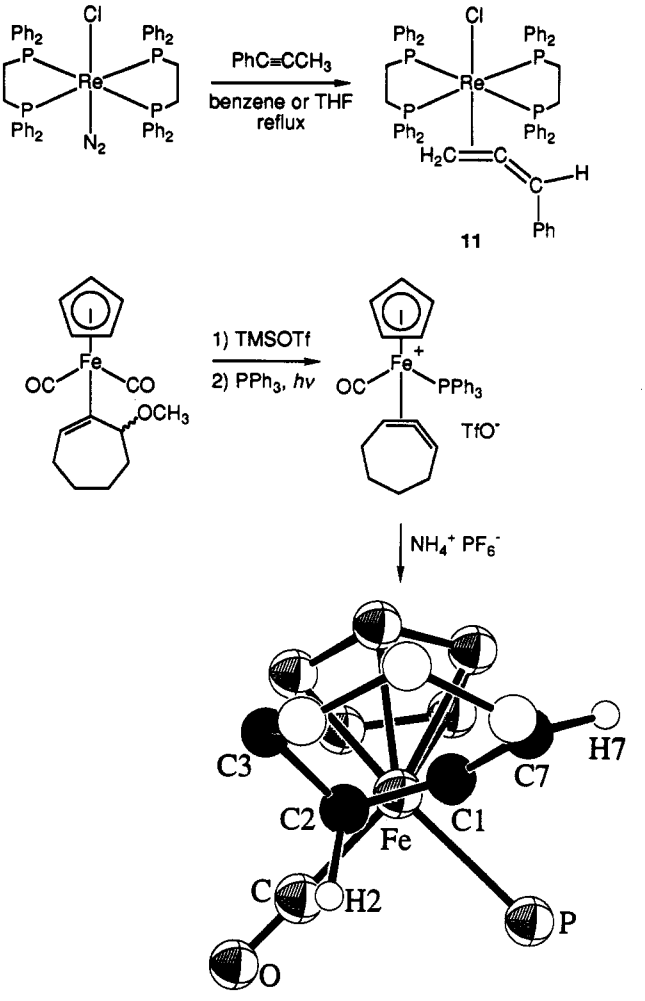
We have previously determined the crystal structures of two monosubstituted alkene complexes that are closely related to **1a**: allylbenzene complex (*RR,SS*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHCH_2C_6H_5)]^+PF_6^-$ (**9**)[5a] and isopropylethylene complex (*RS,SR*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHCH(CH_3)_2)]^+BF_4^-$ (**10**).[5b] As would be expected from frontier MO considerations (Chart I), all three compounds exhibit similar Re—(C=C) conformations, as evidenced by the angles of the Re—P bonds with the Re—C=C planes (24, 18, and 15°, respectively). The length of the coordinated C=C bond in **1a** (1.388 (5) Å) is within experimental error of those of **9** and **10** (1.40 (3), 1.420 (9) Å), and longer than the uncoordinated C=C bond in **1a** (1.311 (5) Å). The Re—CH_2 bond length in **1a** (2.223 (4) Å) is also similar to those in **9** and **10** (2.24 (2), 2.240 (7) Å). However, the Re—CCH_2 distance in **1a** (2.144 (3) Å) is shorter than the Re—CHR distances in **9** and **10** (2.25 (2), 2.278 (7) Å). This likely reflects the reduced steric demand of the π terminus in **1a** and/or the presence of a second π^* acceptor orbital.

The crystal structures of twelve transition-metal complexes of acyclic allenes have been previously reported.[25] These contain a total of 16 independent allene ligands and exhibit C=C=C angles that range from 134.5 to 160°, with an average of 149.6 (7.0)°. The C=C=C angle in **1a** (148.5 (4)°) is close to the average. However, it is much greater than that in another rhenium(I) adduct, the phenylallene complex *trans*-$Re(Cl)(PPh_2CH_2CH_2PPh_2)_2(H_2C{=}C{=}CHPh)$ (**11**, 138.1 (3)°) shown in Scheme V.[26] Interestingly, **11** was accessed by an unanticipated prototropic rearrangement that has a sense opposite to that involved in Scheme III.

