products by fractional crystallization from acetonitrile/ethanol. Interestingly, the methylene protons of the ethyl groups on **7** are diastereotopic and give rise to a complex pattern in the 300-MHz proton NMR spectrum. This arises from differentiation of the two ligand faces by coordinated tricarbonylmanganese.[18]

The alkylation chemistry of anion **5b** stands in contrast to the permethylated system. Treatment of **5b** with excess $CF_3SO_3CH_3$ gave a light-colored solid product which was not readily identified by IR or NMR spectroscopic analysis. The failure of anion **5b** to give a single alkylation product analogous to the permethylated system indicates that additional alkylation sites on the coordinated ring or the metal center itself may exist. Alkylation of a coordinated manganese center has been reported with a coordinated cyclohexadiene system.[4g]

The appearance of protonated products from reactions of anions **5** was a routine difficulty because protonation of the anion at one of the methylene carbons was extremely facile. Handling of the anionic complexes in solution required the use of rigorously dried ether solvents which had been dried over the deep purple colored benzophenone *dianion*.[9,10] By proton NMR analysis, a solution of **5a** in THF-d_8 which had been vacuum distilled from molecular seives indicated that the anion was partially protonated back to **2a**. By contrast, a ^{13}C NMR spectrum of **5a** taken in nondeuterated THF which had been freshly distilled from benzophenone dianion showed no trace of protonation to the neutral complex **2a**.

Although much less reactive than the anions, the exomethylene cyclohexadienyl complexes did react with electrophilic reagents. The protonation of cyclohexadienyl complex **4a** with aqueous HPF_6 gave the cationic toluene complex **3a** in a 34% isolated yield as the PF_6^- salt. A similar protonation of **2a** with NH_4PF_6 was reported.[6] Treatment of **4a** with bromine gave the bromomethyl complex **8**, which was characterized by IR and NMR spectroscopies and elemental analysis. Eyman's group reported[6] a similar iodination of **2a**.

o-Xylylene anions **5a** and **5b** were readily oxidized in solution by molecular oxygen, giving the parent hydrocarbons hexamethylbenzene and *o*-xylene, respectively, as the major organic products, along with additional organic products of uncertain composition by mass spectral analysis.

Cyclohexadienyl complex **2a** in solution or as a solid readily decomposed in the presence of oxygen, giving hexamethylbenzene as the sole organic product. Complex **2a** was found to be unstable in THF solution over a period of days, even under an inert atmosphere, giving stable black crystals of undetermined composition which were insoluble in a variety of solvents.

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Deprotonation of Rhenium Terminal Acetylide Complexes of the Formula $(\eta^5\text{-}C_5R_5)Re(NO)(PPh_3)(C{\equiv}CH)$: Generation and Reactivity of Rhenium/Lithium C_2 Complexes

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Reactions of methyl complexes $(\eta^5\text{-}C_5R_4R')Re(NO)(PPh_3)(CH_3)$ (R/R' = H/H, H/CH_3, CH_3/CH_3) with $HBF_4{\cdot}OEt_2$, chlorobenzene, and R''C≡CH (R'' = H, CH_3) give terminal alkyne complexes $[(\eta^5\text{-}C_5R_4R')Re(NO)(PPh_3)(R''C{\equiv}CH)]^+BF_4^-$ (72–87%). When R'' = CH_3, equilibria with methylvinylidene complexes $[(\eta^5\text{-}C_5R_4R')Re(NO)(PPh_3)(=C{=}CHCH_3)]^+BF_4^-$ can be effected at 90–65 °C (75–99% conversion). Treatment of the alkyne or vinylidene complexes with *t*-BuO^-K^+ gives acetylide complexes $(\eta^5\text{-}C_5R_4R')Re(NO)(PPh_3)(C{\equiv}CR'')$ (R/R'/R'': **1**, H/H/H; **3**, H/H/CH_3; **11**, H/CH_3/H; **12**, H/CH_3/CH_3; **2**, CH_3/CH_3/H; **17**, CH_3/CH_3/CH_3; 81–94%). Reactions of **1** with 1.0 and 2.0 equiv of *n*-BuLi give the lithiated complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C{\equiv}CLi)$ and $(\eta^5\text{-}C_5H_4Li)Re(NO)(PPh_3)(C{\equiv}CLi)$, respectively, as assayed by ^{31}P NMR and subsequent conversion with CH_3I to **3** and **12**. Reaction of **1** with 2.0 equiv of *n*-BuLi and Ph_3SnCl gives the stannylated complex $(\eta^5\text{-}C_5H_4SnPh_3)Re(NO)(PPh_3)(C{\equiv}CSnPh_3)$ (49%), which upon silica gel chromatography yields $(\eta^5\text{-}C_5H_4SnPh_3)Re(NO)(PPh_3)(C{\equiv}CH)$. Reaction of **2** with *n*-BuLi gives $(\eta^5\text{-}C_5(CH_3)_5)Re(NO)(PPh_3)(C{\equiv}CLi)$, as assayed by subsequent reactions with CH_3I, D_2O, Me_3SiCl, and Ph_3SnCl to give **17** (95%), **2**-d_1 (88%; 86–89% labeled), $(\eta^5\text{-}C_5(CH_3)_5)Re(NO)(PPh_3)(C{\equiv}CSi(CH_3)_3)$ (86%), and $(\eta^5\text{-}C_5(CH_3)_5)Re(NO)(PPh_3)(C{\equiv}CSnPh_3)$ (45%).

Transition-metal auxiliaries offer abundant possibilities for modifying the acid/base properties of carbon–hydrogen bonds. Accordingly, diverse types of carbanions have been generated within a metal coordination sphere.[1-3] Their

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reactions with electrophiles have been studied in detail and exploited in numerous syntheses.

Organic terminal acetylenes, RC≡CH, are among the strongest hydrocarbon acids. Typical pK_a values (H_2O, 25 °C, upper limits) range from 21.2 (R = Ph) through 21.7 (R = H) and 22.7 (R = n-C_6H_{13}).[4] Many transition-metal congeners, terminal acetylide complexes $L_nMC{\equiv}CH$, have been synthesized.[5,6] However, to our knowledge, attempts to effect the deprotonation of such compounds as in eq i

$$L_nM\text{-}C{\equiv}C\text{-}H + M^{n+}B:^- \xrightarrow{?} L_nM\text{-}C{\equiv}C^-M^{n+} + B\text{-}H \quad (i)$$

have not been previously reported. The resulting conjugate bases, which can be viewed as C_2 or dicarbide complexes,[7] should be highly nucleophilic and valuable synthons for constructing a variety of species with alkynyl units. Several types of derivatives would be of particular current interest.[8,9]

We have previously described the synthesis of the chiral rhenium terminal acetylide complex (η^5-C_5H_5)Re(NO)(PPh$_3$)(C≡CH) (**1**).[6] We have also found that a number of related neutral complexes of the formula (η^5-C_5H_5)Re(NO)(PPh$_3$)(X) undergo well-defined deprotonations with strong bases such as n-BuLi.[3] Hence, we set out to explore the acid/base chemistry of **1**, and the pentamethylcyclopentadienyl analog (η^5-C_5Me_5)Re(NO)(PPh$_3$)(C≡CH) (**2**). In this paper, we report (1) the ready lithiation of the acetylide ligands in **1** and **2** to give ReC≡CLi species or rhenium/lithium C_2 complexes[7] and (2) their subsequent functionalization with carbon, silicon, and tin electrophiles. Portions of this work have been communicated.[10]

Scheme I. Synthesis of the Cyclopentadienyl Methylacetylide Complex (η^5-C_5H_5)Re(NO)(PPh$_3$)(C≡CCH$_3$) (3)

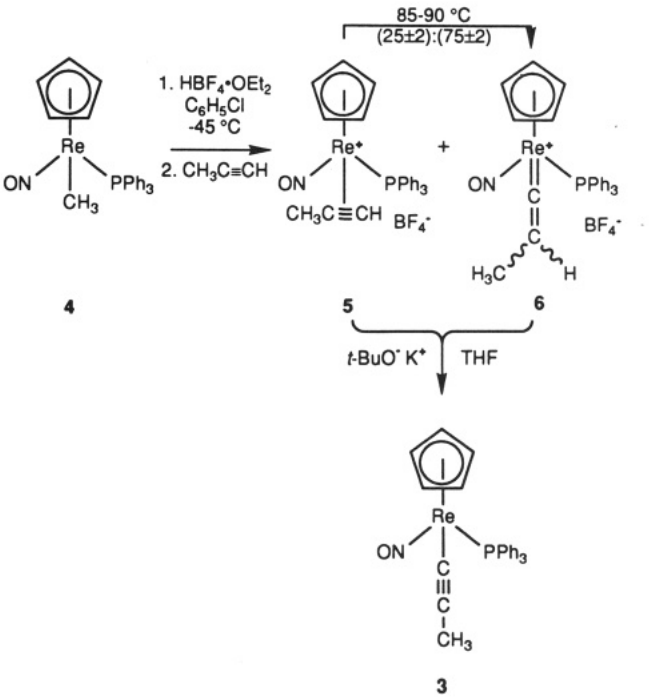
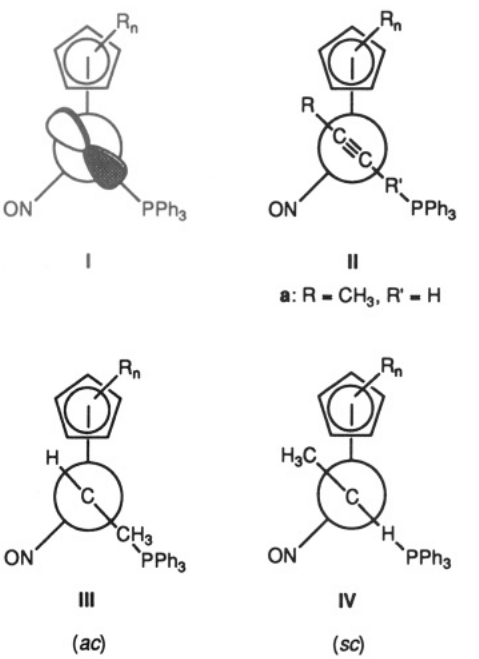


Chart I. (I) d Orbital HOMO of the Chiral Rhenium Fragment [(η^5-C_5H_5)Re(NO)(PPh$_3$)]$^+$ and Methylated Derivatives; (II) Idealized Re—(C≡C) Conformations of Alkyne Complexes of I; (III, IV) Idealized Re=C=CHCH$_3$ Conformations of Methylvinylidene Complexes of I



Results

Prior to attempting the deprotonation of **1** or **2**, we sought authentic samples of potential trapping products.

