Synthesis, Structure, and Reactivity of Chiral Rhenium Alkyne Complexes of the Formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(RC{\equiv}CR')]^+BF_4^-$

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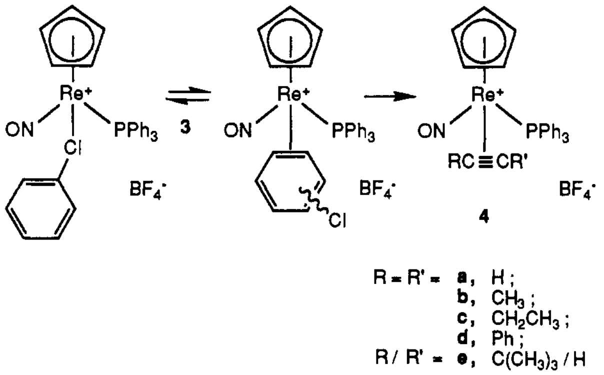
Reactions of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClC_6H_5)]^+BF_4^-$ and $RC{\equiv}CR'$ (R = R' = H (**a**), CH_3 (**b**), CH_2CH_3 (**c**), C_6H_5 (**d**); R/R' = $C(CH_3)_3$/H (**e**)) give alkyne complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(RC{\equiv}CR')]^+BF_4^-$ (**4a–e**; 73–97%). A crystal structure of **4c**·$ClCH_2CH_2Cl$ (orthorhombic, *Pbca*; *a* = 15.724 (1) Å, *b* = 18.593 (2) Å, *c* = 22.128 (2) Å, *Z* = 8) shows a 3-hexyne ligand conformation that directs the ethyl substituents syn and anti to the PPh_3 ligand. The C≡C bond is only slightly longer (1.24 (1) Å) than in free alkynes, but the propargylic carbons are bent back from the C≡C axis (∠C≡C—C = 143.4 (8), 147 (1)°). NMR data show high barriers to alkyne ligand rotation (**4b**,**c**: $\Delta G^{\ddagger}$(180 °C) ≥ 22 kcal/mol). Difference ^{1}H NOE and decoupling experiments enable detailed assignments of NMR resonances. Reactions of **4a**,**e** and *t*-BuO^-K^+ give acetylide complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C{\equiv}CR')$ (**5a**,**e**; 74–97%). Complex **4e** rearranges (80 °C, C_6H_5Cl, 1 h) to vinylidene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}C{=}CHC(CH_3)_3)]^+BF_4^-$, a sample of which can be independently prepared from **5e** and $HBF_4{\cdot}O(CH_2CH_3)_2$ (92%). The physical and chemical properties of **4a–e** are compared to those of other alkyne complexes.

Complexes of alkynes and transition metals are abundant.[1-8] Diverse aspects of their physical and chemical properties have attracted the attention of numerous researchers. The many exploitable features of their chemistry include (a) stabilization of strained cyclic alkynes,[2] (b) activation of the coordinated triple bond toward nucleophilic[3,4] and electrophilic[5] attack, (c) facile coupling reactions with unsaturated organic molecules,[6,7] and (d) propargylic bond activation.[8]

We recently reported that the reaction of the chiral methyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**1**) and $HBF_4{\cdot}O(CH_2CH_3)_2$ in dichloromethane (−78 °C) or chlorobenzene (−45 °C) affords the labile halocarbon complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ (**2**) and $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClC_6H_5)]^+BF_4^-$ (**3**).[9,10] These react with a variety of neutral donor ligands L to give substitution products $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)]^+BF_4^-$ in high yields.[11] When optically active **1** is utilized, substitution products form with overall retention of configuration at rhenium and in high optical yields.[9-11] Hence, **2** and **3** can serve as functional equivalents of the chiral, *optically active*, rhenium Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (I).

Scheme I. Synthesis of the Alkyne Complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(RC{\equiv}CR')]^+BF_4^-$ (4)



We sought to extend the preceding chemistry to both simple alkynes and functionalized alkynes with more than one potential binding site. A variety of interesting asymmetric transformations involving these ligands can be envisioned. As a prelude to such efforts, we set out to delineate the fundamental spectroscopic, structural, and dynamic properties of simple alkyne adducts of I. In this paper we report (a) high-yield syntheses of alkyne complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(RC{\equiv}CR')]^+BF_4^-$ (**4**), (b) a detailed analysis of their spectroscopic properties, (c) a crystal structure of a 3-hexyne complex, (d) the facile deprotonation of terminal acetylene complexes to acetylide complexes, and (e) the rearrangement of a *tert*-butylacetylene complex to a *tert*-butylvinylidene complex.

Results

1. Syntheses of Alkyne Complexes. The chlorobenzene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClC_6H_5)]^+BF_4^-$ (**3**; Scheme I) was generated at −45 °C as previously described.[10] Then the symmetrical alkynes (**b**) 2-butyne, (**c**) 3-hexyne, and (**d**) diphenylacetylene were added (5–10 equiv). These mixtures were stirred for several days at room temperature. Workup gave alkyne complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(RC{\equiv}CR)]^+BF_4^-$ (**4b–d**) in 73–97% yields as tan powders. When analogous reactions

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[1] An extensive review literature exists. For leading references, see: Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1.

[2] Bennett, M. A.; Schwemlein, H. P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1296.

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were attempted with dichloromethane complex **2**, isolated yields were generally lower.

The parent acetylene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(HC{\equiv}CH)]^+BF_4^-$ (**4a**) was sought. Thus, acetylene gas was bubbled through a solution of **3** as the temperature was raised from −45 to +85 °C. Workup gave **4a** in 91% yield. The elevated temperature was employed to accelerate the reaction. Alternatively, the acetylene stream could be maintained for several days at room temperature.

Next, complexes of unsymmetrical alkynes were sought. The reaction of **3** and *tert*-butylacetylene gave $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(HC{\equiv}CC(CH_3)_3)]^+BF_4^-$ (**4e**) in 97% yield. This material was spectroscopically homogeneous. However, in most batches a small amount of a byproduct (identified below) was present. An analogous reaction was conducted with 2-hexyne. The resulting complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3C{\equiv}CCH_2CH_2CH_3)]^+BF_4^-$ (**4f**) was isolated as a spectroscopically inhomogeneous powder and partially characterized as described below.

The reaction of **3** and 3-hexyne was monitored by ^{31}P NMR spectroscopy. No significant reaction occurred below −20 °C. When the sample was warmed to 0 °C, some product **4c** formed from the chlorine-ligated isomer of **3**. However, the chlorine-ligated isomer also transformed to other species (noted earlier)[10] that slowly converted to **4c** over a period of days. Monosubstituted alkenes and THF react much more rapidly with **3**.[10] Thus, despite the presence of a four-electron π system,[1] 3-hexyne is a weaker nucleophile.

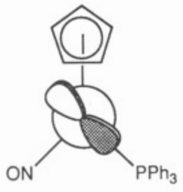
2. Spectroscopic Properties of Alkyne Complexes. Complexes **4a–e** were characterized by microanalysis (Experimental Section) and IR and NMR spectroscopy (Table I). General features were typical of those previously observed for cationic Lewis base adducts $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)]^+X^-$. However, the PPh_3 ^{13}C resonance patterns were considerably more complex in **4b–d**, suggestive of restricted Re–P and/or P–C bond rotation.

Symmetrical alkyne complexes **4a–d** each exhibited *two* C≡C ^{13}C NMR resonances (Table I). Chemical shifts (75–117 ppm) were downfield from those of the corresponding free alkynes. For example, the acetylene and 3-hexyne C≡C resonances in **4a**,**c** were at 84.5/89.7 and 86.8/101.4 ppm, respectively, as compared to 71.9 and 82.0 ppm in the free ligands.[12a] A ^{13}C NMR spectrum of **4a** was recorded without proton decoupling. The 89.7 ppm carbon gave $^1J_{CH}$ and $^2J_{CH}$ values of 242.1 and 23.6 Hz, respectively. The 84.5 ppm carbon gave $^1J_{CH}$ and $^2J_{CH}$ values of 237.7 and 23.5 Hz, respectively.

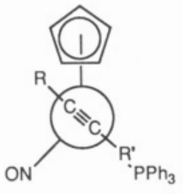
The doubled C≡C ^{13}C NMR resonances suggested restricted rotation about the Re—(C≡C) axis. Accordingly, 2-butyne complex **4b** and 3-hexyne complex **4c** also exhibited two sets of CH_2 and CH_3 ^1H and ^{13}C NMR resonances (Table I). Similarly, acetylene complex **4a** showed two ^1H NMR resonances for the ≡CH protons (δ 6.72/8.63). These were considerably downfield from that of free acetylene (δ 1.80),[13] but close to that of neat cyclopropene (δ 7.06),[14] and were not directly coupled ($^3J_{HH} < 2$ Hz).