Metal complexes of chiral 1,3-disubstituted allenes have previously been studied in detail.[2,3] In particular, Jones has reported the synthesis of the racemic iron 1,2-cycloheptadiene complex $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(HC{=}C{=}CH(CH_2)_4)]^+PF_6^-$ (**12**) shown in Scheme V.[3a,b] The iron fragment $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)]^+$ can be viewed as "isoelectronic" with I. However, frontier MO interactions appear to be less important determinants of ligand conformation than for rhenium analogs.[9a]

Jones showed **12** to be a 60:40 equilibrium mixture of *two* diastereomers in solution—in accord with our initial expectations for cyclic allenes based upon Chart III. These interconverted with an activation energy of ca. 23 kcal/mol, and a mechanism involving an iron-substituted allyl cation (X)[17c] was proposed. The crystal structure of one diastereomer was determined, and is shown in Scheme V.[3a] Interestingly, the M—(C=CHR) conformation differs from that of **1a** and roughly corresponds to that in XI (Chart IV). However, the alkyl substituent of the bound =CHR group occupies the more hindered position closest to the cyclopentadienyl ligand.

Scheme V. Some Other Structurally Characterized Allene Complexes



The reactions of **1a** with *t*-BuO^-K^+ (Scheme III) and methyllithium, together with the supporting control experiments, constitute to our knowledge the first demonstration that allene complexes can undergo deprotonation at the coordinated $=CH_2$ terminus. We are surprised that this reactivity mode has not been observed previously, since it leads to a *more* stable product (an allenyl complex) than deprotonation of the free $=CH_2$ terminus (a propargyl complex). Excellent precedent has also been provided for each step of the mechanism proposed for the subsequent isomerization of the allenyl complex **4** to the methyl acetylide complex **3**. These transformations establish the overall stability order **3** > **4** > **6**, which parallels well-known acidity trends for sp, sp^2, and sp^3 carbon—hydrogen bonds.[27]

In summary, this study has demonstrated the ready accessibility of allene complexes of the rhenium fragment I. Their structures follow from simple stereoelectronic considerations. Although I does not appear to show a high degree of chiral recognition upon binding to 1,3-disubstituted allenes, fully equilibrating conditions likely remain to be investigated. Also, efficient routes to the new allenyl

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and propargyl complexes **4** and **6** have been established. The former synthesis involves a new type of allene ligand carbon—hydrogen bond activation. Additional properties of **4** and **6**, and those of other classes of π C=C complexes of **I**, will be further described in subsequent reports.[10]

Experimental Section

General Data. General procedures were identical to those in a previous paper.[5b] Chemicals not utilized earlier were obtained as follows: THF-d_8 (Cambridge Isotopes), vacuum-transferred from $LiAlH_4$; allene (Baker), 1,2-butadiene, 3-methyl-1,2-butadiene (Wiley), 2,3-pentadiene (Chemical Samples), *t*-BuO^-K^+/THF, and CH_3Li/ether (Aldrich), used as received; 3,4-heptadiene,[28,29] 1,2-cyclononadiene,[29] propargyl tosylate,[30] prepared by literature procedures; Florisil, treated with concentrated NH_4OH (30% v/w).

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}C{=}CH_2)]^+BF_4^-$ (1a). A thick-walled, 12-mm-radius Schlenk tube equipped with an O-ring-sealed Teflon stopcock was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**13**, 0.557 g, 1.000 mmol),[31] chlorobenzene (10 mL), and a stir bar, and cooled to −45 °C (CH_3CN/CO_2 bath). Then $HBF_4{\cdot}OEt_2$ (110 μL, 1.000 mmol) was added with stirring.[12] After 30 min, excess allene was condensed into the tube (1–2-mm layer). The stopcock was closed, and the cold bath was removed. After 20 h, the tube was transferred to a 85 °C bath. After an additional 21 h, the mixture was concentrated to ca. 3 mL. The resulting precipitate was collected by filtration and dissolved in CH_2Cl_2 (2 mL). This solution was added dropwise to hexane (80 mL). The resulting pale yellow powder was collected by filtration, washed with pentane (2 × 2 mL), and dried under oil pump vacuum to give **1a** (0.550 g, 0.821 mmol, 82%), mp 214–217 °C dec. Anal. Calcd for $C_{26}H_{24}BF_4NOPRe$: C, 46.58; H, 3.61. Found: C, 46.52; H, 3.65. Chlorobenzene was removed from the initial filtrate, and the residue was reprecipitated as above to give a second crop of **1a** (0.050 g) for a total yield of 0.600 g (0.895 mmol, 90%).