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(7) Formally, a carbide is a binary compound of carbon with a more electropositive element. Thus, one way to designate compounds of the type $L_nMCCM'L'_{n'}$ is as dimetallo*di*carbides, which denotes stoichiometry and can be extended to C_x homologs. Other conventions (e.g., ethynediyls)[8a] are often equally appropriate or even more descriptive, but can carry connotations regarding the bond orders between atoms in the MCCM′ linkage.

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A variety of lithiated derivatives of (η^5-C_5H_5)Re(NO)(PPh_3)(X) compounds have been previously generated—including several classes of lithiocyclopentadienyl complexes (η^5-C_5H_4Li)Re(NO)(PPh_3)(X).[3] In all cases, simple methyl electrophiles have proved to be effective trapping agents. Thus, we set out to prepare appropriate methylated derivatives of **1** and **2**.

1. Syntheses of Cyclopentadienyl Complexes. The methyl acetylide complex (η^5-C_5H_5)Re(NO)(PPh_3)(C≡CCH_3) (**3**) has been prepared previously.[6a] However, an improved route to this class of compounds involving terminal alkyne complexes has recently been developed.[6b] Thus, the methyl complex (η^5-C_5H_5)Re(NO)(PPh_3)(CH_3) (**4**) was treated with HBF_4·OEt_2 in chlorobenzene at −45 °C to generate the substitution-labile chlorobenzene complex [(η^5-C_5H_5)Re(NO)(PPh_3)(ClC_6H_5)]$^+BF_4^-$.[11] Then excess propyne was added. Workup gave the π adduct [(η^5-C_5H_5)Re(NO)(PPh_3)(HC≡CCH_3)]$^+BF_4^-$ (**5**) in 85% yield (Scheme I). The IR and NMR properties of **5** resembled those described earlier for the corresponding acetylene and 2-butyne complexes[6b] and are summarized in Table I.

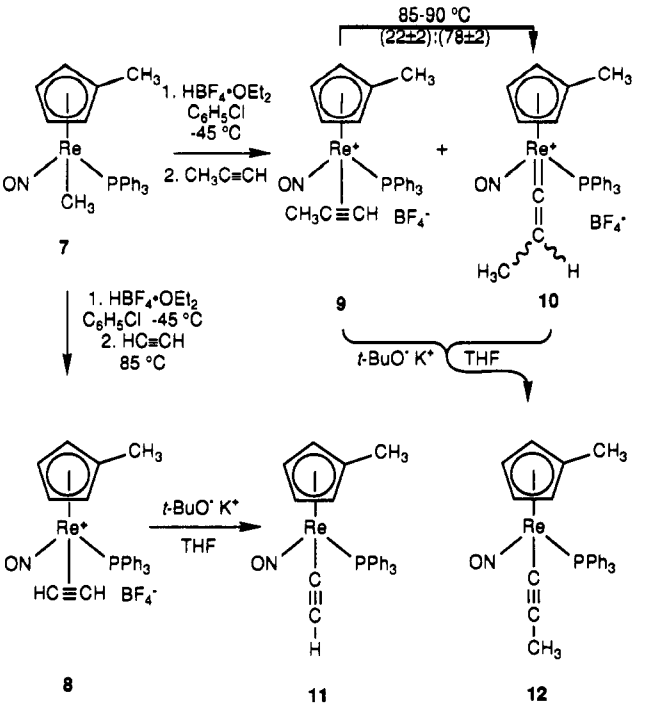
The rhenium fragment [(η^5-C_5H_5)Re(NO)(PPh_3)]$^+$ (I) is a strong π base with the d orbital HOMO shown in Chart I.[12] Hence, alkyne adducts adopt the idealized Re—(C≡C) conformation depicted in II, with rotational barriers of >22 kcal/mol (180 °C).[6b] Some unsymmetrical alkynes (e.g., 2-hexyne) give mixtures of Re—(C≡C) rotamers.[6b] However, the propyne complex **5** appeared homogeneous. The ^{1}H and ^{13}C NMR properties of the ≡CH and ≡CCH_3 moities indicated the conformation shown in IIa,[6b] which has the larger methyl C≡C substituent anti to the bulky PPh_3 ligand.

As a complement to observations made below, a chlorobenzene solution of **5** was kept at 85 °C for 0.5 h. Isomerization occurred to give a (84 ± 2):(16 ± 2) mixture of **5** and the previously characterized methylvinylidene complex [(η^5-C_5H_5)Re(NO)(PPh_3)(=C=$CHCH_3$)]$^+BF_4^-$ (**6**),[6a] as assayed by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy in $CDCl_3$. Complex **6** was a (50 ± 2):(50 ± 2) mixture of *ac*/*sc* Re=C=C geometric isomers, the structures of which are shown in III and IV (Chart I). A chlorobenzene solution of **5** was subsequently kept at 90 °C for 2 h. A (25 ± 2):(75 ± 2) **5**/**6** mixture formed ((53 ± 2):(47 ± 2) *ac*/*sc*). These ratios were unchanged after an additional 2 h, thus showing equilibration to be complete. This type of rearrangement, which has also been observed by Bullock and Selegue in related cyclopentadienyl ruthenium complexes,[13] is further exemplified elsewhere.[6b]

Terminal alkyne and vinylidene complexes closely related to **5** and **6** have previously been shown to undergo deprotonation to the corresponding neutral acetylide complexes when treated with *t*-BuO^-K^+ in THF.[6] Hence, **5** or mixtures of **5** and **6** were reacted analogously (Scheme I). Workup gave the methylacetylide complex **3** in 94% yield. The ^{1}H and ^{31}P NMR spectra matched those reported earlier.[6a]

2. Syntheses of Methylcyclopentadienyl Complexes. Next, similar methylcyclopentadienyl complexes were sought. Thus, the methyl complex (η^5-$C_5H_4CH_3$)Re(NO)(PPh_3)(CH_3) (**7**)[14] was treated with HBF_4·OEt_2 and chlorobenzene in a protocol analogous to that in Scheme I. In separate experiments, excess acetylene and propyne were added (Scheme II). Workup gave the analytically pure alkyne complexes [(η^5-$C_5H_4CH_3$)Re(NO)(PPh_3)(HC≡CH)]$^+BF_4^-$ (**8**) and [(η^5-$C_5H_4CH_3$)Re(NO)(PPh_3)(HC≡CCH_3)]$^+BF_4^-$ (**9**) in 79–83% yields. The NMR properties of **9** (Table I) established the propyne ligand conformation shown in IIa.[6b]

Scheme II. Synthesis of the Methylcyclopentadienyl Acetylide Complexes (η^5-$C_5H_4CH_3$)Re(NO)(PPh_3)(C≡CR)



Complexes **8** and **9** exhibited ^{1}H and ^{13}C NMR resonance patterns characteristic of methylcyclopentadienyl ligands.[15] Otherwise, spectroscopic properties resembled those of the cyclopentadienyl analogs. Weak IR $\nu_{\equiv CH}$ (3102–3109 cm^{-1}) were observed under some conditions. A chlorobenzene solution of **8** was kept at 85 °C for 0.5 h. No vinylidene complex could be detected. However, a careful examination of isolated **9** showed ca. 8% of the isomeric methylvinylidene complex [(η^5-$C_5H_4CH_3$)Re(NO)(PPh_3)(=C=$CHCH_3$)]$^+BF_4^-$ (**10**, (52 ± 2):(48 ± 2) *ac*/*sc*).

Thus, a chlorobenzene solution of **9** was kept at 85 °C for 0.5 h. A (22 ± 2):(78 ± 2) mixture of **9** and **10** ((52 ± 2):(48 ± 2) *ac*/*sc*) formed, as assayed by ^{31}P NMR spectroscopy ($CDCl_3$). A second sample was kept at 90 °C for 4 h. An identical product ratio was obtained. Thus, this equilibrium is attained more rapidly than that in Scheme I. However, the equilibrium constants are identical within experimental error. The spectroscopic properties of **10** are summarized in Table I, and NMR resonances were assigned to *ac* and *sc* isomers on the basis of chemical shift trends established earlier.[6a]

As shown in Scheme II, **8**, **9**, or **9**/**10** mixtures were treated with *t*-BuO^-K^+ in THF. Workup gave the parent acetylide complex (η^5-$C_5H_4CH_3$)Re(NO)(PPh_3)(C≡CH)

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Table I. Spectroscopic Characterization of New Alkyne, Vinylidene, and Acetylide Complexes