The preceding data suggested that two inequivalent Re—(C≡C) rotamers should be possible for unsymmetrical alkyne complexes. However, *tert*-butylacetylene complex **4e**, which contains two sterically differentiated C≡C substituents, gave only a single set of ^1H, ^{13}C, and ^{31}P NMR resonances (Table I). Two explanations were considered. First, **4e** might exist essentially as one Re—(C≡C) rotamer. Second, the two rotamers might rapidly interconvert. However, the ^{31}P NMR spectrum of 2-hexyne complex **4f** showed two PPh_3 resonances (16.1/15.5 ppm, ca. 64:36 height ratios). The ^1H NMR spectrum of **4f** exhibited one cyclopentadienyl resonance (δ 5.86) but two sets of $\equiv CCH_3$ and CH_2CH_3 resonances (δ (major/minor) 1.81/2.96 and 1.06/0.72). Thus, we conclude that **4e** is isolated as a single Re—(C≡C) rotamer, while **4f** forms as a mixture of rotamers.

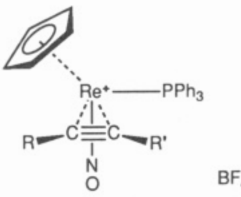
3. Crystal Structure of 3-Hexyne Complex 4c. The rhenium fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (I) is a powerful π donor, with the d orbital HOMO shown in the formula.[15]



I



II



III

Thus, the alkyne ligands in **4a–e** might be expected to adopt conformations that maximize overlap of the HOMO with a C≡C π^* acceptor orbital, as shown in idealized structures II and III. However, this orientation would direct an alkyne substituent at the bulky PPh_3 ligand. Thus, a crystal structure was sought. Note that the angle of the $\overline{\mathrm{Re{-}C{\equiv}C}}$ plane with the Re—P bond, which is 0° in II and III, provides a convenient measure of conformation.

Crystals of the solvate **4c**·$ClCH_2CH_2Cl$ were grown, and X-ray data were collected as summarized in Table II. Refinement, described in the Experimental Section, yielded the structures shown in Figure 1. Atomic coordinates and key bond lengths, bond angles, and torsion angles are given in Tables III and IV. Atoms C3 and C4 gave larger thermal ellipsoids, resulting in an abnormally short bond length. Additional data are provided in the supplementary material.

As shown in Figure 1b, **4c**·$ClCH_2CH_2Cl$ exhibited the expected Re—(C≡C) conformation. The angle of the $\overline{\mathrm{Re{-}C{\equiv}C}}$ plane with the Re—P bond, was found to be 10.6°, with the 3-hexyne ligand rotated very slightly counterclockwise from the conformation shown in II. The corresponding angle with the Re—N bond was 75.4°. Both propargylic carbons were bent distinctly back from the

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(12) (a) Levy, G. C.; Lichter, R. L.; Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance Spectroscopy*, 2nd ed.; Wiley: New York, 1980; p 92. (b) *Ibid.*, pp 33–36.

(13) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; Wiley: New York, 1981; p 230.

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(15) (a) Schilling, B. E. R.; Hoffmann, R.; Faller, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 592. (b) Kiel, W. A.; Lin, G.-Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4865. (c) Czech, P. T.; Gladysz, J. A.; Fenske, R. F. *Organometallics* **1989**, *8*, 1810.

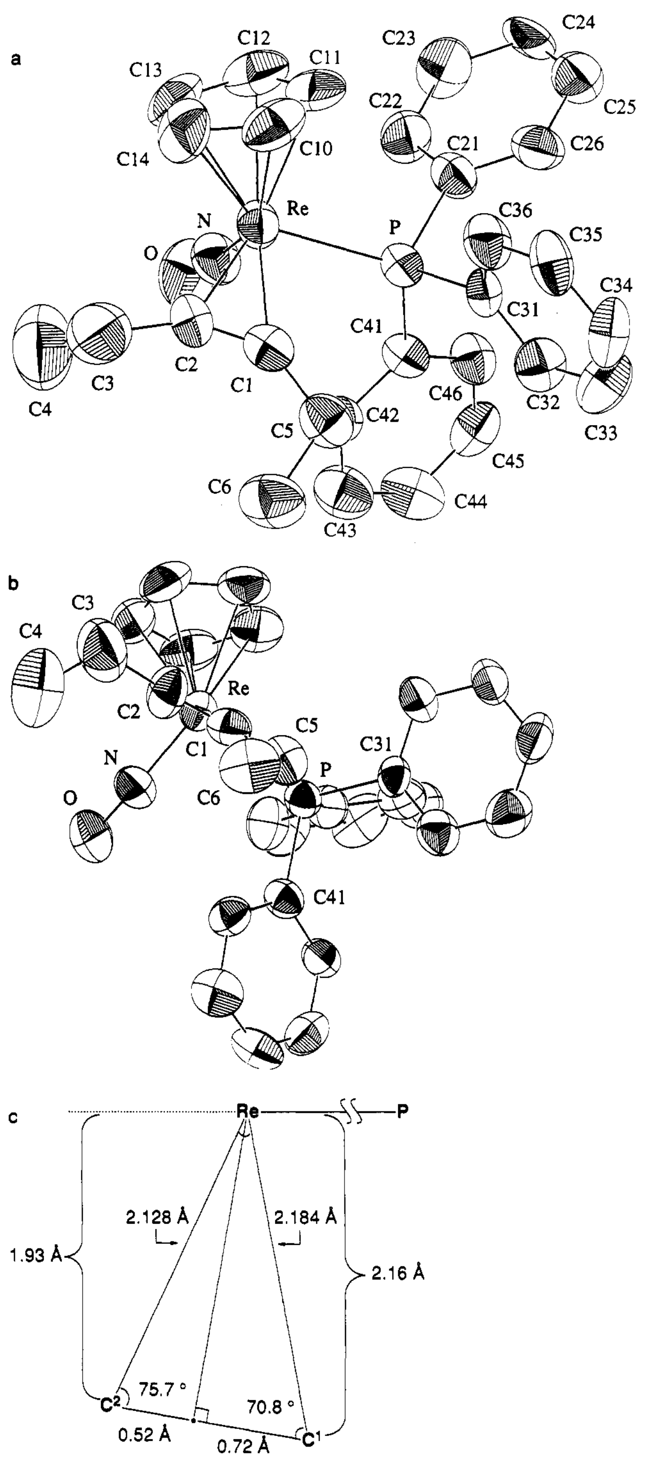

Figure 1. Structure of the cation of the 3-hexyne complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3CH_2C{\equiv}CCH_2CH_3)]^+BF_4^-\cdot ClCH_2CH_2Cl$ ($4c\cdot ClCH_2CH_2Cl$): (a) numbering diagram; (b) Newman-type projection; (c) view of $\overline{Re{-}C{\equiv}C}$ plane.

C≡C axis (∠C—C≡C = 143.4, 147°). Also, the $\overline{Re{-}C{\equiv}C}$ plane defined the distorted triangle shown in Figure 1c. Distances were calculated from the C≡C carbons to the nearest point on the Re—P vector. The carbon syn to the bulky PPh$_3$ ligand, C1, was farther from rhenium and the Re—P vector (2.184 and 2.16 Å) than C2 (2.128 and 1.93 Å).

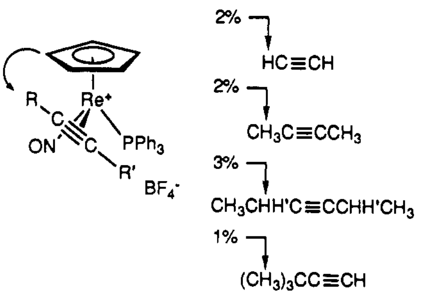

Figure 2. Summary of ^1H difference NOE data (from cyclopentadienyl ligand irradiation).

4. Dynamic and NOE NMR Experiments. We sought to probe the dynamic and conformational properties of the alkyne ligands of **4a–e** in solution. Thus, C_6D_5Cl solutions of symmetrical alkyne complexes **4b,c** were heated to 180 °C. No coalescence was observed for any of the alkyne ligand ^{13}C or ^1H NMR resonances. Also, little thermal decomposition occurred during the brief exposures to these elevated temperatures. The ^{13}C NMR data bound $\Delta G^{\ddagger}$(180 °C) for Re—(C≡C) rotation as >21.6 kcal/mol for **4b** and >22.6 kcal/mol for **4c**.[16]

Next, difference NOE experiments were conducted, as summarized in Figure 2.[17] First, the cyclopentadienyl ^1H NMR resonance of acetylene complex **4a** was irradiated. A 2% enhancement was observed in the downfield HC≡ resonance (δ 8.63), but none in the upfield HC≡ resonance (δ 6.72). Thus, the downfield resonance was assigned to the proton closer to the cyclopentadienyl ligand, or anti to the PPh$_3$ ligand, in II. The upfield proton, which must be syn to the PPh$_3$ ligand, exhibited a considerably larger J_{HP} value (Table I).