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}C{=}CHCH_3)]^+BF_4^-$ (1b). Complex **13** (0.116 g, 0.209 mmol), chlorobenzene (14 mL), $HBF_4{\cdot}OEt_2$ (22.0 μL, 0.200 mmol), and excess 1,2-butadiene were combined in a procedure analogous to that given for **1a**. The mixture was stirred at room temperature for 5 days. Solvent was removed under oil pump vacuum, and the residue was precipitated from CH_2Cl_2/hexane as for **1a**. This gave **1b** as a tan powder (0.129 g, 0.189 mmol, 90%). Crystallization from layered CH_2Cl_2/ether gave tan prisms, dec pt 103–104 °C (no melting). Anal. Calcd for $C_{27}H_{26}BF_4NOPRe$: C, 47.38; H, 3.83. Found: C, 47.23; H, 3.89.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}C{=}C(CH_3)_2)]^+BF_4^-$ (1c). Complex **13** (0.112 g, 0.200 mmol), chlorobenzene (3.5 mL), $HBF_4{\cdot}OEt_2$ (22.0 μL, 0.200 mmol), and 3-methyl-1,2-butadiene (100 μL, 1.000 mmol) were reacted in a procedure analogous to that given for **1b**. An identical workup gave **1c** (0.126 g, 0.182 mmol, 91%) as a light tan powder, dec pt 130–136 °C (no melting). Anal. Calcd for $C_{28}H_{28}BF_4NOPRe$: C, 48.15; H, 4.03. Found: C, 48.13; H, 4.12.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3CH{=}C{=}CHCH_3)]^+BF_4^-$ (1d).
A. Complex **13** (0.056 g, 0.100 mmol), chlorobenzene (3 mL), $HBF_4{\cdot}OEt_2$ (11.8 μL, 0.110 mmol), and 2,3-pentadiene (50 μL, 0.510 mmol) were reacted in a procedure analogous to that given for **1b**. A similar workup gave **1d** (0.066 g, 0.094 mmol, 94%) as a tan powder and mixture of four diastereomers:[19] ^1H NMR (δ, $CDCl_3$) C_5H_5 at 5.88, 5.84, 5.80, 5.75 (ca. 40:11:38:12); IR (cm^{-1}, thin film) ν_{NO} 1734 (s). Minor impurities were also evident by ^{31}P NMR (ppm, $CDCl_3$): 13.5, 4.2, 0.7. The preceding sample was dissolved in chlorobenzene (3 mL), and the solution was stirred at 100 °C for 24 h. An identical workup gave **1d** (0.050 g, 0.072 mmol, 76%) as a ca. 18:14:61:7 mixture of the same diastereomers.

B. Complex **13** (0.056 g, 0.100 mmol), chlorobenzene (3 mL), $HBF_4{\cdot}OEt_2$ (11.8 μL, 0.110 mmol), and 2,3-pentadiene (50 μL, 0.510 mmol) were combined in a procedure analogous to (A), and stirred at 100 °C for 30 min. An identical workup gave **1d** (0.063 g, 0.096 mmol, 96%) as a ca. 21:13:59:7 mixture of diastereomers. Another reaction was conducted on an identical scale but was stirred at 100 °C for 30 h. Workup gave **1d** as a ca. 18:14:61:7 mixture of diastereomers.