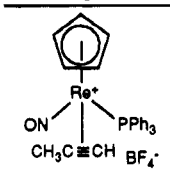
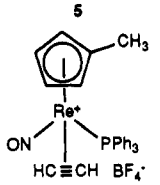
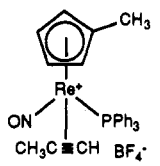
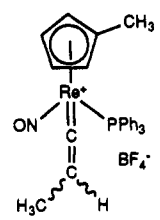
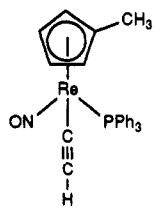
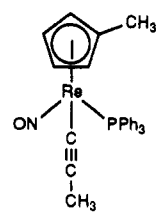
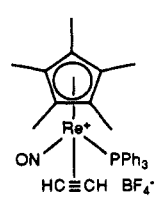
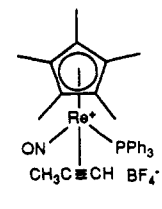
complex	IR (cm^{-1})	^1H NMR[a] (δ)	$^{13}C\{^1H\}$ NMR[b] (ppm)	$^{31}P\{^1H\}$ NMR[c] (ppm)
 **5**	ν_{NO} 1716 (vs) (CH_2Cl_2); ν_{NO} 1700 (vs), ν_{CH} 3124 (w) (KBr)	7.75–7.50 (m, 6 H of 3 C_6H_5), 7.43–7.20 (m, 9 H of 3 C_6H_5), 6.15 (dq, J_{HP} 19.7, J_{HH} 2.0, ≡CH syn to PPh_3), 5.85 (s, C_5H_5), 3.03 (d, J_{HH} 2.0, H_3CC≡ anti to PPh_3)[e]	PPh_3 at[d] 133.2 (d, J 10.2, ortho), 132.5 (d, J 2.7, para), 129.8 (d, J 9.8, meta); 99.2 (s, C_5H_5), 102.1 (s, CC≡ anti to PPh_3), 76.0 (d, J 14.3, HC≡ syn to PPh_3), 17.6 (d, J 2.2, CC≡)[e]	16.7 (s)[e]
 **8**	ν_{NO} 1717 (vs) (CH_2Cl_2); ν_{NO} 1703 (vs), ν_{CH} 3102 (m) (KBr)	8.42 (d, J_{HP} 4.3, ≡CH anti to PPh_3), 7.47–7.39 (m, 9 H of 3 C_6H_5), 7.20–7.12 (m, 6 H of 3 C_6H_5), 6.57 (d, J_{HP} 19.0, ≡CH syn to PPh_3); $C_5H_4CH_3$ at 5.78, 5.66, 5.51, 5.18 (br s); 1.97 (s, $C_5H_4CH_3$)[e]	PPh_3 at[d] 133.1 (d, J 10.5, ortho), 132.5 (d, J 2.8, para), 129.8 (d, J 11.3, meta); 119.2 (s, HC≡ anti to PPh_3), 86.5 (d, J 14.4, HC≡ syn to PPh_3); $C_5H_4CH_3$ at 99.4, 99.0, 97.5, 94.3, 93.8 (s); 30.3 (s, $C_5H_4CH_3$)[e]	17.6 (s)[e]
 **9**	ν_{NO} 1708 (vs) (CH_2Cl_2); ν_{NO} 1696 (vs), ν_{CH} 3109 (m) (KBr)	7.69–7.47 (m, 8 H of 3 C_6H_5), 7.37–7.14 (m, 7 H of 3 C_6H_5), 6.29 (dq, J_{HP} 19.9, J_{HH} 2.0, ≡CH syn to PPh_3); $C_5H_4CH_3$ at 6.10, 5.70, 5.54, 5.31 (br s); 3.09 (d, J_{HH} 2.0, H_3CC≡ anti to PPh_3), 2.12 (s, $C_5H_4CH_3$)[e]	PPh_3 at[d] 133.2 (d, J 10.3, ortho), 132.5 (d, J 2.6, para), 129.7 (d, J 11.3, meta); 118.1 (s, CC≡ anti to PPh_3), 78.4 (d, J 15.8, HC≡ syn to PPh_3); $C_5H_4CH_3$ at 104.4, 99.3, 99.2, 98.3, 95.2 (s); 17.5 (s, $C_5H_4CH_3$), 12.5 (s, CC≡)[e]	17.0 (s)[e]
 *anti/syn*-**10**	ν_{NO} 1721 (vs), $\nu_{C=C}$ 1655 (m) (CH_2Cl_2); ν_{NO} 1704 (vs), $\nu_{C=C}$ 1655 (m) (KBr)	6.07/5.37 (q, J_{HH} 8.1/7.9, =$CHCH_3$); $C_5H_4CH_3$ at 5.89, 5.86, 5.71, 5.67 (br s); 2.26, 2.24 (s, $C_5H_4CH_3$), 1.23/1.90 (d, J_{HH} 8.1/7.9, =$CHCH_3$)[e,f]	328.5/329.4 (d, J 10.4/9.5, C_α); PPh_3 at[d] 132.9, 132.8 (d, J = 10.4, 9.5, ortho), 132.4 (s br, para), 129.7, 129.5 (d, J 9.1, 9.2, meta); 124.8/124.7, (s, C_β); $C_5H_4CH_3$ at 117.9/117.5; 99.28, 99.26; 98.2, 98.3; 97.3, 97.2, 96.22, 96.18 (s); 14.0, 13.7 (s, $C_5H_4CH_3$), 8.0/9.9 (s, =$CHCH_3$)[e,f]	19.1/ 18.7 (s)[e]
 **11**	ν_{NO} 1654 (vs), $\nu_{C=C}$ 1946 (m), ν_{CH} 3051 (w) (CH_2Cl_2); ν_{NO} 1648 (vs), $\nu_{C=C}$ 1944 (m) (KBr)	7.94–7.50 (m, 6 H of 3 C_6H_5), 7.46–7.04 (m, 9 H of 3 C_6H_5); $C_5H_4CH_3$ at 5.41, 5.01, 4.76, 4.44 (br s); 2.64 (d, J_{HP} 2.0, ≡CH), 2.06 (s, $C_5H_4CH_3$)[e]	PPh_3 at 135.4 (d, J 55.1, ipso), 133.7 (d, J 10.5, ortho), 130.0 (d, J 2.4, para), 128.0 (d, J 10.5, meta); 111.0 (s, ≡CH), 90.3 (d, J 15.2, ReC≡); $C_5H_4CH_3$ at 110.2 (s), 91.5 (d, J 2.0), 88.9 (s), 87.9 (s), 86.3 (d, J 3.0); 14.0 (s, $C_5H_4CH_3$)[e]	20.4 (s)[e]
 **12**	ν_{NO} 1646 (vs) (CH_2Cl_2); ν_{NO} 1648 (vs), $\nu_{C=C}$ 2110 (w) (KBr)	7.56–7.46 (m, 6 H of 3 C_6H_5), 7.44–7.31 (m, 9 H of 3 C_6H_5); $C_5H_4CH_3$ at 5.36, 4.99, 4.61, 4.37 (br s); 2.01 (d, J_{HP} 2.1, ≡CCH_3), 1.99 (s, $C_5H_4CH_3$)[e]	PPh_3 at 135.8 (d, J 53.6, ipso), 133.8 (d, J 10.5, ortho), 129.9 (d, J 2.3, para), 128.1 (d, J 10.4, meta); 119.2 (d, J 1.3, ≡CC), 77.4 (d, J 16.9, ReC≡); $C_5H_4CH_3$ at 91.1 (d, J 2.4), 88.3 (s, 2C), 87.6 (s), 85.6 (d, J 3.2); 13.9 (s, $C_5H_4CH_3$), 6.5 (d, J 1.2, ≡CC)[e]	21.1 (s)[e]
 **14**	ν_{NO} 1705 (vs), ν_{CH} 3054 (m) (CH_2Cl_2); ν_{NO} 1684 (vs), ν_{CH} 3058 (m) (KBr)	7.87 (d, J_{HP} 4.8, ≡CH anti to PPh_3), 7.81–7.12 (m, 3 C_6H_5, broad), 6.94 (d, J_{HP} 18.9, ≡CH syn to PPh_3), 1.79 (s, $C_5(CH_3)_5$)[g]	PPh_3 at 134.3–133.2 and 130.1–128.7; 108.9 (s, $C_5(CH_3)_5$), 100.6 (d, J 2.0, HC≡ anti to PPh_3), 91.4 (d, J 16.2, HC≡ syn to PPh_3), 9.7 (s, $C_5(CH_3)_5$)[g]	20.4 (s)[g]
 **15**	ν_{NO} 1698 (vs) (CH_2Cl_2); ν_{NO} 1681 (vs) (KBr)	7.74–6.95 (m, 3 C_6H_5, broad), 6.31 (dq, J_{HP} 20.3, J_{HH} 2.0, ≡CH syn to PPh_3), 2.90 (dd, J_{HP} 1.2, J_{HH} 2.0, CH_3C≡ anti to PPh_3), 1.82 (d, J_{HP} 0.8, $C_5(CH_3)_5$)[g]	PPh_3 at[d] 134.0 (br, ortho), 132.2 (br, para), 129.8 (br, meta); 109.3 (s, $C_5(CH_3)_5$), 94.7 (d, J 1.6, CC≡ anti to PPh_3), 82.5 (d, J 15.8, HC≡ syn to PPh_3), 14.3 (d, J 2.2, CC≡), 9.8 (s, $C_5(CH_3)_5$)[g]	18.0 (s)[g]

Table I (Continued)