The cyclopentadienyl ^1H NMR resonance of 2-butyne complex **4b** was similarly irradiated. A 2% enhancement was observed in the downfield methyl resonance (δ 2.89), but none in the upfield methyl resonance (δ 1.77). Accordingly, these were assigned as the methyl groups anti and syn to the PPh$_3$ ligand in II, respectively (Table I). An identical experiment with 3-hexyne complex **4c** showed an enhancement (3%) in one of the four CHH′ resonances (δ 2.86). From coupling constant relationships, similar anti/syn assignments could be made as summarized in Table I.

An analogous NOE experiment was conducted with *tert*-butylacetylene complex **4e**. Only the *tert*-butyl protons showed an enhancement (1%), suggestive of an anti relationship to the PPh$_3$ ligand. Further, a large J_{HP} value was observed for the ≡CH proton, consistent with a syn relationship to the PPh$_3$ ligand as established in **4a** above. The alternative ligand conformation would place the *tert*-butyl group syn to the PPh$_3$ ligand, resulting in severe steric interactions.

Next, a ^{13}C NMR spectrum of **4e** was recorded with off-resonance proton decoupling. The upfield C≡C resonance (75.6 ppm, J_{CP} = 11.5 Hz) showed a doubling indicative of one directly bound hydrogen, while the downfield resonance (117.1 ppm, J_{CP} < 2 Hz) was essentially unaffected. Accordingly, these were assigned to the ≡CH and ≡*C*(CH$_3$)$_3$ carbons, respectively. On the basis of the above NOE data, the ≡CH and ≡*C*(CH$_3$)$_3$ carbons are also syn and anti to the PPh$_3$ ligand, respectively. Thus, J_{CP} is much larger for the upfield syn C≡C carbon of **4e** than for the downfield anti carbon. Significantly, the upfield C≡C resonances of **4a–e** all show greater J_{CP} values (11.5–14.6 Hz) than the downfield resonances (<2 Hz; Table I). Hence, these are assigned to the carbons syn to the PPh$_3$ ligand in each case. The ^1H NMR assignments

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[16] Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982; Chapter 7.

[17] Neuhaus, D.; Williamson, M. *The Nuclear Overhauser Effect in Structure and Conformational Analyses*; VCH: New York, 1989; Chapter 7.

Table I. Spectroscopic Characterization of Alkyne Complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(RC{\equiv}CR')]^+BF_4^-$ (4) and Other New Complexes

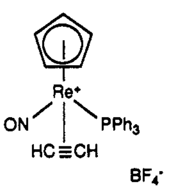
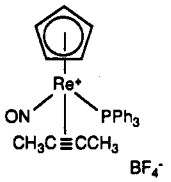
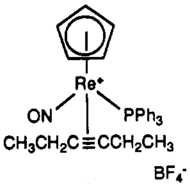
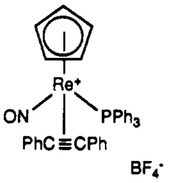
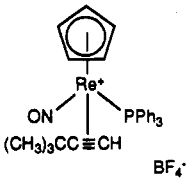
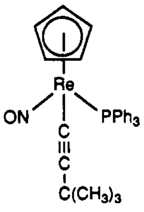
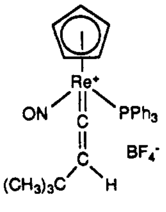
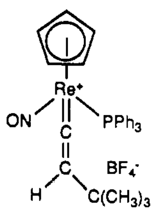
complex	IR (KBr), cm^{-1}	^{1}H NMR,[a] δ	$^{13}C\{^1H\}$ NMR,[b,c] ppm	$^{31}P\{^1H\}$ NMR,[d] ppm
 **4a**	ν_{NO} 1710 vs	8.63 (d, J_{HP} 4.7, $\equiv$CH anti to PPh_3), 7.64–7.26 (m, 3 C_6H_5), 6.72 (d, J_{HP} 18.7, $\equiv$CH syn to PPh_3), 5.88 (s, C_5H_5)	C$\equiv$C at 89.7 (s, anti to PPh_3), 84.5 (d, *J* 14.1, syn to PPh_3); 99.3 (s, C_5H_5)	16.8 (s)
 **4b**	ν_{NO} 1703 vs	7.69–7.14 (m, 3 C_6H_5), 5.84 (s, C_5H_5), 2.89 (s, CH_3 anti to PPh_3), 1.77 (s, CH_3 syn to PPh_3)	C$\equiv$C at 95.6 (s, anti to PPh_3), 83.5 (d, *J* 11.7, syn to PPh_3); 99.1 (s, C_5H_5), 17.8 (s, CH_3 anti to PPh_3), 12.0 (d, *J* 5.9, CH_3 syn to PPh_3)	15.8 (s)
 **4c**	ν_{NO} 1696 vs	7.72–7.07 (m, 3 C_6H_5), 5.83 (s, C_5H_5), 3.70 (dq, *J* 16.2, 7.5, C*H*H anti to PPh_3, 1 H), 2.86 (dq, *J* 16.2, 7.5, CH*H* anti to PPh_3, 1 H), 1.90 (dq, *J* 17.7, 7.4, C*H*H syn to PPh_3, 1 H), 1.75 (dq, *J* 17.7, 7.4, CH*H* syn to PPh_3, 1 H), 1.34 (t, *J* 7.5, CH_3 anti to PPh_3), 1.12 (t, *J* 7.4, CH_3 syn to PPh_3)	C$\equiv$C at 101.4 (s, anti to PPh_3), 86.8 (d, *J* 11.9, syn to PPh_3); 99.0 (s, C_5H_5), 26.2 (s, CH_2 anti to PPh_3), 23.0 (d, *J* 5.7, CH_2 syn to PPh_3), 15.3 (s, CH_3), 14.7 (s, $C'H_3$)	15.2 (s)
 **4d**	ν_{NO} 1726 vs	7.66–6.87 (m, 23 H of 5 C_6H_5), 6.61 (d, *J* 7.5, 2 H of 5 C_6H_5), 6.07 (s, C_5H_5)	C$\equiv$C at 104.3 (s, anti to PPh_3), 95.8 (d, *J* 11.5, syn to PPh_3); 99.7 (s, C_5H_5)	11.2 (s)
 **4e**	ν_{NO} 1702 vs	7.73–7.08 (m, 3 C_6H_5), 6.23 (d, J_{HP} 20.1, $\equiv$CH), 5.93 (s, C_5H_5), 1.49 (s, $C(CH_3)_3$)	C$\equiv$C at 117.1 (s, anti to PPh_3), 75.6 (d, *J* 14.6, syn to PPh_3); 97.8 (s, C_5H_5), 36.0 (s, $C(CH_3)_3$), 30.6 (s, $C(CH_3)_3$)[e]	15.0 (s)
 **5e**	ν_{NO} 1649 vs, 1637 vs; $\nu_{C\equiv C}$ 2091 w	7.58–7.52 (m, 6 H of 3 C_6H_5), 7.40–7.34 (m, 9 H of 3 C_6H_5), 5.11 (s, C_5H_5), 0.90 (s, $C(CH_3)_3$)	C$\equiv$C at 128.5 (s, C_β), 69.4 (d, *J* 17.0, C_α); 90.7 (s, C_5H_5), 32.9 (s, $C(CH_3)_3$), 29.8 (s, $C(CH_3)_3$)	19.7 (s)
 ***sc*-6e**	ν_{NO} 1728 vs; $\nu_{C=C}$ 1669 sh, 1648 sh[f]	7.66–7.55 (m, 9 H of 3 C_6H_5), 7.40–7.34 (m, 6 H of 3 C_6H_5), 5.94 (s, C_5H_5), 5.25 (s, =CH), 1.19 (s, $C(CH_3)_3$)	C=C at 328.7 (d, *J* 10.1 C_α), 140.8 (s, C_β); 98.8 (s, C_5H_5), 34.4 (s, $C(CH_3)_3$), 31.1 (s, $C(CH_3)_3$)	17.4 (s)

Table I (Continued)

complex	IR (KBr), cm^{-1}	^1H NMR,[a] δ	$^{13}C\{^1H\}$ NMR,[b,c] ppm	$^{31}P\{^1H\}$ NMR,[d] ppm
 *ac*-**6e**	ν_{NO} 1728 vs; $\nu_{C=C}$ 1669 sh, 1648 sh[f]	7.83–7.42 (m, 9 H of 3 C_6H_5), 7.37–7.18 (m, 6 H of 3 C_6H_5), 6.15 (s, =CH), 6.02 (s, C_6H_5), 0.83 (s, $C(CH_3)_3$)[g]	C=C at 143.0 (s, C_β);[h] 98.6 (s, C_5H_5), 35.5 (s, $C(CH_3)_3$), 30.9 (s, $C(CH_3)_3$)	18.7 (s)

[a] At 300 MHz in CD_2Cl_2 at ambient probe temperature, referenced to internal $Si(CH_3)_4$ (0.00 ppm) unless noted; couplings (Hz) are to hydrogen unless noted. [b] At 75.4 MHz in CD_2Cl at ambient probe temperature, referenced to CD_2Cl_2 (53.8 ppm) unless noted; couplings (Hz) are to phosphorus. [c] Data for PPh_3 resonances: **4a**, 133.3 (d, *J* 10.4, *o*), 132.8 (d, *J* 2.7, *p*), 130.0 (d, *J* 11.3, *m*), ipso resonance obscured; **4b–e**, many resonances at 135–126 ppm due to inequivalent aryl groups (restricted Re–P and/or P–C rotation); **5e**, 136.2 (d, *J* 54.0, ipso), 134.1, (d, *J* 10.4, *o*), 130.3 (d, *J* 2.3, *p*), 128.3 (d, *J* 10.1, *m*); *sc*-**6e**, 133.4 (d, *J* 11.1, *o*), 133.0 (s, *p*), 130.0 (d, *J* 62.1, ipso), 129.8 (d, *J* 12.2, *m*). [d] At 121 MHz in CD_2Cl_2 at ambient probe temperature, referenced to external 85% H_3PO_4 (0.00 ppm). [e] Spectrum recorded at −86 °C. [f] Data for mixture of *sc*/*ac* isomers. [g] Spectrum recorded at −78 °C; the last three resonances appear at δ 6.04, 5.96, and 0.84 at ambient temperature. [h] C_α not observed at ambient temperature.