NMR data for the most stable isomer of **1d** ($CDCl_3$): ^1H (δ) 7.80–7.00 (m, 3 C_6H_5), 5.80 (s, C_5H_5), 5.23 (m, =CHR/free), 4.06 (m, =CHR/bound), 2.08 (d, J_{HH} 5.8 Hz, CH_3), 1.88 (dd, J_{HH} 6.4, J_{HP} 1.8 Hz, CH_3'); $^{13}C\{^1H\}$ (ppm) 134.4 (br s, =CHR/free), 133.0 (d, J_{CP} 9.8 Hz, *o*-Ph), 132.2 (s, *p*-Ph), 129.7 (d, J_{CP} 10.9 Hz, *m*-Ph),[32] 126.9 (d, J_{CP} 8.8 Hz, =C=), 97.7 (s, C_5H_5), 22.6/21.4/16.3 (3 s, =CHR/bound, CH_3, CH_3'); $^{31}P\{^1H\}$ (ppm) 16.4 (s). Partial NMR data for the major kinetic isomer ($CDCl_3$): ^1H (δ) 5.88 (s, C_5H_5), 3.07 (m, =CHR/bound), 2.04 (dd, J_{HH} 6.6, J_{HP} 2.2 Hz, CH_3), 0.72 (d, J_{HH} 6.4 Hz, CH_3'); $^{13}C\{^1H\}$ (ppm) 98.0 (s, C_5H_5), 23.5 (d, J_{CP} 5.7 Hz, =CHR/bound), 20.2/17.7 (2 s, CH_3, CH_3'); $^{31}P\{^1H\}$ (ppm) 10.7 (s).

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C_2H_5CH{=}C{=}CHC_2H_5)]^+BF_4^-$ (1e). Complex **13** (0.224 g, 0.400 mmol), chlorobenzene (8 mL), $HBF_4{\cdot}OEt_2$ (44 μL, 0.400 mmol), and 3,4-heptadiene (0.321 g in 300 μL of ether, 3.35 mmol) were reacted in a procedure analogous to that given for **1b**. The mixture was stirred at room temperature for 3 days and then at 90 °C for 40 h. An identical workup gave **1e** (0.265 g, 0.360 mmol, 91%) as a mixture of five diastereomers:[19] ^1H NMR (δ, $CDCl_3$) C_5H_5 at 5.97, 5.90, 5.85, 5.80, 5.76 (ca. 6:11:15:62:6); IR (cm^{-1}, thin film) ν_{NO} 1726 (s).

NMR data for the most stable isomer of **1e** ($CDCl_3$): ^1H (δ) 7.57–7.26 (m, 3 C_6H_5), 5.80 (s, C_5H_5), 5.24 (dt, J_{HH} 7.0, 2.9 Hz, =CHR/free), 3.99 (m, =CHR/bound), 2.24 (dq, J_{HH} 7.0, 7.0 Hz, CH_2CH=/free), 1.81 (m, CH_2CH=/bound), 1.26 (t, J_{HH} 7.0 Hz, CH_3), 0.77 (t, J_{HH} 7.3 Hz, CH_3'); $^{31}P\{^1H\}$ (ppm) 17.1 (s).

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\overline{CH{=}C{=}CH(CH_2)_6})]^+BF_4^-$ (1f).
A. Complex **13** (0.224 g, 0.400 mmol), chlorobenzene (8 mL), $HBF_4{\cdot}OEt_2$ (45 μL, 0.410 mmol), and 1,2-cyclononadiene (110 μL, 0.80 mmol) were reacted in a procedure analogous to that given for **1b**. An identical workup gave **1f** (0.303 g, 0.400 mmol, >99%) as a mixture of four diastereomers:[19] ^1H NMR (δ, $CDCl_3$) C_5H_5 at 5.99, 5.83, 5.81, 5.76; ca. 18:14:31:37. Impurities were also evident (δ 5.69–4.80).

B. Complex **13** (0.028 g, 0.050 mmol), chlorobenzene (0.5 mL), $HBF_4{\cdot}OEt_2$ (5.5 μL, 0.050 mmol), and 1,2-cyclononadiene (20 μL, 0.15 mmol) were similarly combined in a 5-mm NMR tube. The mixture was kept at room temperature for 4 days and then at 95 °C for 24 h. An identical workup gave **1f** (0.028 g, 0.037 mmol, 74%) as a mixture of three diastereomers: ^1H (δ, $CDCl_3$) C_5H_5 at 5.83, 5.80, 5.76; ca. 19:53:28.