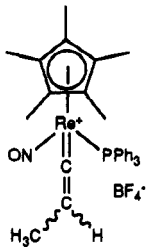
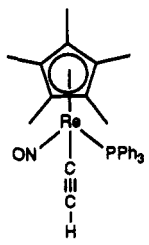
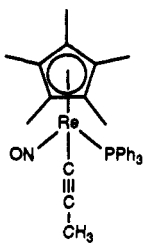
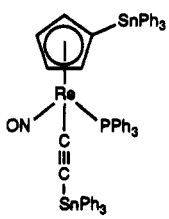
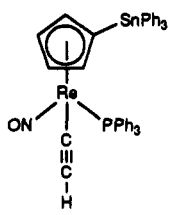
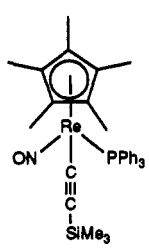
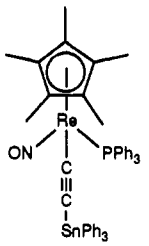
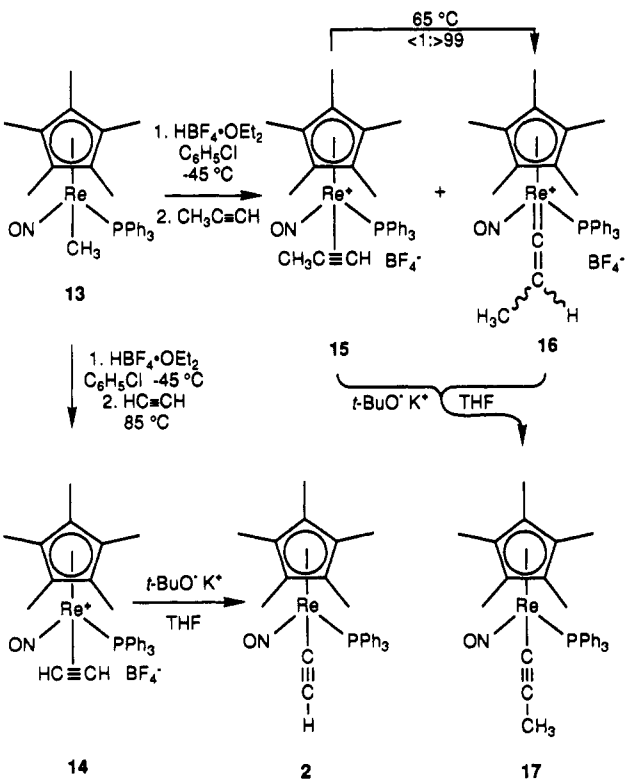
complex	IR (cm^{-1})	^1H NMR[a] (δ)	$^{13}C\{^1H\}$ NMR[b] (ppm)	$^{31}P\{^1H\}$ NMR[c] (ppm)
 *ac/sc*-16	ν_{NO} 1698 (vs), ν_{C-C} 1655 (w) (CH_2Cl_2); ν_{NO} 1681 (vs), ν_{C-C} 1656 (w) (KBr)	7.68–7.23 (m, 3 C_6H_5), 5.91/5.61 (dq/q, J_{HP} 1.5, J_{HH} 8.0/7.8, =C*H*CH$_3$), 1.45/1.97 (d, J_{HH} 8.0/7.8, =CHC*H*$_3$), 1.92/1.95 (d, J_{HH} 8.1/7.9, $C_5(CH_3)_5$)[f,g]	329.0/329.3 (d, J 10.0/10.6, C_α); PPh_3 at[d] 133.5/133.6 (d, J 11.5/11.8, ortho), 132.8/132.8 (d, J 2.7/2.4, para), 129.9/129.7 (d, J 11.3/11.6, meta); 123.8/125.1 (s, C_β), 109.4/110.0 (s, $C_5(CH_3)_5$), 10.4/10.1 (s, $C_5(CH_3)_5$), 8.5/9.3 (s, =CH*C*H$_3$)[f,g]	26.2/ 24.8 (s)[f,g]
 2	ν_{NO} 1637 (vs), $\nu_{C\equiv C}$ 1939 (m) (CH_2Cl_2); ν_{NO} 1629 (vs), $\nu_{C\equiv C}$ 1936 (m), ν_{CH} 3049 (w) (KBr)	7.89–7.70 (m, 6 H of 3 C_6H_5), 7.14–6.92 (m, 9 H of 3 C_6H_5), 3.24 (d, J_{HP} 2.3, ≡CH), 1.67 (s, $C_5(CH_3)_5$)[h]	PPh_3 at 136.1 (d, J 50.4, ipso), 134.6 (d, J 10.6, ortho), 130.0 (d, J 2.2, para), 128.2 (d, J 10.2, meta); 116.0 (s, ≡CH), 98.0 (d, J 15.8, ReC≡), 99.8 (d, J 1.5, $C_5(CH_3)_5$), 10.2 (s, $C_5(CH_3)_5$)[h]	21.5 (s)[h]
 17	ν_{NO} 1630 (vs), $\nu_{C\equiv C}$ 2107 (w) (CH_2Cl_2); ν_{NO} 1633 (vs), $\nu_{C\equiv C}$ 2104 (w) (KBr)	7.91–7.72 (m, 6 H of 3 C_6H_5), 7.20–6.88 (m, 9 H of 3 C_6H_5), 2.42 (d, J_{HP} 2.6, ≡CCH$_3$), 1.68 (s, $C_5(CH_3)_5$)[h]	PPh_3 136.5 (d, J 49.9, ipso), 134.6 (d, J 10.6, ortho), 139.8 (d, J 1.5, para), 128.1 (d, J 10.5, meta); 118.5 (d, J 1.5, ≡*C*C), 86.2 (d, J 17.7 ReC≡), 99.6 (d, J 1.9, $C_5(CH_3)_5$), 10.3 (s, $C_5(CH_3)_5$), 7.5 (s, ≡C*C*)[h]	22.2 (s)[h]
 20	ν_{NO} 1660 (vs), $\nu_{C\equiv C}$ 1992 (m) (CH_2Cl_2); ν_{NO} 1655 (vs), $\nu_{C\equiv C}$ 1991 (m) (KBr)	7.93–6.74 (m, 9 C_6H_5); C_5H_4Sn at 5.51, 4.95, 4.88, 4.32 (br s)[g]	PPh_3 at 136.0 (d, J 54.1, ipso), 134.2 (d, J 10.4, ortho), 130.2 (d, J 2.4, para), 128.3 (d, J 10.4, meta); $SnPh_3$ at[i] 140.6/138.0 (s, ipso), 137.8/137.4 (s, J_{CSn} 39.8/41.8 ortho), 129.5, 129.0, 128.8, 128.6 (s, meta/para); 122.5 (d, J 14.6, J_{CSn} 97.5, ReC≡), 122.4 (s, ≡CSn); C_5H_4Sn at[i,j] 105.5 (s, J_{CSn} 42.2), 98.3 (s, J_{CSn} 36.2), 92.9 (s, J_{CSn} 44.5), 90.9 (s, J_{CSn} 20.5)[g]	19.4 (s)[g]
 21	ν_{NO} 1654 (vs), $\nu_{C\equiv C}$ 1951 (vs) (CH_2Cl_2); ν_{NO} 1654 (vs), $\nu_{C\equiv C}$ 1951 (vs), ν_{CH} 3040 (w) (KBr)	7.87–6.89 (m, 6 C_6H_5); C_5H_4Sn at 5.40, 5.24 (2 H), 4.47 (br s); 2.40 (d, J 2.4, ≡CH)[g]	PPh_3 at 135.8 (d, J 55.7, ipso), 134.2 (d, J 10.2, ortho), 130.6 (d, J 2.4, para), 128.5 (d, J 10.6, meta); $SnPh_3$ at[i] 153.0 (s, ipso), 138.0 (s, J_{CSn} 20.0, ortho), 129.6 (s, J_{CSn} 11.3, para), 129.0 (s, J_{CSn} 31.3, meta); 112.5 (s, ≡CSn), 84.0 (d, J 15.6, ReC≡); C_5H_4Sn at[i,j] 102.6 (s, J_{CSn} 41.1), 99.3 (s, J_{CSn} 35.8), 92.9 (s, J_{CSn} 44.1), 92.1 (s, J_{CSn} 34.8)[g]	20.2 (s)[g]
 23	ν_{NO} 1633 (vs), $\nu_{C\equiv C}$ 2008 (s) (CH_2Cl_2); ν_{NO} 1627 (vs), $\nu_{C\equiv C}$ 2002 (s) (KBr)	7.80–7.74 (m, 6 H of 3 C_6H_5), 7.10–6.99 (m, 9 H of 3 C_6H_5), 1.63 (s, $C_5(CH_3)_5$), 0.24 (s, $Si(CH_3)_3$)[h]	PPh_3 at 136.0 (d, J 51.1, ipso), 134.6 (d, J 10.6, ortho), 129.9 (d, J 2.1, para), 128.1 (d, J 10.3, meta); 131.4 (d, J 15.6, ReC≡), 131.1 (s, ≡CSi), 99.9 (d, J 1.7, $C_5(CH_3)_5$), 10.1 (s, $C_5(CH_3)_5$), 2.1 (s, $Si(CH_3)_3$)[h]	21.2 (s)[h]

Table I (Continued)

complex	IR (cm^{-1})	^1H NMR[a] (δ)	$^{13}C\{^1H\}$ NMR[b] (ppm)	$^{31}P\{^1H\}$ NMR[c] (ppm)
 24	ν_{NO} 1637 (vs), $\nu_{C\equiv C}$ 1983 (s) (CH_2Cl_2); ν_{NO} 1638 (vs), $\nu_{C\equiv C}$ 1983 (s) (KBr)	7.66–7.16 (m, 6 C_6H_5), 1.76 (s, $C_5(CH_3)_5$)[g]	PPh_3 at[d] 134.4 (d, J 10.6, ortho), 130.2 (d, J 2.2, para), 128.3 (d, J 10.2, meta); $SnPh_3$ at[i] 140.4 (s, ipso), 137.0 (s, J_{CSn} 41.8, ortho), 128.9 (s, J_{CSn} 10.8, para), 128.5 (s, meta); 138.6 (d, J 15.8, J_{CSn} 96.4, ReC≡), 119.7 (d, J 1.5, ≡CSn), 100.7 (d, J 1.7, $C_5(CH_3)_5$), 10.3 (s, $C_5(CH_3)_5$).[g]	22.2 (s)[g]

[a] At 300 MHz and ambient probe temperature and referenced to internal $Si(CH_3)_4$ (0.00 ppm); couplings are in Hz. [b] At 75.4 MHz and ambient probe temperature and referenced to $CDCl_3$ (77.0 ppm), CD_2Cl_2 (53.2 ppm), or C_6D_6 (128.0 ppm); couplings (Hz) are to phosphorus unless noted. [c] At 121 MHz and ambient probe temperature and referenced to external 85% H_3PO_4 (0.00 ppm). [d] The ipso resonance is obscured. [e] In $CDCl_3$. [f] Data separated by a slash (/) can be assigned to *ac* and *sc* isomers, respectively. In some cases where a definitive assignment cannot be made, data are separated by a comma. [g] In CD_2Cl_2. [h] In C_6D_6. [i] Satellites due to ^{13}C–^{119}Sn coupling are not observed for all resonances. [j] The CSn resonance is not observed.

Scheme III. Synthesis of the Pentamethylcyclopentadienyl Acetylide Complexes (η^5-$C_5(CH_3)_5$)Re(NO)(PPh_3)(C≡CR)



(11, 91%) and the methylacetylide complex (η^5-$C_5H_4CH_3$)Re(NO)(PPh_3)(C≡CCH_3) (12, 81%), respectively, in analytically pure form. Except for the NMR resonances associated with the methylcyclopentadienyl ligands, spectroscopic properties (Table I) closely matched those of cyclopentadienyl analogs.[6a]

3. Syntheses of Pentamethylcyclopentadienyl Complexes. Next, samples of the pentamethylcyclopentadienyl acetylide complex **2** and methylated homologs were sought. Thus, the methyl complex (η^5-$C_5(CH_3)_5$)-Re(NO)(PPh_3)(CH_3) (**13**)[16] was treated with HBF_4•OEt_2 and chlorobenzene in a procedure analogous to that in Scheme II. In separate experiments, excess acetylene and propyne were added (Scheme III). Workup gave the alkyne complexes [(η^5-$C_5(CH_3)_5$)Re(NO)(PPh_3)(HC≡CH)]$^+BF_4^-$ (**14**, 72%) and [(η^5-$C_5(CH_3)_5$)Re(NO)(PPh_3)-(HC≡CCH_3)]$^+BF_4^-$ (**15**).