Table II. Summary of Crystallographic Data for the 3-Hexyne Complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3CH_2C{\equiv}CCH_2CH_3)]^+BF_4^-\bullet ClCH_2CH_2Cl$ (4c•$ClCH_2CH_2Cl$)

molecular formula	$C_{31}H_{34}BCl_2F_4NOPRe$
fw	811.507
cryst syst	orthorhombic
space group	*Pbca*
cell dimens	
a, Å	15.724 (1)
b, Å	18.593 (2)
c, Å	22.128 (2)
V, $Å^3$	6469.50
Z	8
temp of collecn, °C	16 (1)
d_{calcd}, g/cm^3	1.666
d_{obsd}, g/cm^3	1.642
cryst dimens, mm	0.20 × 0.15 × 0.10
radiation, Å	λ(Mo Kα) = 0.71073
data collecn method	$\theta/2\theta$
scan speed, deg/min	3.0
range/indices (*hkl*)	0–15; 0–20; 1–24
scan range, deg	$K\alpha_1 - 1.3$ to $K\alpha_2 + 1.6$
total bkgd time/scan time	0.0
no of rflns between stds	98
total no. of unique data	4721
no. of obsd data, $I > 3\sigma(I)$	2126
abs coeff (μ), cm^{-1}	40.699
min transmissn factor	0.8564
max transmissn factor	1.1968
no. of variables	363
goodness of fit	5.17
$R = \sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$	0.0414
$R_w = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$	0.0467
Δ/σ (max)	0.012
$\Delta\rho$ (max), e $Å^{-3}$	0.706

established above also show that groups syn to the PPh_3 ligand are upfield of those that are anti.

5. Reactions of Alkyne Ligands. Many transformations have been proposed to occur via the deprotonation of intermediate cationic terminal alkyne complexes. However, explicit precedents for such reactions are not abundant.[18,19] Thus, a THF suspension of acetylene complex **4a** was treated with $t\text{-BuO}^-K^+$ (Scheme II). Workup gave the previously synthesized acetylide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C{\equiv}CH)$ (**5a**)[20] in 74% yield. A

Table III. Atomic Coordinates and Equivalent Isotropic Thermal Parameters for Non-Hydrogen Atoms in 4c•$ClCH_2CH_2Cl$[a]

atom	*x*	*y*	*z*	*B*, $Å^2$
Re	0.81733 (4)	0.87413 (4)	0.78771 (3)	4.71 (1)
P	0.8950 (3)	0.9177 (2)	0.8741 (2)	4.03 (9)
O	0.9789 (8)	0.8295 (8)	0.7325 (5)	7.9 (4)
N	0.9133 (8)	0.8440 (7)	0.7571 (6)	5.5 (3)
C1	0.784 (1)	0.7876 (9)	0.8501 (7)	4.8 (4)
C2	0.762 (1)	0.771 (1)	0.7982 (7)	6.3 (5)
C3	0.715 (2)	0.716 (1)	0.758 (1)	10.8 (7)
C4	0.769 (2)	0.689 (2)	0.719 (1)	14 (1)
C5	0.789 (1)	0.7619 (9)	0.9126 (8)	6.0 (5)
C6	0.771 (1)	0.680 (1)	0.9157 (9)	7.9 (6)
C10	0.687 (1)	0.935 (1)	0.7841 (8)	7.2 (4)
C11	0.753 (1)	0.986 (1)	0.7822 (8)	7.4 (5)
C12	0.800 (1)	0.977 (1)	0.7304 (8)	7.2 (5)
C13	0.762 (1)	0.919 (1)	0.7006 (7)	7.4 (5)
C14	0.694 (1)	0.893 (1)	0.7321 (7)	7.5 (5)
C21	0.936 (1)	1.0087 (8)	0.8605 (7)	4.9 (4)
C22	0.983 (1)	1.021 (1)	0.8074 (7)	5.9 (4)
C23	1.013 (1)	1.089 (1)	0.7966 (8)	6.9 (5)
C24	1.000 (1)	1.1449 (8)	0.8380 (8)	7.0 (5)
C25	0.954 (1)	1.132 (1)	0.8914 (7)	6.1 (4)
C26	0.922 (1)	1.0627 (9)	0.9022 (7)	5.6 (4)
C31	0.8387 (9)	0.9265 (8)	0.9451 (6)	4.0 (3)
C32	0.875 (1)	0.9046 (9)	0.9997 (7)	5.6 (4)
C33	0.830 (1)	0.914 (1)	1.0539 (7)	7.0 (5)
C34	0.748 (1)	0.941 (1)	1.0533 (7)	6.6 (5)
C35	0.711 (1)	0.960 (1)	0.9992 (7)	5.8 (4)
C36	0.755 (1)	0.953 (1)	0.9438 (7)	5.9 (5)
C41	0.9918 (9)	0.8678 (8)	0.8927 (6)	4.4 (3)
C42	1.000 (1)	0.7954 (8)	0.8772 (7)	4.8 (4)
C43	1.072 (1)	0.755 (1)	0.8936 (8)	6.6 (5)
C44	1.135 (1)	0.792 (1)	0.9222 (8)	6.1 (5)
C45	1.131 (1)	0.864 (1)	0.9344 (6)	5.6 (4)
C46	1.060 (1)	0.9029 (8)	0.9199 (7)	4.8 (4)
C50	0.568 (2)	0.364 (1)	0.552 (2)	11.0 (8)
C51	0.494 (2)	0.363 (2)	0.541 (1)	7.9 (7)
Cl1	0.6275 (4)	0.2898 (4)	0.5745 (3)	10.7 (2)
Cl2	0.4222 (4)	0.3228 (4)	0.5864 (4)	11.7 (2)
B*	0.491 (2)	0.552 (1)	0.630 (1)	4.4 (5)
F1*	0.456 (1)	0.609 (1)	0.6495 (7)	16.1 (6)
F2*	0.499 (1)	0.4952 (9)	0.6655 (7)	13.6 (5)
F3*	0.570 (2)	0.576 (2)	0.648 (1)	12.6 (9)
F4*	0.491 (2)	0.537 (1)	0.568 (1)	12.9 (7)

[a] Starred atoms were refined isotropically. Atoms refined anisotropically are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

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(18) (a) Appel, M.; Heidrich, J.; Beck, W. *Chem. Ber.* **1987**, *120*, 1087. (b) Akita, M.; Terada, M.; Oyama, S.; Moro-oka, Y. *Organometallics* **1990**, *9*, 816. (c) Frank, K. G.; Selegue, J. P. *J. Am. Chem. Soc.* **1990**, *112*, 6414.

(19) See also: (a) Nicklas, P. N.; Selegue, J. P.; Young, B. A. *Organometallics* **1988**, *7*, 2248. (b) Löwe, C.; Hund, H.-U.; Berke, H. *J. Organomet. Chem.* **1989**, *378*, 211.