C. Complex **13** (0.117 g, 0.209 mmol), chlorobenzene (2 mL), $HBF_4{\cdot}OEt_2$ (23.0 μL, 0.209 mmol), and 1,2-cyclononadiene (80 μL, 0.584 mmol) were reacted in a procedure analogous to (A). The mixture was stirred at room temperature for 4 days and then 85 °C for 13 h. The sample was concentrated to ca. 0.5 mL. The resulting precipitate was collected by filtration and dissolved in CH_2Cl_2 (2 mL). This solution was added dropwise to hexane (80 mL). The resulting pale yellow powder was collected by filtration, washed with pentane (2 × 2 mL), and dried under oil pump vacuum to give **1f** (0.082 g, 0.108 mmol, 51%) as a mixture of three diastereomers: ^1H (δ, $CDCl_3$): C_5H_5 at 5.83, 5.80, 5.76 (ca. 21:66:13); IR (cm^{-1}, thin film) ν_{NO} 1724 (s). Anal. Calcd for $C_{32}H_{34}BF_4NOPRe$: C, 51.07; H, 4.55. Found: C, 50.89; H, 4.62.

NMR data for the most stable isomer of **1f** ($CDCl_3$): ^1H (δ) 7.57–7.26 (m, 3 C_6H_5), 5.80 (s, C_5H_5), 5.45 (m, =CHR/free), 4.10 (m, =CHR/bound), 2.62/2.28/2.09/1.86/1.98–0.95 (m/m/m/m/m, 1 H/1 H/1 H/2 H/7 H, $(CH_2)_6$); $^{13}C\{^1H\}$ (ppm) 144.3 (d, J_{CP} 8.8 Hz, =C=), 134.5 (br s, =CHR/free), 133.8 (d, J_{CP} 9.8 Hz, *o*-Ph), 132.3 (s, *p*-Ph), 131.6 (d, J_{CP} 8.9 Hz, *m*-Ph),[32] 97.7 (s, C_5H_5), 34.9/34.3/29.6/26.0/25.4/23.7/21.2 (7 s, =CHR/bound, $(CH_2)_6$); $^{31}P\{^1H\}$ (ppm) 16.3 (s).

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(32) The ipso carbon is not located or one line of the doublet is obscured.

Reaction of 1a and *t*-BuO⁻K⁺. A Schlenk tube was charged with **1a** (0.067 g, 0.100 mmol), THF (2 mL), and a stir bar and was cooled to −80 °C (acetone/CO_2 bath). Then *t*-BuO⁻K⁺/THF (1.0 M, 125 μL, 0.125 mmol) was added with stirring. Over the course of 3 h, the bath was allowed to warm to room temperature. The mixture was filtered, and solvent was removed from the filtrate under oil pump vacuum to give $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C{\equiv}CCH_3)$ (**3**, 0.054 g, 0.092 mmol, 92%), which was pure by NMR. The IR and NMR (^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$) spectra were identical with those of an authentic sample.[21]

$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH{=}C{=}CH_2)$ (4). Complex **1a** (0.041 g, 0.061 mmol), THF (2 mL), and CH_3Li/ether (1.4 M, 85 μL, 0.120 mmol) were combined at −80 °C in a procedure analogous to the preceding one. After 2 h, the mixture was filtered through 0.5 cm of Florisil. Solvent was removed from the filtrate under oil pump vacuum to give **4** as a dark red oil (0.025 g, 0.042 mmol, 70%), which was pure by NMR. Mass spectrum (EI, 17 eV; *m/z* (relative intensity), ^{187}Re): 583 (M^+, 63%), 467 ($M^+ - C_3H_3 - C_6H_5$, 27%), 262 (Ph_3P^+, 100%).