No vinylidene complex could be detected in isolated **14**. However, the latter sample was a (65 ± 2):(22 ± 2):(13 ± 2) mixture of **15** and *ac*/*sc* isomers of the corresponding methylvinylidene complex [(η^5-$C_5(CH_3)_5$)Re(NO)(PPh_3)-(=C=$CHCH_3$)]$^+BF_4^-$ (**16**; 87% total yield). A chlorobenzene solution of this mixture was kept at 65 °C for 1 h. Complete conversion to **16** occurred ((57 ± 2):(43 ± 2) *ac*/*sc*). Thus, this isomerization occurs much more readily than those in Schemes I and II, and the equilibrium constant is appreciably greater. Also, the *ac*/*sc* ratio is slightly higher, presumably due to steric interactions between the =CCH_3 group and the pentamethylcyclopentadienyl ligand in the *sc* isomer (see IV).

As shown in Scheme III, **14** or the **15**/**16** mixture was treated with *t*-BuO^-K^+ in THF. Workup gave the analytically pure parent acetylide complex **2** (91%) and the methylacetylide complex (η^5-$C_5(CH_3)_5$)Re(NO)(PPh_3)-(C≡CCH_3) (**17**, 81%), respectively. Spectroscopic properties of the new pentamethylcyclopentadienyl complexes **2** and **14**–**17** are summarized in Table I. In all cases, the IR ν_{NO} were significantly lower than those of the methylcyclopentadienyl and cyclopentadienyl analogs, reflecting the greater basicity of the pentamethylcyclopentadienyl ligand.[17] Also, the alkyne complexes **14** and **15** exhibited broadened or decoalesced PPh_3 ligand ^{13}C NMR resonances, consistent with the greater steric congestion in these compounds.[6b]

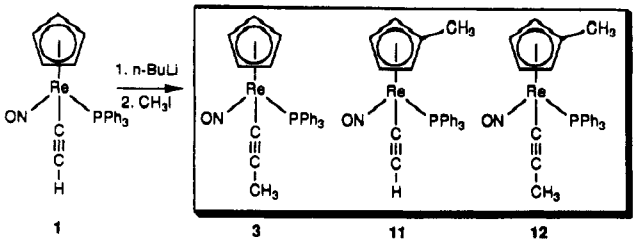
Maitlis has recently shown that the cyclopentadienyl methyl groups in the d^6 iridium complex (η^5-$C_5(CH_3)_5$)Ir-(CO)(C_6H_5)(CH_3), which is isoelectronic with **13**, can be sequentially lithiated and alkylated.[18] A similar transformation of **13** would provide a convenient route to *ethyl*tetramethylcyclopentadienyl homologs of **2** and **14**–**17**. Thus, THF solutions of **13** were treated with *n*-BuLi (1.0 equiv, −80 °C) and *t*-BuLi (2.0 equiv, −30 °C). No reactions were detected by ^{31}P NMR spectroscopy. Excesses of methyl iodide were added, and the samples were warmed to room temperature. Again, no reactions

(16) Patton, A. T.; Strouse, C. E.; Knobler, C. B.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5804.

(17) (a) Lichtenberger, D. L.; Kellogg, G. E. *Acc. Chem. Res.* **1987**, *20*, 379. (b) Elschenbroich, C.; Salzer, A. *Organometallics*; VCH: New York, 1989; p 47. (c) Sowa, J. R., Jr.; Angelici, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 2537. (d) Choi, M.-G.; Angelici, R. J. *Ibid.* **1991**, *113*, 5651.

(18) Miguel-Garcia, J. A.; Adams, H.; Bailey, N. A.; Maitlis, P. M. *J. Organomet. Chem.* **1991**, *413*, 427; *J. Chem. Soc., Dalton Trans.* **1992**, 131.

Chart II. Deprotonation and Methylation of the Terminal Acetylide Complex 1



Entry	Solvent	*n*-BuLi	CH_3I addn.	Yield (%)	Product Distribution (%) 1	3	11	12
1	THF	1.0 equiv. -80 °C, 1.5 h	0 °C	79	8	66	0	26
2	THF	1.5 equiv. -80 °C, 1.5 h	0 °C	89	0	46	0	54
3	THF	2.0 equiv. -80 °C, 1.5 h	0 °C	91	0	0	0	>99
4	1:1 THF/ hexane	1.0 equiv. 20 °C, 3 min	20 °C	71	10	80	0	10
5	1:1 THF/ hexane	2.0 equiv. 20 °C, 3 min	20 °C	53	0	8	0	92

were detected, and **13** was recovered from the first experiment in 89% yield.

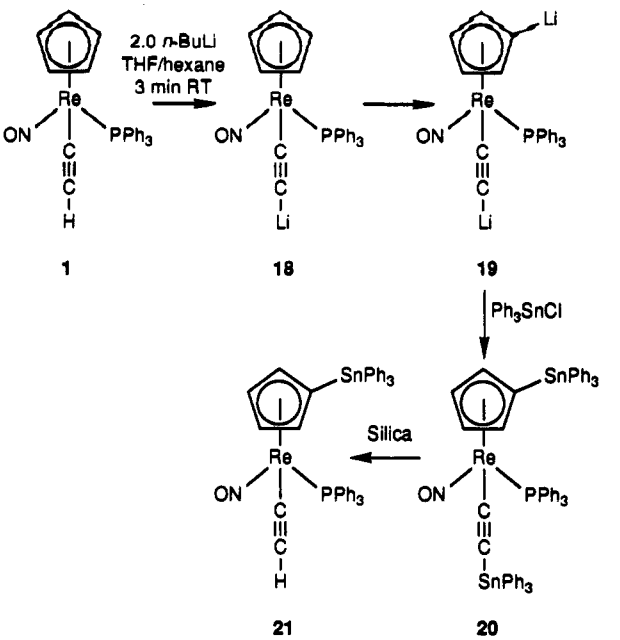
4. Deprotonation and Functionalization of 1. The cyclopentadienyl acetylide complex **1** was treated with freshly standardized *n*-BuLi (2–3 M in hexane) under a variety of conditions. Subsequently, excesses of methyl iodide were added (generally 6.0 equiv). Some representative experiments are summarized in Chart II. For example, **1** and *n*-BuLi (1.0 equiv) were combined in THF at −80 °C. The sample was warmed to 0 °C, and methyl iodide was added. Workup gave a 79% yield of a (8 ± 2):(66 ± 2):(26 ± 2) mixture of **1**, the desired methylacetylide complex **3**, and the dimethylated compound **12**, as assayed by ^{31}P NMR spectroscopy (entry 1, Chart II). Product identities were confirmed by ^{1}H NMR.

The formation of **3** was taken as evidence for the intermediacy of the target rhenium/lithium C_2 complex (η^5-C_5H_5)Re(NO)(PPh$_3$)(C≡CLi) (**18**). The absence of any methylcyclopentadienyl acetylide complex **11** suggested that competing lithiation of the cyclopentadienyl ligand to give (η^5-C_5H_4Li)Re(NO)(PPh$_3$)(C≡CH) did not occur.[19] However, we were unable to find conditions that eliminated the minor quantities of dimethylation product **12**. Although more intricate explanations remain possible, this was taken as evidence for a facile *second* lithiation of **18** to give (η^5-C_5H_4Li)Re(NO)(PPh$_3$)(C≡CLi) (**19**), as shown in Scheme IV. The best selectivity was achieved when *n*-BuLi and a THF/hexane solution of **1** were reacted for a 3-min period at 20 °C prior to methylation (entry 4, Chart II). A variety of other alkyllithium bases were investigated, but no improvements in selectivity were realized.

Complex **1** was similarly reacted with increasing amounts of *n*-BuLi (entries 2 and 3, Chart II). When 1.5 equiv of *n*-BuLi was utilized, subsequent methylation gave a ca. 50:50 mixture of **3** and **12**. When 2.0 equiv of *n*-BuLi was utilized, only **12** was isolated. This was taken as evidence for the essentially quantitative generation of the dilithio compound **19**.

(19) The reaction of (η^5-C_5H_5)Re(NO)(PPh$_3$)(C≡CD) (1-d_1, 58% labeled) with CH_3Li and then methyl iodide has been previously examined (D. Senn, Ph.D. Thesis, University of Utah, 1988). Complex **3** formed with deuterium at natural-abundance levels, as assayed by mass spectrometry. This eliminates more complex but precedented[3c,e] routes to **18** involving initial cyclopentadienyl ligand lithiation, followed by proton transfer.

Scheme IV. Synthesis of Lithiated and Stannylated Derivatives of 1



Spectroscopic data on the proposed intermediates were sought. Thus, NMR tubes were charged with THF/hexane solutions of **1**, and 1.0 and 2.0 equiv of *n*-BuLi was added. After 3 min at room temperature, the mixtures were cooled to −80 °C and ^{31}P NMR spectra recorded. The first sample exhibited a resonance at 21.4 ppm—identical with that of **1**. However, upon addition of methyl iodide (−80 °C), **3** (major) and **12** (minor) cleanly formed. The sample with 2.0 equiv of *n*-BuLi exhibited a very broad resonance at 24 ppm. Typically, downfield shifts of 3–5 ppm have been observed upon cyclopentadienyl ligand lithiation in (η^5-C_5H_5)Re(NO)(PPh$_3$)(X) compounds.[3] Addition of methyl iodide (room temperature) gave **12** (>95%). These data suggest that the monolithio compound **18** has nearly the same ^{31}P NMR chemical shift as **1**, whereas that of the dilithio compound **19** is ca. 3 ppm downfield.