Table IV. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) in 4c • $ClCH_2CH_2Cl$

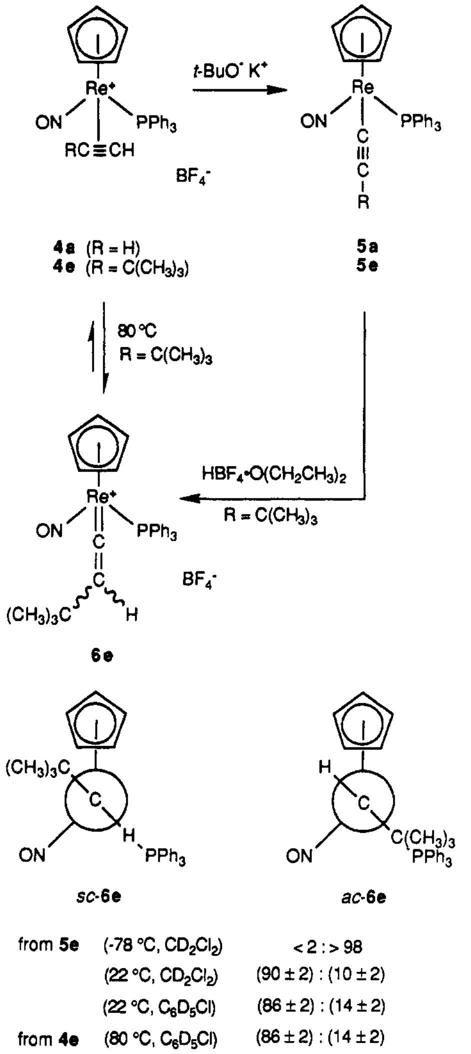
Re-P	2.409 (2)	C2-C3	1.55 (1)
Re-N	1.747 (6)	C3-C4	1.32 (1)
Re-C1	2.184 (7)	C5-C6	1.54 (1)
Re-C2	2.128 (9)	C10-C11	1.40 (1)
Re-C10	2.341 (8)	C10-C14	1.40 (1)
Re-C11	2.307 (9)	C11-C12	1.37 (1)
Re-C12	2.316 (8)	C12-C13	1.40 (1)
Re-C13	2.277 (7)	C13-C14	1.37 (1)
Re-C14	2.328 (7)	C21-C22	1.404 (9)
N-O	1.198 (7)	P-C21	1.836 (7)
C1-C2	1.24 (1)	P-C31	1.810 (6)
C1-C5	1.464 (9)	P-C41	1.828 (7)
P-Re-N	88.7 (2)	C2-C1-C5	143.4 (8)
P-Re-C1	82.3 (2)	C1-C2-C3	147 (1)
P-Re-C2	115.2 (3)	C2-C3-C4	109 (1)
N-Re-C1	102.4 (3)	C1-C5-C6	110.8 (7)
N-Re-C2	96.2 (3)	Re-N-O	173.2 (6)
C1-Re-C2	33.5 (3)	C10-C11-C12	110 (1)
Re-C1-C2	70.8 (5)	C10-C14-C13	106.1 (8)
Re-C2-C1	75.7 (5)	C11-C12-C13	104.5 (9)
Re-C1-C5	145.7 (5)	C11-C10-C14	107.2 (9)
Re-C2-C3	137.0 (8)	C12-C13-C14	111.8 (8)
P-Re-C1-C2	-169 (1)		
P-Re-C2-C1	12 (1)		
N-Re-C2-C1	103 (1)		
Re-C1-C5-C6	-162 (2)		
C5-C1-C2-Re	-177 (3)		
C5-C1-C2-C3	9 (5)		
C1-C2-C3-C4	-119 (3)		
C2-C1-C5-C6	13 (3)		

similar reaction of *tert*-butylacetylene complex **4e** gave the new *tert*-butylacetylide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C{\equiv}CC(CH_3)_3)$ (**5e**, 97%).

The spectroscopic properties of **5e** (Table I) were similar to those previously reported for other rhenium acetylide complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C{\equiv}CR)$.[20] Two IR ν_{NO} values were reproducibly observed in KBr (Table I), but only one in thin films (1650 cm^{-1}). Hence, the doubling was attributed to a solid-state splitting. These syntheses of acetylide complexes **5** are considerably shorter than the multistep routes described earlier.[20]

The attempted generation of cationic terminal acetylene complexes $[L_nM(RC{\equiv}CH)]^+$ often gives the corresponding vinylidene complexes $[L_nM({=}C{=}CHR)]^+$.[21-23] Accordingly, facile prototropic rearrangements have been proposed. However, direct observations of such alkyne ligand isomerizations are scarce.[22,23] Acetylene complex **4a** remained unchanged after 2 h in C_6D_5Cl at 90 °C. However, over the course of 1 h in C_6D_5Cl at 80 °C, *tert*-butylacetylene complex **4e** converted to a mixture of the two Re=C=C geometric isomers (*sc*, *ac*)[20] of the *tert*-butylvinylidene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}C{=}CHC(CH_3)_3)]^+BF_4^-$ (**6e**; Scheme II) and **4e**. Integration of the *tert*-butyl and cyclopentadienyl ^1H NMR resonances indicated a (74 ± 2):(12 ± 2):(14 ± 2) *sc*-**6e**:*ac*-**6e**:**4e** ratio (or 86 ± 2):(14 ± 2) *sc*:*ac*). The sample was kept at 80 °C for an additional 7 h. Compound ratios remained constant, within experimental error. The isomerization of **4e** was considerably slower at 60 °C (ca. 50% conversion, 4 h), but small amounts of **6e** appeared in all but the most carefully purified batches of **4e** prepared via Scheme I.

Scheme II. Reactions of Terminal Alkyne Complexes 4a,e



The new complex **6e** was independently prepared in 92% yield from **5e** and $HBF_4{\cdot}O(CH_2CH_3)_2$ (Scheme II). A sample was dissolved in cold chlorobenzene. A (85 ± 2):(15 ± 2) ratio of Re=C=C isomers *sc*:*ac*-**6e** was observed (−30 °C). No **4e** was present, and the *sc*:*ac* ratio remained constant when the sample was warmed to room temperature. The reaction of **5e** and $HBF_4{\cdot}O(CH_2CH_3)_2$ in CD_2Cl_2 was monitored by ^1H and ^{31}P NMR spectroscopy at −78 °C. In accord with previous rhenium acetylide complex protonations,[20] only the less stable Re=C=C isomer, *ac*-**6e**, formed. Above 10 °C, equilibration to a (90 ± 2):(10 ± 2) *sc*/*ac*-**6e** mixture occurred. Spectroscopic data for both isomers are given in Table I and closely match those reported earlier for other rhenium vinylidene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}C{=}CHR)]^+X^-$.[20]

Finally, a C_6D_5Cl solution of **6e** was kept at 80 °C for 2 h. A (77 ± 2):(10 ± 2):(13 ± 2) *sc*-**6e**/*ac*-**6e**/**4e** mixture cleanly formed. This ratio is identical, within experimental error, with that obtained from **4e** above. This demonstrates that the acetylene and vinylidene complexes achieve a true thermal equilibrium when heated in chlorobenzene.

Discussion

1. Synthesis of Alkyne Complexes. As previously described, the starting material for the synthesis of alkyne complexes **4**, the chlorobenzene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClC_6H_5)]^+BF_4^-$ (**3**), is inhomogeneous (Scheme I).[10] In fact, when Lewis bases are not sufficiently nu-

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(20) Senn, D. R.; Wong, A.; Patton, A. T.; Marsi, M.; Strouse, C. E.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 6096.

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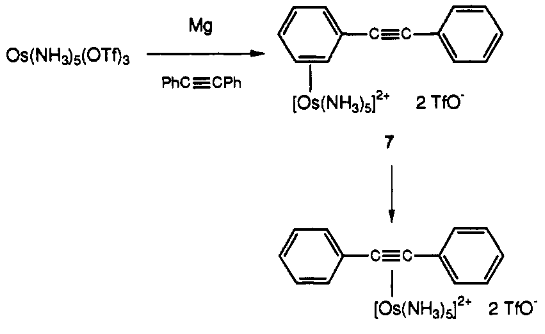
(22) (a) Birdwhistell, K. R.; Burgmayer, S. J. N.; Templeton, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 7789. (b) Werner, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1077. (c) Werner, H.; Hampp, A.; Peters, K.; Peters, E. M.; Walz, L.; von Schnering, H. G. *Z. Naturforsch.* **1990**, *45B*, 1548.

(23) Bullock, R. M. *J. Chem. Soc., Chem. Commun.* **1989**, 165.

cleophilic to react with **3** below 0 °C, decomposition to numerous products occurs. However, all species retain their *chemical* integrity as functional equivalents of the chiral Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (I), as evidenced by the high product yields from Scheme I.

Equation i shows a linkage isomerization that is relevant to Scheme I.[24] The generation of pentaammineosmium η^2-arene complex **7** is followed by a rearrangement to the alkyne complex **8**. This establishes that arene and alkyne functionalities exhibit contrasting kinetic and thermodynamic binding affinities for the osmium fragment $[Os(NH_3)_5]^{2+}$. Although our studies are still in progress, it is clear at this stage that alkynes also exhibit some of the poorer kinetic binding affinities, but some of the better thermodynamic binding affinities, for the rhenium fragment I.



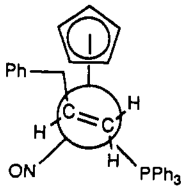
8

(i)

Preliminary data indicate that the methodology in Scheme I works equally well for the preparation of optically active alkyne complexes.[25] The ≡CH protons of the enantiomers of racemic **4e** are easily differentiated with chiral NMR shift reagents. Optically active **3**[10] gives **4e** that is, within detection limits, optically pure.