$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2C{\equiv}CH)$ (6). A 5-mm NMR tube was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ (0.055 g, 0.100 mmol)[23] and THF (1.0 mL), and fitted with a septum. The solution was cooled to −15 °C (ethylene glycol/CO_2 bath), and *n*-BuLi/hexane (1.58 M, 160 μL, 0.24 mmol) was added dropwise with shaking to generate $Li^+[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^-$.[23] After 15 min, propargyl tosylate (30 μL, 0.046 g, 0.175 mmol) was added. The tube was shaken and transferred to a −15 °C NMR probe. A ^{31}P NMR spectrum showed the formation of **6** and an unknown compound (24.8/24.5, ca. 92:8). Solvent was removed under oil pump vacuum, and the residue was extracted with benzene (2 mL). The extract was filtered under N_2 through a small plug of Florisil. Solvent was removed from the filtrate under oil pump vacuum to give a yellow-orange foam that was a ca. 86:11:2 mixture of **6**, the unknown compound, and **4** (0.051 g). The foam was dissolved in CH_2Cl_2 (1 mL). Hexane (5 mL) was added, and the solution was concentrated to ca. 4 mL. After 2 days at room temperature, orange plates formed and were collected by filtration and dried under oil pump vacuum to give **6** (0.027 g, 0.046 mmol, 46%), mp 168–170 °C dec. Mass spectrum (EI, 17 eV; *m/z* (relative intensity), ^{187}Re): 583 (M^+, 68%), 544 ($M^+ - C_3H_3$, 21%), 467 ($M^+ - C_3H_3 - C_6H_5$, 27%), 262 (Ph_3P^+, 100%). Anal. Calcd for $C_{26}H_{23}NOPRe$: C, 53.60; H, 3.98; N, 2.40. Found: C, 53.51; H, 3.98; N, 2.37.

Reaction of 4 and $HBF_4{\cdot}OEt_2$. A Schlenk tube was charged with **4** (0.025 g, 0.042 mmol), C_6H_5Cl (2 mL), and a stir bar, and cooled to −45 °C. Then $HBF_4{\cdot}OEt_2$ (5.5 μL, 0.050 mmol) was added with stirring. After 15 min, the cold bath was removed. After 3 h, the mixture was filtered, and solvent was removed from the filtrate under oil pump vacuum. The resulting residue was reprecipitated with CH_2Cl_2/hexane to give $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(HC{\equiv}CCH_3)]^+BF_4^-$ (**5**, 0.019 g, 0.028 mmol, 67%). The IR and NMR (^1H, $^{31}P\{^1H\}$) spectra were identical with those of an authentic sample[9b,21b] and showed the presence of several minor impurities (see text).

Isomerization of 6. The following experiment is representative. A 5-mm NMR tube was charged with **6** (0.0178 g, 0.031 mmol) and THF (0.6 mL), capped with a septum, and cooled to −80 °C. Then *t*-BuOH (2.8 μL, 0.030 mmol) and *t*-BuO⁻K⁺/THF (1.0 M, 30 μL, 0.030 mmol) were added. The tube was shaken and transferred to a −80 °C NMR probe. Data: see text.

^1H NOE Experiments. The ^1H NOED spectra[16] were acquired at ambient probe temperature in CD_2Cl_2 (**1a,b**) or $CDCl_3$ (**1c**) using septum-sealed tubes. Experimental details were similar to those previously described (82–88% cyclopentadienyl resonance irradiation; block size 32 transients; 0–1 steady states/block; 1472–1920 transients; pulse delay 6.0–7.0 s).[33]

Crystal Structure of 1a. An acetone solution of **1a** was layered with hexane. This gave a yellow prism which was mounted for data collection on a Syntex $P\bar{1}$ diffractometer as summarized in Table II. Cell constants were obtained from 42 reflections with $10° < 2\theta < 20°$. The space group was determined from systematic absences ($h0l$ $h + l = 2n$, $0k0$ $k = 2n$) and subsequent least-squares refinement. Lorentz, polarization, and empirical absorption (ψ scans) corrections were applied to the data. The structure was solved by standard heavy-atom techniques with the SDP/VAX package.[34] Non-hydrogen atoms were refined with anisotropic thermal parameters. The $=CH_2$ hydrogen atoms (H1–H4) were located and refined. Other hydrogen atom positions were calculated and added to the structure factor calculations. Scattering factors, and $\Delta f'$ and $\Delta f''$ values, were taken from the literature.[35]

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Supplementary Material Available: Tables of hydrogen atom coordinates and anisotropic thermal parameters for **1a** (3 pages). Ordering information is given on any current masthead page.

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