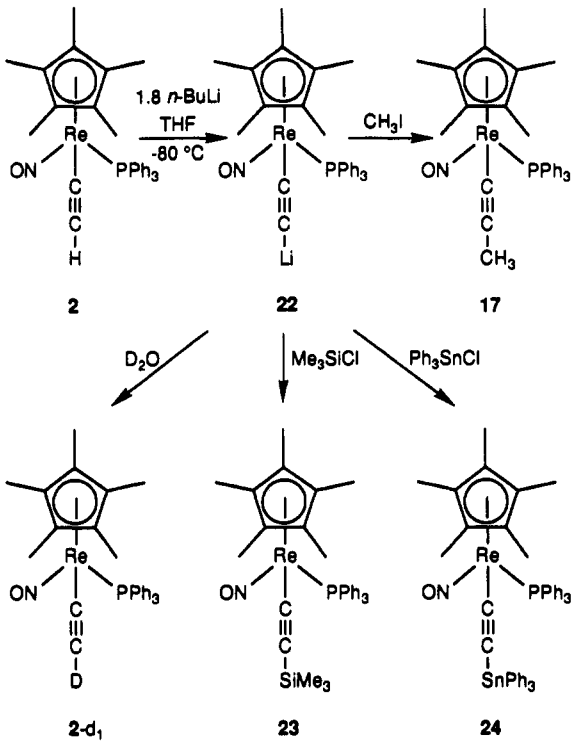
Since **1** could be cleanly dimethylated, additional bis derivatives were sought. Thus, **1** and *n*-BuLi (2.0 equiv) were reacted as in entry 5, Chart II. Then the tin electrophile Ph$_3$SnCl was added (Scheme IV). Workup gave the bis stannylated complex (η^5-C_5H_4SnPh$_3$)Re(NO)(PPh$_3$)(C≡CSnPh$_3$) (**20**) in 49% yield as an analytically pure, air-stable solid.[20] The structure of **20** followed from its mass spectrum (Experimental Section), and the NMR properties summarized in Table I. In particular, all cyclopentadienyl carbon resonances exhibited $J_{^{13}C^{119}Sn}$ satellites (21–45 Hz). Also, the ReC≡CSn carbon (C_α) gave a $^2J_{^{13}C^{119}Sn}$ value typical of tin acetylides (97.5 Hz),[21] and a $^2J_{^{13}C^{31}P}$ value characteristic for this series of rhenium complexes (15 Hz).[6] The ReC≡CSn carbon (C_β) gave a less intense resonance, and the $^1J_{^{13}C^{119}Sn}$ satellites (which should be 400–1000 Hz)[21] were not resolved.

During exploratory effects to purify **20**, silica gel chromatography was attempted. A new compound was isolated in 23% yield. The NMR properties (Table I) unambiguously showed this substance to be the stannylcyclopentadienyl acetylide complex (η^5-C_5H_4SnPh$_3$)Re(NO)(PPh$_3$)(C≡CH) (**21**, Scheme IV). Tin–carbon bonds are

(20) Reaction of **1**, *n*-BuLi, and Ph$_3$SnCl at −80 °C (analogous to entry 3 of Chart II) did not give an improved yield of **20**.

(21) Cauletti, C.; Furlani, C.; Sebald, A. *Gazz. Chim. Ital.* **1988**, *118*, 1.

Scheme V. Synthesis and Derivatization of the Rhenium/Lithium Dicarbide Complex 22



well-known to be susceptible toward hydrolysis,[22] and an initial C_β protonation of **20** would give a vinylidene complex that bears a partial positive charge on a carbon β to tin.

5. Deprotonation and Functionalization of 2. We sought to study terminal acetylide complexes that would not be as prone to competing acid/base processes involving auxiliary ligands. We thought that adding a cyclopentadienyl alkyl substituent to **1** might render the remaining cyclopentadienyl protons less acidic. However, exploratory experiments with the methylcyclopentadienyl acetylide complex **11** gave evidence for facile dilithiation. Hence, efforts were focused on the pentamethylcyclopentadienyl acetylide complex **2**. Although pentamethylcyclopentadienyl ligands have been deprotonated,[18] they appear to be much less acidic than cyclopentadienyl ligands where reasonable comparisons exist.[3a,c]

Thus, **2** and *n*-BuLi (1.8 equiv) were reacted in THF at −80 °C. After 1.5 h, methyl iodide (10 equiv) was added (Scheme V). Workup gave the methyl acetylide complex **17** in 95% yield. A comparable experiment was conducted with *n*-BuLi and D_2O. Workup gave the deuterated acetylide complex (η^5-$C_5(CH_3)_5$)Re(NO)(PPh_3)(C≡CD) (**2-d_1**) in 88% yield. A mass spectrum showed the sample to be 86% labeled, and the $^+PPh_3$ ion contained deuterium at natural-abundance levels. A ^1H NMR spectrum showed only a small residual ≡CH resonance, and integration versus either the *o*-PPh_3 or pentamethylcyclopentadienyl resonances indicated 89% deuteration.

Similar reactions were conducted with $(CH_3)_3SiCl$ and Ph_3SnCl (1.6–2.6 equiv, Scheme V). Workup gave the analytically pure rhenium/group 14 C_2 derivatives (η^5-$C_5(CH_3)_5$)Re(NO)(PPh_3)(C≡CSi$(CH_3)_3$) (**23**, 86%) and (η^5-$C_5(CH_3)_5$)Re(NO)(PPh_3)(C≡CSnPh_3) (**24**, 45%), respectively. Both compounds exhibited mass spectral parent ions and were stable for days in air as solids. The ^{13}C NMR properties of the ReC≡CSn linkage in **24** (Table I) were similar to those noted for **20** above. Interestingly, the ReC≡C (C_α) resonances of **20** and **24** (122–138 ppm) were considerably downfield from those of the other acetylide complexes (77–98 ppm). Similar deshielding has been found in organic tin acetylides.[21]

The preceding data suggested that the pentamethylcyclopentadienyl rhenium/lithium C_2 complex (η^5-$C_5(CH_3)_5$)Re(NO)(PPh_3)(C≡CLi) (**22**) was cleanly generated under the conditions of Scheme V. In order to check for the possibility of initial deprotonation at the pentamethylcyclopentadienyl or PPh_3 ligands, **2-d_1** prepared above was treated with *n*-BuLi and then methyl iodide. The resulting methylacetylide complex **17** (86%) contained deuterium at natural-abundance levels, as assayed by mass spectrometry. Hence, **22** must be the kinetic deprotonation product.

Finally, reactions of **2** and *n*-BuLi were monitored by ^{31}P NMR spectroscopy at −80 °C. Complex spectra, consisting of a broad hump at 23.4 ppm, a cluster of four peaks at 22.4–21.8 ppm, and a resonance close to that of **2** (21.2 ppm), were reproducibly obtained. Methyl iodide was added, and spectra were recorded after 20 min. In all cases, **17** cleanly formed (21.6 ppm), accompanied only by small amounts of **2**. Broad and/or multiple ^{31}P NMR resonances—possibly arising from different aggregates—have sometimes been observed with other lithiated (η^5-C_5H_5)Re(NO)(PPh_3)(X) complexes.[3]

Discussion

1. Acid/Base Properties of Rhenium Acetylide Complexes. The results in Schemes IV and V, together with supporting deuterium labeling experiments, provide the first demonstration of the viability of generalized eq i. However, several problems complicate the acquisition of quantitative acidity data for **1** and **2**. For example, the ^{31}P NMR resonances of **1** and the conjugate base **18**, which are potentially convenient probes of equilibrium, appear to be degenerate. Also, the conjugate base of **2** is spectroscopically inhomogeneous.

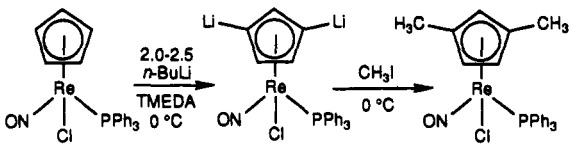
However, other data provide very rough limits on the pK_a values of **1** and **2**. For example, the cyclopentadienyl protons of methyl complex **4** (Scheme I) have a pK_a per hydrogen (THF) of ca. 35.9 based upon equilibria with lithium diisopropylamide.[3c] The cyclopentadienyl protons in **1** are probably slightly more acidic due to the enhanced electronegativity of the alkynyl substituents.[4,23] From the absence of any detectable amount of methylcyclopentadienyl complex **11** among the products in Chart II, it is furthermore likely that the cyclopentadienyl protons in **1** are at least 1 pK_a unit *less* acidic than the acetylide proton. Thus, a conservative upper bound on the pK_a (THF) of the acetylide proton in **1** would be 34.

The rhenium fragment [(η^5-C_5H_5)Re(NO)(PPh_3)]$^+$ (**I**) is both electropositive and a strong π donor.[6,12] Accordingly, **I** has previously been shown to *destabilize* an α-carbanion relative to a proton.[3e] Thus, the pK_a of acetylene (21.7, H_2O)[4] provides a conservative lower bound for that of **1**. We suggest that in actuality, the pK_a(THF) of **1** is approximately halfway between the boundary values of 34 and 22. That of the more electron-rich[17] pentamethylcyclopentadienyl complex **2** should be slightly greater.

(22) Davies, A. G.; Smith, P. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 2, pp 536–542.

(23) As would be expected, the reaction of methyl acetylide complex **3** and CH_3Li gives the lithiocyclopentadienyl complex (η^5-C_5H_4Li)Re(NO)(PPh_3)(C≡CCH_3), as assayed by ^{31}P NMR and subsequent reaction with methyl iodide to give **12**. F. Agbossou, unpublished results, University of Utah, 1989.