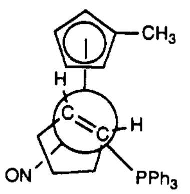
2. Structures of Alkyne Complexes 4. The NMR coupling constant, chemical shift, and NOE data described strongly suggest that alkyne complexes **4a–e** adopt similar structures in solution, analogous to that found for **4c** in the solid state (Figure 1). The absence of a bent nitrosyl or slipped cyclopentadienyl ligand indicates that the alkyne ligand functions as a simple two-electron donor, as opposed to a four-electron donor as observed in some complexes.[1] As a starting point, structural features of **4c** will be compared to those of the corresponding alkene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(RCH{=}CHR)]^+X^-$.

Allylbenzene complex (*RR*,*SS*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHCH_2C_6H_5)]^+PF_6^-$ (**9**)[11b] and cyclopentene complex $[(\eta^5\text{-}C_5H_4CH_3)Re(NO)(PPh_3)(\overline{HC{=}CHCH_2CH_2CH_2})]^+BF_4^-$ (**10**)[26] exhibit the structures shown in Newman projections IV and V. Analogously to **4c**, the alkene ligands adopt Re—(C⋯C) conformations that allow a high degree of overlap of the C=C π^* acceptor orbital with the d orbital HOMO of I. The angles of the Re—C⋯C plane with the Re—P and Re—N bonds in **10** are 8.8 and 73.6°, respectively, as compared to 10.6 and 75.4° in **4c**.



IV

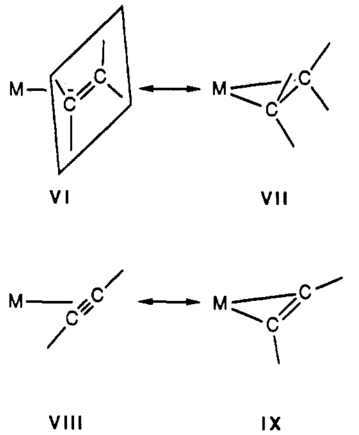
9



V

10

Scheme III. Limiting Resonance Formulations for Alkene and Alkyne Complexes



The C⋯C bond lengths in alkene complexes **9** and **10** (1.40 (3), 1.48 (1) Å) are intermediate between those of the C=C bond in propene (1.318 Å) and the C—C bond in propane (1.526 Å).[11b,26] Also, the C⋯C substituents lie considerably out of the C=C nodal plane of the free alkenes. Structures of alkene complexes are commonly analyzed in the context of two limiting resonance forms, π complex VI and "metallacyclopropane" VII (Scheme III). Our data indicate that **9** and **10** have considerable metallacyclopropane characters.

Structures of alkyne complexes are similarly analyzed in the context of π and "metallacyclopropene" resonance forms (VIII, IX; Scheme III).[1] Interestingly, the C≡C bond in **4c** (1.24 (1) Å) is not much longer than those in acetylene and 2-butyne (1.21 Å)[27] and shorter than the C=C bonds in cyclopropenes (1.28–1.30 Å).[28,29] This suggests at first glance a substantial contribution from π resonance form VIII. However, both propargylic carbons in **4c** are bent considerably back from the C≡C axis (∠C≡C—C = 143.4 (8), 147 (1)°). The analogous C=C—R angles in cyclopropene and 3-substituted 1,2-diphenylcyclopropenes are ca. 150 and 151–153°, respectively.[28,29] Also, the IR ν_{NO} values of **4a–e** (1696–1726 cm^{-1}) are slightly lower than those of analogous alkene complexes.[11b,26] This and NMR chemical shift trends suggest that the alkyne ligands in **4a–e** are better π acceptors than the alkene ligands in **9**, **10**, and related complexes.

One-bond carbon/hydrogen coupling constants, $^1J_{CH}$, are considered diagnostic of carbon hybridization.[12b] However, correlations to π character in metal complexes are viewed as much less reliable.[30] Nonetheless, the $^1J_{CH}$ values of the acetylene ligand in parent complex **4a** (242, 238 Hz) are much closer to that of free acetylene (249 Hz) than to that of ethylene (156 Hz).[12b] Cyclopropene exhibits a =CH $^1J_{CH}$ value of 226–228 Hz.[14]

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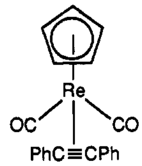
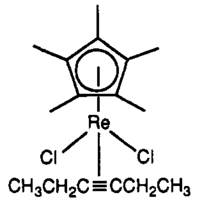
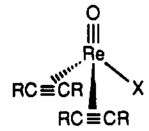
3. Structures of Other Alkyne Complexes. A search of the Cambridge Crystallographic Data Base located several other structurally characterized rhenium alkyne complexes.[31-34] These included the diphenylacetylene complex $(\eta^5\text{-}C_5H_5)Re(CO)_2(C_6H_5C{\equiv}CC_6H_5)$ (11),[31] the 3-hexyne complex $(\eta^5\text{-}C_5(CH_3)_5)Re(Cl)_2(CH_3CH_2C{\equiv}CCH_2CH_3)$ (12),[7,32] and a series of bis(alkyne) complexes of the formula $Re(O)(X)(RC{\equiv}CR)_2$ (13).[33] Complexes



11



12



13

4c and 11 contain rhenium in a +1 oxidation state and are the most closely related. Complex 11 crystallizes with two independent molecules in the unit cell. Their alkyne Re—C distances (2.18–2.19 Å) are comparable to those in **4c** (2.13–2.18 Å). The C≡C bond lengths (1.23–1.26 Å) are also close to that of **4c** (1.24 Å), whereas the C—C≡C bond angles (150–153°) are slightly greater.

The higher oxidation state complexes **12** and **13** exhibit distinctly different structures. The alkyne Re—C distances (**12**, 1.96–1.97 Å; **13**, 1.98–2.07 Å) are markedly shorter than those in **4c**. The C≡C bonds (**12**, 1.33 Å; **13**, 1.27–1.29 Å) are significantly longer than in **4c**. In all cases, smaller C—C≡C angles are evident. Hence, metallacyclopropene resonance form IX is comparatively more important in these complexes.

Spectroscopic features of many metal alkyne complexes have been studied in detail.[35] For example, the rhenium acetylene complex $(\eta^5\text{-}C_5H_5)Re(CO)_2(HC{\equiv}CH)$, which is related to the crystallographically characterized **11**, exhibits a ≡CH $^1J_{CH}$ value (237 Hz)[35a] that is similar to those of **4a** (242–238 Hz). The corresponding ^1H and ^{13}C NMR resonances (δ 5.61 and 64.5 ppm) are upfield of those in **4a**. The rhenium(V) acetylene complex $(CH_3)Re({=}O)_2(HC{\equiv}CH)$ exhibits ≡CH $^1J_{CH}$ values (225–227 Hz) that are lower than those of **4a** and ^1H and ^{13}C NMR resonances (δ 9.33–9.50, 129–139 ppm) that are downfield from those of **4a**.[34c] The crystal structure of the corresponding diphenylacetylene complex shows bond lengths and angles similar to those noted for **12** and **13**.[34c]

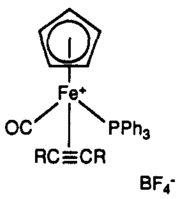
4. Dynamic and Conformational Properties of Alkyne Ligands. The 3-hexyne ligand orientation in **4c** indicates an overwhelming *electronic* influence upon conformation, as one ethyl substituent is directed at the bulky PPh_3 ligand. Figure 1 shows that a cleft can open between two PPh_3 phenyl rings to accommodate the ethyl group. This likely accounts for the NMR shielding of alkyne ligand substituents that are syn to the PPh_3 ligand. However, the ≡C—CH_2 (C1–C5) bond adopts a conformation that minimizes penetration of the methyl group into the cleft.

The distortions evident in Figure 1c suggest that considerable strain is nonetheless associated with the 3-hexyne ligand conformation. In related π-aldehyde complexes, the distances from the ligating atoms to the Re–P vector are nearly equal.[11c] Interestingly, alkyl ligand conformations that direct substituents at PPh_3 ligands in closely related compounds have been considered unattainable without severe perturbation of the core structures.[36]

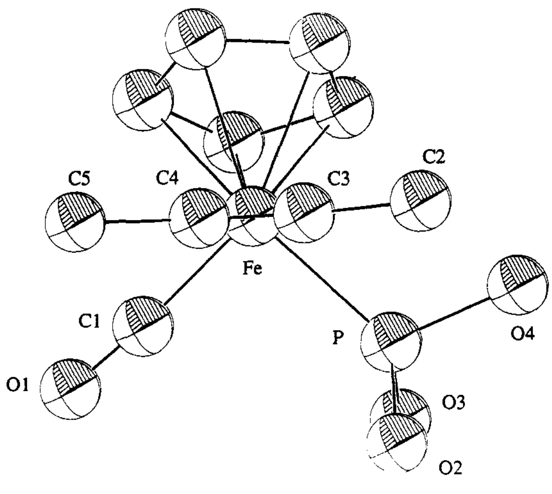
The Re—(C≡C) rotational barriers in **4b,c** (>22 kcal/mol, 180 °C) are much higher than the Re—(C=C) rotational barrier in the ethylene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CH_2)]^+PF_6^-$ (16.4 kcal/mol, 96 °C).[1b] We presume that there is a sizable electronic component to all of these barriers. However, there should also be a significant steric component to the alkyne complex barriers that is associated with moving the C≡C substituents through the PPh_3 phenyl rings. An upper bound on this contribution can be established, as described below.