Under the conditions in Chart II, the rate of the second lithiation of **1** appears to be quite close to that of the first. Although the dilithio compound **19** may have utility for the synthesis of polymeric materials, milder bases can potentially give greater selectivity for the precursor **18**. However, exploratory reactions with lithium dialkylamides gave less tractable chemistry. Interestingly, the dilithiation of (η^5-C_5H_5)Re(NO)(PPh_3)(X) compounds has precedent. As shown in eq ii, the chloride complex (η^5-C_5H_5)Re-



(ii)

(NO)(PPh_3)(Cl) cleanly reacts with 2.0–2.5 equiv of *n*-BuLi/TMEDA to give (η^5-1,3-$C_5H_3Li_2$)Re(NO)(PPh_3)(Cl), as assayed by ^{31}P NMR and subsequent trapping as the 1,3-dimethylcyclopentadienyl complex (η^5-1,3-C_5H_3-$(CH_3)_2$)Re(NO)(PPh_3)(Cl) (63%).[3b]

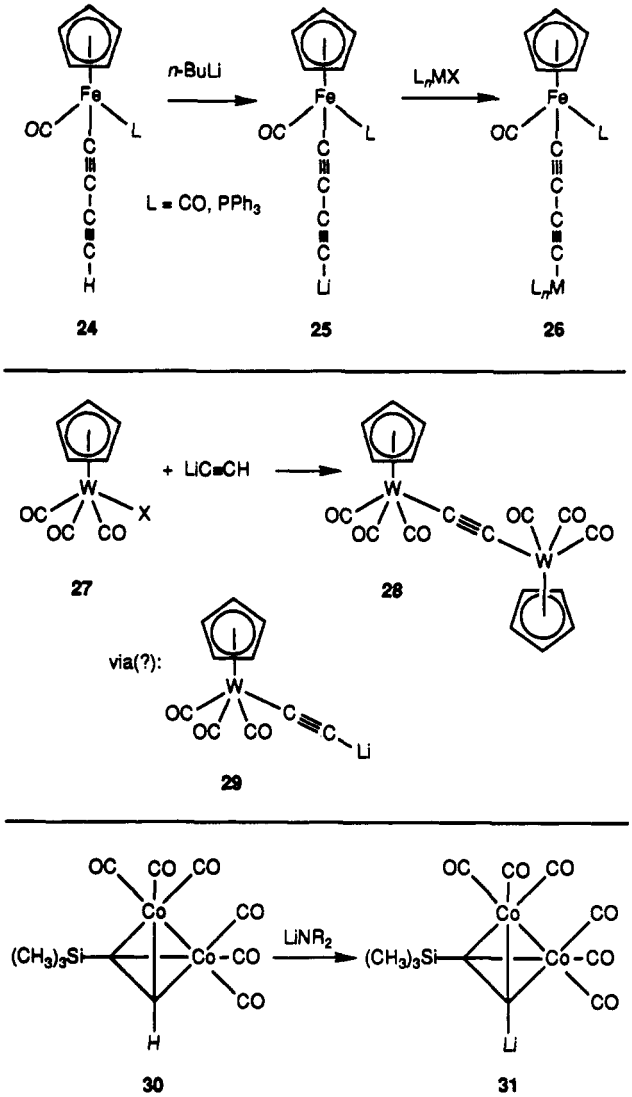
Acetylide complexes such as **3** are readily protonated by HBF_4·OEt_2 or triflic acid to cationic vinylidene complexes.[6] As shown in Schemes I–III, these conjugate acids can equilibrate with the corresponding π terminal alkyne complexes. Additional examples are given elsewhere.[6b] Significantly, the rates of isomerization of propyne complexes **5**, **9**, and **15**—and the methylvinylidene/propyne equilibrium ratios—become progressively greater as the number of methyl groups on the cyclopentadienyl ligand increases.

These trends follow logically from both electronic and steric considerations. First, vinylidene ligands are stronger π acceptors than alkynes,[24] and the π basicity of the rhenium fragment is increased by methyl substitution on the cyclopentadienyl ligand.[17] Second, vinylidene ligands are monohapto (η^1), whereas alkyne ligands are dihapto (η^2). Thus, *two* carbons are held close to the congested rhenium center in the latter, and in a conformation (II, Chart I) that directs one ≡CR substituent at the bulky PPh_3 ligand.[6b] Consistent with this rationale, the smaller acetylene ligands in **8** and **14** are much less prone to isomerization than the propyne ligands in **9** and **15**. Analogous trends have been documented with ruthenium alkyne complexes of the formula [(η^5-C_5H_5)Ru(PRR'_2)$_2$(R″C≡CH)]$^+X^-$.[13a,b]

2. Lithiocarbon Complexes and Derivatives. Intermediates **18**, **19**, and **22** constitute members of a very rare class of substances—lithiocarbon complexes, or compounds that contain ligands of the formula C_xLi_y. Many lithiated organic molecules exhibit unusual solid-state structures.[25] Thus, lithiocarbon complexes have considerable promise for novel and unprecedented bonding modes. Accordingly, attempts to isolate and crystallize species such as **18**, **19**, and **22** are in progress.

To our knowledge, the only previous well-documented examples of lithiocarbon complex intermediates have been reported by Wong.[26] In pioneering work, he reacted iron complexes of the formula (η^5-C_5H_5)Fe(CO)(L)(C≡CC≡CH) (**24**) and *n*-BuLi as shown in Scheme VI. The C_4Li complexes (η^5-C_5H_5)Fe(CO)(L)(C≡CC≡CLi) (**25**) subsequently formed, as assayed by reactions with transition-metal electrophiles to give a variety of bimetallic C_4 or

Scheme VI. Generation of Other Lithiocarbon Complexes



tetracarbide derivatives (η^5-C_5H_5)Fe(CO)(L)(C≡CC≡C)-ML_n (**26**).

Other reactions that may involve lithiocarbon complexes have been described.[27] For example, reactions of tungsten halide complexes (η^5-C_5H_5)$W(CO)_3$(X) (**27**) and LiC≡CH give the ditungsten C_2 complex (η^5-C_5H_5)$(CO)_3$W(C≡C)-$W(CO)_3$(η^5-C_5H_5) (**28**, Scheme VI).[28] This transformation requires a proton-transfer step either prior to or following initial tungsten–carbon bond formation. Both pathways would likely proceed via the intermediate tungsten/lithium C_2 complex (η^5-C_5H_5)$W(CO)_3$(C≡CLi) (**29**).

Some deprotonations of other complexes with CCH linkages also merit note. For example, Magnus found that the dicobalt terminal μ-alkyne complex **30** can be converted to the lithiated derivative **31** (Scheme VI).[29] Chisholm has described reactions of platinum terminal acetylide complexes with tungsten alkoxides that result

(24) Kostić, N. M.; Fenske, R. F. *Organometallics* **1982**, *1*, 974.

(25) (a) Apeloig, Y.; Schleyer, P. v. R.; Binkley, J. S.; Pople, J. A.; Jorgensen, W. L. *Tetrahedron Lett.* **1976**, *43*, 3923. (b) Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353. (d) Maercker, A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 584.

(26) Wong, A.; Kang, P. C. W.; Tagge, C. D.; Leon, D. R. *Organometallics* **1990**, *9*, 1992.

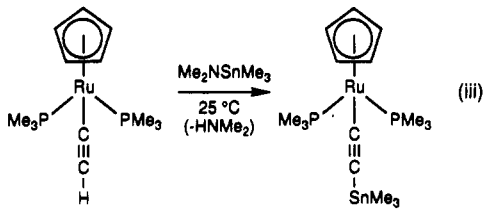
(27) (a) Ferrocene can be lithiated up to seven times. However, the generation of a C_5Li_5 ligand (as opposed to $C_5Li_{5-x}H_x$ ligands) has not been verified: Halasa, A. F.; Tate, D. P. *J. Organomet. Chem.* **1970**, *24*, 769. (b) Transformations that may involve $Li^+[(\eta^5\text{-}C_5H_5)Mn(CO)_2(C{\equiv}CLi)]^-$: Berke, H. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1980**, *35*, 86.

(28) Ustynyuk, N. A.; Vinogradova, V. N.; Krautsov, D. N.; Oprunenko, Yu. F.; Piven, V. A. *Metallorg. Khim.* **1988**, *1*, 884; *Chem. Abstr.* **1989**, *111*, 233074c.

(29) Magnus, P.; Becker, D. P. *J. Chem. Soc., Chem. Commun.* **1985**, 640.

in ≡CH bond cleavage and the formation of heterobimetallic σ,π C_2 adducts.[30]

Only a few other complexes in which an unsupported C_2 linkage spans a main-group metal and a transition metal appear to have been previously reported. For example, Bullock has recently characterized the ruthenium/stannyl complex **32** shown in eq iii.[8b] His synthesis features a



(iii)

32

facile ≡CH bond cleavage by a tin-substituted amine. Also, unpublished platinum/stannyl C_2 complexes have been cited in a review.[21] Organic tin acetylides have been shown to be useful precursors to transition-metal acetylide complexes.[21] Thus, stannylated complexes such as **20** and **24**, both of which exhibit good air stability, may prove to be versatile synthons for bimetallic C_2 complexes.

In conclusion, we have established that transition-metal terminal acetylide complexes, $L_nMC{\equiv}CH$, can be deprotonated in a manner analogous to organic terminal acetylenes (eq i). Although the pK_a values appear somewhat higher than for organic analogs, there is no obvious reason why this transformation should not have considerable generality. The conjugate bases can be derivatized by organic and inorganic electrophiles in high yields. In particular, they are useful building blocks for novel heterobimetallic C_2 complexes,[10b] as well as other unusual types of organometallic compounds that will be reported in the near future.