Metal alkyne complexes have previously been found to exhibit M—(C≡C) rotational barriers ranging from 9 to 20 kcal/mol.[34c,35,36] Available data indicate that barriers in the rhenium(I) complex **11** (Scheme III) and derivatives are lower than those in **4b,c**.[31] However, NMR spectra of higher oxidation state rhenium complexes such as **13** and $(CH_3)Re({=}O)_2(RC{\equiv}CR)$ bound rotational barriers as >20 kcal/mol.[33a,34c]

Reger has previously studied the dynamic and conformational properties of iron alkyne complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(RC{\equiv}CR)]^+BF_4^-$ (**14**) and $[(\eta^5\text{-}C_5H_5)Fe(CO)(P(OPh)_3)(RC{\equiv}CR)]^+BF_4^-$ (**15**).[37] He finds Fe—



14 R = **b**, CH_3
c, CH_2CH_3



$[(\eta^5\text{-}C_5H_5)Fe(CO)(P(OPh)_3)(CH_3C{\equiv}CCH_3)]^+SbF_6^-$ (X)

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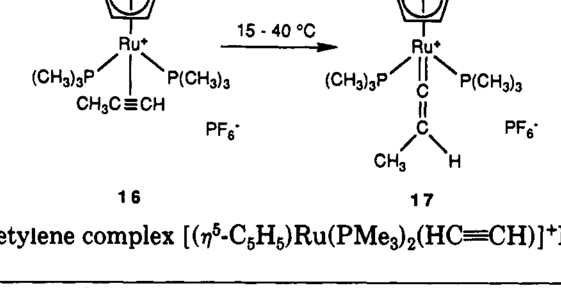
(C≡C) rotational barriers of 14.3 and 15.0 kcal/mol (1–18 °C) for the 2-butyne and 3-hexyne complexes **14b,c**. These complexes are "isoelectronic" with **4b,c**. However, metal–ligand bonds commonly differ by 6–9% in this series of rhenium and iron compounds. The shorter bond lengths in **14b,c** should increase the steric component of the alkyne ligand rotational barriers. Thus, these values provide *upper limits* on the steric components of the rotational barriers in **4b,c**.

Reger finds Fe—(C≡C) rotational barriers in the phosphite-substituted complexes **15** to be somewhat lower. Also, the crystal structure of the hexafluoroantimonate salt of phosphite-substituted 2-butyne complex **15b** has been determined.[39] The C≡C bond length (1.19 Å) and C≡C—C angles (158°) suggest a greater contribution from π resonance form VIII than in **4c**. The alkyne ligand adopts a conformation somewhat different from those in **4**, as shown in Newman projection X. The Fe—C≡C plane and Fe—P and Fe—C bonds define angles of 45.5 and 42.3°, respectively. We presume that, in the absence of electronic effects, similar alkyne ligand conformations would be observed in **4**.

5. Reactions of Alkyne Complexes. Terminal alkynes exhibit pK_a(H_2O) values of ca. 25.[40] Tertiary alcohols are much more acidic (pK_a(H_2O) ca. 17).[40] Thus, the facile deprotonation of terminal alkyne complexes **4a,e** by the conjugate base t-BuO$^-$K$^+$ shows that the acidities of terminal alkynes are markedly enhanced by coordination to the cationic rhenium fragment I. The thermal stability of **4a** and the previously synthesized[20] vinylidene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=C=CH_2)]^+X^-$ under the deprotonation conditions rules out the possibility of an initial isomerization step.

Interestingly, an analogous acidity enhancement of *vinylic* protons in alkene complexes of I has recently been documented.[26,41] Also, preliminary data show that the propargylic protons of internal alkyne complexes such as **4b,c** are also readily abstracted by t-BuO$^-$K$^+$.[25]

The prototropic rearrangement of terminal alkyne to vinylidene ligands has been the subject of a detailed theoretical analysis.[21b] Interestingly, the relative thermal stabilities of **4a,e** (Scheme II) parallel those of ruthenium terminal alkyne complexes recently studied by Bullock.[23] The propyne complex $[(\eta^5\text{-}C_5H_5)Ru(PMe_3)_2(HC{\equiv}CCH_3)]^+PF_6^-$ (**16**) readily rearranges to the vinylidene complex $[(\eta^5\text{-}C_5H_5)Ru(PMe_3)_2(=C=CHCH_3)]^+PF_6^-$ (**17**) at 15–40 °C, as shown in eq ii. However, the less bulky acetylene complex $[(\eta^5\text{-}C_5H_5)Ru(PMe_3)_2(HC{\equiv}CH)]^+PF_6^-$ undergoes an analogous rearrangement only at higher temperatures (60–90 °C). Finally, the methylvinylidene ligand in **17** is displaced by acetonitrile at 80–100 °C, liberating propyne. This suggests that **16** and **17** remain in equilibrium, as observed for **4e** and **6e**.



16 17

(ii)

6. Conclusion. This study has established that alkyne complexes of the chiral rhenium fragment I can be readily prepared. They exhibit conformational properties that are predicted by simple electronic considerations, and very high barriers to Re—(C≡C) rotation. The thermal and acid/base chemistry of the terminal acetylene complexes provides precedent for some widely postulated but rarely observed transformations. Studies of polyfunctional acetylene ligands will be reported in the future.

Experimental Section

General Data. All reactions were carried out under a dry N_2 atmosphere. FT-IR spectra were recorded on a Mattson Polaris spectrometer. NMR spectra were recorded on Varian XL-300 spectrometers as outlined in Table I. Microanalyses were conducted by Atlantic Microlab. Melting points were determined in evacuated capillaries with use of a calibrated thermometer.[42]

Solvents and reagents were purified as follows: C_6H_5Cl, distilled from P_2O_5; CH_2Cl_2, distilled from CaH_2; ether, distilled from $LiAlH_4$; THF, hexane, and benzene, distilled from Na/benzophenone; CD_2Cl_2 and C_6D_6, vacuum transferred from CaH_2; $CDCl_3$, dried over sieves and filtered through alumina; acetone, pentane, and $ClCH_2CH_2Cl$ (all spectral reagent grade), used as received; $HBF_4{\cdot}O(CH_2CH_3)_2$ (Aldrich), standardized as previously described;[9] acetylene gas (Matheson, minimum 99.6%), passed through Drierite; other alkynes (Aldrich), used as received.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(HC{\equiv}CH)]^+BF_4^-$ (4a). A Schlenk tube was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (1;[43] 0.446 g, 0.798 mmol) and chlorobenzene (10 mL), capped with a septum, and cooled to −45 °C (acetonitrile/liquid N_2 slurry). Then $HBF_4{\cdot}O(CH_2CH_3)_2$ (0.128 mL, 0.800 mmol) was added via syringe. After 10 min, a needle was inserted through the septum, and acetylene gas was bubbled through the solution. After 10 min, the cold bath was replaced by a water bath, which was warmed to 85 °C over the course of 1–2 h. The bath was maintained at 85 °C for 20 min and then cooled to room temperature over the course of 1–2 h. Some black precipitate appeared. The acetylene stream was stopped, and the brown reaction mixture was transferred via a cannula/filtration assembly (Celite) to a flask that had been charged with rapidly stirred hexane/benzene (60 mL, 2:1 v/v). The resulting precipitate was collected by filtration, washed with hexane and pentane, and then dried under oil pump vacuum at room temperature to give **4a** (0.476 g, 0.725 mmol, 91%) as a brown powder, mp 129–131 °C dec. Anal. Calcd for $C_{25}H_{22}BF_4NOPRe$: C, 45.74; H, 3.38. Found: C, 45.83; H, 3.40.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3C{\equiv}CCH_3)]^+BF_4^-$ (4b). A Schlenk flask was charged with 1 (0.352 g, 0.629 mmol) and chlorobenzene (7 mL), capped with a septum, and cooled to −45 °C. Then $HBF_4{\cdot}O(CH_2CH_3)_2$ (0.101 mL, 0.629 mmol) was added. After 10 min, 2-butyne (0.490 mL, 6.29 mmol) was added via a chilled syringe. The reaction mixture was slowly warmed to room temperature under a static sealed atmosphere (to minimize evaporation of 2-butyne). After 6 days, the brown solution was added dropwise to rapidly stirred hexane (ca. 50 mL, in air). The resulting precipitate was collected by filtration, washed with pentane, and dried under oil pump vacuum at 56 °C (24 h) to give **4b** (0.413 g, 0.603 mmol, 96%) as a yellow-tan powder that was nearly analytically pure. A sample was flash-chromatographed on silica (230–400 mesh, 10:90 v/v acetone/CH_2Cl_2) and dried under oil pump vacuum at 56 °C to give **4b** as a golden powder (75–85% recovery), mp 122–126 °C dec. Anal. Calcd for $C_{27}H_{26}BF_4NOPRe$: C, 47.83; H, 3.83. Found: C, 47.66; H, 3.99.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3CH_2C{\equiv}CCH_2CH_3)]^+BF_4^-$ (4c). Complex 1 (0.345 g, 0.618 mmol), chlorobenzene (9 mL), $HBF_4{\cdot}O(CH_2CH_3)_2$ (0.099 mL, 0.618 mmol), and 3-hexyne (0.350 mL,

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3.09 mmol) were combined in a procedure analogous to that given for **4b**. An identical workup gave crude **4c** (0.319 g, 0.448 mmol, 73%) as a maroon-tan powder. A sample was flash-chromatographed on silica as above (10:90 v/v ethyl acetate/CH_2Cl_2) and dried under oil pump vacuum at 56 °C to give **4c** as an amber powder (75–85% recovery), mp 192–197 °C dec. Anal. Calcd for $C_{29}H_{30}BF_4NOPRe$: C, 48.88; H, 4.24. Found: C, 48.78; H, 4.26. A sample was crystallized from layered 1,2-dichloroethane/pentane. Amber cubes of **4c**·$ClCH_2CH_2Cl$ formed, which were collected by filtration, washed with pentane, and dried under a nitrogen stream; mp 215–216 °C dec (gas evolution). Anal. Calcd for $C_{31}H_{34}BCl_2F_4NOPRe$: C, 45.88; H, 4.22; Cl, 8.74. Found: C, 45.70; H, 4.16; Cl, 8.66. The solvate and stoichiometry were confirmed by ^1H NMR spectroscopy ($CDCl_3$: δ 3.74, s, 4 H).

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(PhC{\equiv}CPh)]^+BF_4^-$ (4d). Complex **1** (0.208 g, 0.372 mmol), chlorobenzene (5 mL), $HBF_4{\cdot}O(CH_2CH_3)_2$ (0.060 mL, 0.37 mmol), and diphenylacetylene (0.332 g, 1.86 mmol) were combined in a procedure analogous to that given for **4b**. An identical workup gave crude **4d** (0.253 g, 0.313 mmol, 84%) as a tan powder. A sample (0.093 g, 0.115 mmol) was flash-chromatographed on silica as above (0–10:100–90 v/v acetone/CH_2Cl_2 gradient) and dried under aspirator vacuum to give **4d**·CH_2Cl_2 (0.074 g, 0.083 mmol) as orange-yellow microcrystals. Anal. Calcd for $C_{38}H_{32}BCl_2F_4NOPRe$: C, 51.08; H, 3.61; Cl, 7.94. Found: C, 51.13; H, 3.61; Cl, 7.87. This material was dried under oil pump vacuum at 56 °C to give unsolvated **4d** (0.067 g, 0.083 mmol) as an orange-yellow microcrystalline powder, mp 244–247 °C dec. Anal. Calcd for $C_{37}H_{30}BF_4NOPRe$: C, 54.96; H, 3.74. Found: C, 55.02; H, 3.77.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(HC{\equiv}CC(CH_3)_3)]^+BF_4^-$ (4e). Complex **1** (0.213 g, 0.381 mmol), chlorobenzene (5 mL), $HBF_4{\cdot}O(CH_2CH_3)_2$ (0.061 mL, 0.38 mmol), and *tert*-butylacetylene (0.470 mL, 3.81 mmol) were combined in a procedure analogous to that given for **4b**. An identical workup gave **4e** (0.263 g, 0.369 mmol, 97%) as a tan powder, mp 116–122 °C dec. Traces of **6e** were best removed by flash chromatography (silica gel, 10:90 v/v acetone/CH_2Cl_2). Anal. Calcd for $C_{29}H_{30}BF_4NOPRe$: C, 48.88; H, 4.24. Found: C, 48.74; H, 4.28.

$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C{\equiv}CH)$ (5a). A Schlenk flask was charged with **4a** (0.140 g, 0.213 mmol), THF (3.5 mL), and a stirbar and cooled to −80 °C. Then $t\text{-}BuO^-K^+$ (0.250 mL, 1.0 M in THF) was added to the suspension with stirring. The bath was warmed to room temperature over 3 h, and the mixture was stirred for an additional 3 h. Solvent was removed under oil pump vacuum, and the red-brown residue was extracted with benzene (2 × 3 mL, 2 × 2 mL). Each extract was transferred via cannula to a Kramer filter containing a 1 × 3 cm column of Celite topped with ca. 0.3 cm of deactivated Florisil.[11c] The orange filtrate was collected in a tared flask. The benzene was concentrated to ca. 3 mL under oil pump vacuum. Then hexane (5 mL) was added to precipitate an orange powder. Solvents were removed under oil pump vacuum (12 h) to give **5a** (0.089 g, 0.157 mmol, 74%) as an orange powder, mp 187–190 °C dec. Anal. Calcd for $C_{25}H_{21}NOPRe$: C, 52.81; H, 3.72. Found: C, 52.72; H, 3.73. The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra matched those previously reported.[20]

$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C{\equiv}CC(CH_3)_3)$ (5e). Complex **4e** (0.108 g, 0.151 mmol), THF (2 mL), and $t\text{-}BuO^-K^+$ (0.166 mL) were combined in a procedure analogous to that given for **5a**. The mixture was stirred for 15 min at −80 °C and then 45 min at room temperature. Solvent was removed under oil pump vacuum, and the orange-red residue was extracted with benzene (2 × 2 mL, 2 × 1 mL). Each extract was transferred via cannula to a Kramer filter containing a 1 × 2.5 cm column of Celite. Solvent was removed from the filtrate to give **5e** (0.092 g, 0.147 mmol, 97%) as an orange powder, mp 172–175 °C dec. Anal. Calcd for $C_{29}H_{29}NOPRe$: C, 57.22; H, 4.80. Found: C, 57.04; H, 4.85.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}C{=}CHC(CH_3)_3)]^+BF_4^-$ (6e). A Schlenk flask was charged with **5e** (0.090 g, 0.143 mmol), chlorobenzene (4 mL), and a stirbar and cooled to −45 °C. Then $HBF_4{\cdot}O(CH_2CH_3)_2$ (0.025 mL, 0.16 mmol) was added. The solution was stirred for 15 min at −45 °C, during which time an orange powder precipitated and redissolved. The cold bath was removed. The solution was stirred at room temperature for 1 h and then transferred via cannula (with a ca. 1 mL chlorobenzene rinse) to a flask that had been charged with rapidly stirred hexane (30 mL). The resulting precipitate was collected by filtration, washed with pentane, and dried under oil pump vacuum (4 h) to give **6e** (0.094 g, 0.132 mmol, 92%) as a dull yellow granular powder, mp 107–110 °C dec. Anal. Calcd for $C_{29}H_{30}BF_4NOPRe$: C, 48.88; H, 4.24. Found: C, 48.78; H, 4.24.

NMR Experiments. The ^1H NOE difference spectra were acquired at 21–26 °C in CD_2Cl_2 or $CDCl_3$ (**4c**) in septum-sealed tubes. Details were similar to experiments previously described (90% cyclopentadienyl resonance irradiation; block size 32–16 transients; 0–1 steady state/block; 512–3072 transients; pulse delay 6.5–7.0 s).[44] Probe temperatures were calibrated in VT experiments with either ethylene glycol or methanol.

Crystal Structure of 4c·$ClCH_2CH_2Cl$. An amber cube, obtained as described above, was mounted for data collection on a Syntex $P\bar{1}$ diffractometer as summarized in Table II. Cell constants were determined from 20 centered reflections with 20° < 2θ < 30°. The space group was determined from systematic absences ($0kl$, $k = 2n$; $h0l$, $l = 2n$; $h00$, $h = 2n$; $0k0$, $k = 2n$; $00l$, $l = 2n$) and subsequent least-squares refinement. Lorentz, polarization, and empirical absorption corrections were applied. The structure was solved by standard heavy-atom techniques with the SDP/VAX package.[45] Hydrogen atom positions were calculated. Non-hydrogen atoms (except BF_4^- atoms) were refined with anisotropic thermal parameters. Anomalous dispersion corrections were applied throughout the refinement. Scattering factors, and $\Delta f'$ and $\Delta f''$ values, were taken from the literature.[46]

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Supplementary Material Available: A table of anisotropic thermal parameters for 4c·$ClCH_2CH_2Cl$ (1 page); a table of calculated and observed structure factors (8 pages). Ordering information is given on any current masthead page.

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