Experimental Section

General Data. All reactions were carried out under a dry N_2 atmosphere. IR spectra were recorded on a Mattson Polaris FT spectrometer. NMR spectra were recorded on Varian XL-300 spectrometers as outlined in Table I. Mass spectra were obtained on VG 7050E (EI) and Finnigan MAT 95 (FAB) high-resolution instruments. Microanalyses were conducted by Atlantic Microlab. Melting points were determined in evacuated capillaries using a calibrated thermometer.[31]

Solvents and reagents were purified as follows: C_6H_5Cl, distilled from P_2O_5; CH_2Cl_2, distilled from CaH_2; ether, THF, hexane, and benzene, distilled from Na/benzophenone; $CDCl_3$ and CD_2Cl_2, vacuum-transferred from CaH_2; C_6D_6, vacuum-transferred from $LiAlH_4$; acetylene (Matheson, ≥99.6%) and propyne (Farchan, Matheson), passed through Drierite; $(CH_3)_3SiCl$ (Aldrich), dried over 4A molecular sieves and distilled; *n*-BuLi and $HBF_4{\cdot}OEt_2$ (Aldrich), standardized[32,33] before use. Other reagents and solvents were used as received from commercial suppliers.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(HC{\equiv}CCH_3)]^+BF_4^-$ (5). A Schlenk tube was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**4**,[34] 0.152 g, 0.272 mmol), C_6H_5Cl (5 mL), and a stir bar, capped with a septum, and cooled to −45 °C (acetonitrile/liquid N_2). Then $HBF_4{\cdot}OEt_2$ (48 μL, 0.51 mmol) was added with stirring. After 10 min, propyne (ca. 1 mL) was condensed into the solution, and the septum was replaced by a stopper that was securely wired to the Schlenk tube. The mixture was stirred for 6 days at room temperature, and the solvent was removed under oil pump vacuum. The residue was dissolved in CH_2Cl_2 (5 mL), and the solution was added dropwise to rapidly stirred ether (75 mL). The resulting light tan powder was collected by filtration and dried under oil pump vacuum to give **5** (0.155 g, 0.231 mmol, 85%), mp 103–108 °C dec.

$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C{\equiv}CCH_3)$ (3). A Schlenk flask was charged with **5** (0.075 g, 0.112 mmol), *t*-BuO^-K^+ (0.019 g, 0.17 mmol), and a stir bar and cooled to −80 °C. Then THF (5 mL) was added with stirring. After 20 min, the cooling bath was removed. After an additional 1 h, solvent was removed under oil pump vacuum. The residue was extracted with benzene (3 × 3 mL), and the extract was filtered through Celite. Solvent was removed from the filtrate under oil pump vacuum to give previously characterized[6a] **3** as an orange foam (0.061 g, 0.105 mmol, 94%), which was pure by ^1H and ^{31}P NMR spectroscopy.

$[(\eta^5\text{-}C_5H_4CH_3)Re(NO)(PPh_3)(HC{\equiv}CH)]^+BF_4^-$ (8). Complex $(\eta^5\text{-}C_5H_4CH_3)Re(NO)(PPh_3)(CH_3)$ (**7**,[14] 0.0642 g, 0.112 mmol), C_6H_5Cl (5 mL), and $HBF_4{\cdot}OEt_2$ (20 μL, 0.21 mmol) were reacted in a procedure analogous to that given for **5**. Acetylene was then bubbled through the −45 °C mixture. After 10 min, the tube was transferred to a 90 ± 5 °C oil bath. After 30 min, the acetylene stream was halted. The tube was removed from the bath and allowed to cool to room temperature. The solvent was removed under oil pump vacuum, and the residue dissolved in a minimum of CH_2Cl_2. The sample was filtered through a medium frit into rapidly stirred ether (75 mL). The resulting cream precipitate was collected by filtration, washed with ether, and dried under oil pump vacuum to give **8** as an off-white powder (0.0593 g, 0.088 mmol, 79%), mp 198–202 °C dec. Anal. Calcd for $C_{26}H_{24}BF_4NOPRe$: C, 46.58; H, 3.61. Found: C, 46.53; H, 3.59.

$[(\eta^5\text{-}C_5H_4CH_3)Re(NO)(PPh_3)(HC{\equiv}CCH_3)]^+BF_4^-$ (9). Complex **7** (0.0946 g, 0.165 mmol), C_6H_5Cl (6 mL), $HBF_4{\cdot}OEt_2$ (30 μL, 0.30 mmol), and propyne (ca. 1 mL) were reacted in a procedure analogous to that given for **5**. An identical workup gave **9** as a pale tan powder (0.0940 g, 0.137 mmol, 83%), mp 103–110 °C. Anal. Calcd for $C_{27}H_{26}BF_4NOPRe$: C, 47.38; H, 3.83. Found: C, 47.16; H, 3.87.

$(\eta^5\text{-}C_5H_4CH_3)Re(NO)(PPh_3)(C{\equiv}CH)$ (11). A Schlenk tube was charged with **8** (0.0381 g, 0.057 mmol), THF (5 mL), and a stir bar and cooled to −80 °C. Then *t*-BuO^-K^+ (85 μL, 1.0 M in THF) was added. After 20 min, the cooling bath was removed, and the mixture was stirred overnight. Solvent was removed under oil pump vacuum. The residue was extracted with benzene (2 × 5 mL), and the extract was filtered through Celite. Solvent was removed from the filtrate under oil pump vacuum. The resulting orange oil was dissolved in CH_2Cl_2, and hexane was added. Solvent was removed by rotary evaporation and then oil pump vacuum to give **11** as a bright orange powder (0.0302 g, 0.052 mmol, 91%), mp 162–165 °C dec. Anal. Calcd for $C_{26}H_{23}NOPRe$: C, 53.59; H, 3.98. Found: C, 53.67; H, 4.02.

$(\eta^5\text{-}C_5H_4CH_3)Re(NO)(PPh_3)(C{\equiv}CCH_3)$ (12). Complex **9** (0.106 g, 0.155 mmol), *t*-BuO^-K^+ (0.026 g, 0.23 mmol), and THF (6 mL) were combined in a procedure analogous to that given for **3**. A workup identical to that used for **11** gave **12** as an orange powder (0.075 g, 0.126 mmol, 81%), mp 144–147 °C dec. Anal. Calcd for $C_{27}H_{25}NOPRe$: C, 54.35; H, 4.22. Found: C, 54.45; H, 4.25.

$[(\eta^5\text{-}C_5(CH_3)_5)Re(NO)(PPh_3)(HC{\equiv}CH)]^+BF_4^-$ (14). Complex $(\eta^5\text{-}C_5(CH_3)_5)Re(NO)(PPh_3)(CH_3)$ (**13**,[16] 0.190 g, 0.302 mmol), C_6H_5Cl (8 mL), $HBF_4{\cdot}OEt_2$ (50 μL, 1.1 equiv, 33 mmol), and acetylene were reacted in a procedure analogous to that given for **8** (maximum oil bath temperature 85 °C). The mixture was filtered under N_2 into rapidly stirred ether (50 mL). The resulting cream precipitate quickly gummed. The solvent was decanted, and an oil pump vacuum was applied. This gave **14** as a pale gray foam (0.158 g, 0.217 mmol, 72%), mp 110–115 °C dec. Anal. Calcd for $C_{30}H_{32}NOPReBF_4$: C, 49.59; H, 4.44. Found: C, 49.49; H, 4.41.

$[(\eta^5\text{-}C_5(CH_3)_5)Re(NO)(PPh_3)(HC{\equiv}CCH_3)]^+BF_4^-$ (15). Complex **13** (0.100 g, 0.159 mmol), C_6H_5Cl (5 mL), $HBF_4{\cdot}OEt_2$ (34 μL, 0.21 mmol), and propyne (ca. 1.5 mL) were reacted in a procedure analogous to that given for **9**. Solvent was removed under oil pump vacuum, and the residue was dissolved in THF (4 mL). The solution was transferred via cannula into rapidly

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stirred hexane (50 mL). The resulting white precipitate quickly gummed. The solvent was decanted, and an oil pump vacuum was applied. This gave **15** as a pale tan foam (0.102 g, 0.138 mmol, 87%), mp 105–117 °C dec, for which carbon analyses were ca. 1.6% low.

(η^5-$C_5(CH_3)_5$)Re(NO)(PPh_3)(C≡CH) (2). Complex **14** (0.112 g, 0.154 mmol), *t*-BuO^- K^+ (0.022 g, 0.20 mmol), and THF (5 mL) were combined in a procedure analogous to that given for **3**. The mixture was stirred at room temperature overnight. The solvent was removed under oil pump vacuum, and the residue was extracted with benzene (2 × 2 mL, 1 × 4 mL). The extracts were sequentially filtered through Celite (2 cm). Solvent was removed from the filtrate under oil pump vacuum. The residue was dissolved in CH_2Cl_2 (1 mL), and hexane (5 mL) was added. Solvent was removed by rotary evaporation and then oil pump vacuum to give **2** as an orange powder (0.087 g, 0.136 mmol, 88%), mp 212–216 °C. Anal. Calcd for $C_{30}H_{31}NOPRe$: C, 56.41; H, 4.89. Found: C, 56.32; H, 4.91. In similar experiments, the CH_2Cl_2/hexane solution was stored at −20 °C for 14 h. Orange needles of **2** were subsequently isolated in ca. 90% yields.

(η^5-$C_5(CH_3)_5$)Re(NO)(PPh_3)(C≡CCH_3) (17). Complexes **15**/**16** (0.0761 g, 0.103 mmol), *t*-BuO^- K^+ (0.015 g, 0.13 mmol), and THF (5 mL) were combined in a procedure analogous to that given for **2**. An identical workup gave **17** as an orange powder (0.0539 g, 0.083 mmol, 81%), mp 58–62 °C dec. Anal. Calcd for $C_{31}H_{33}NOPRe$: C, 57.04; H, 5.10. Found: C, 57.10; H, 5.11.

Conversion of (η^5-C_5H_5)Re(NO)(PPh_3)(C≡CH) (1) to 3. A Schlenk tube was charged with **1** (0.057 g, 0.100 mmol),[6b] THF (2.5 mL), hexane (2.5 mL), and a stir bar at room temperature. Then *n*-BuLi (33 μL, 3.01 M in hexane) was added with stirring. After 3 min, CH_3I (33 μL, 0.53 mmol) was added. After 10 min, solvent was removed under oil pump vacuum. The residue was extracted with benzene (3 mL). Hexane (6 mL) was added, and the sample was filtered through a fine frit. The solvent was removed under oil pump vacuum. The resulting orange oil was dissolved in CH_2Cl_2, and hexane was added. Solvent was removed by rotary evaporation and then oil pump vacuum to give a bright orange powder (0.0411 g, ca. 0.071 mmol, 71%). Composition: Chart II, entry 4.

Conversion of 1 to 12. Complex **1** (0.057 g, 0.100 mmol), THF (2.5 mL), hexane (2.5 mL), *n*-BuLi (86 μL, 2.36 M in hexane) and CH_3I (80 μL, 1.3 mmol) were combined in a procedure analogous to the preceding one. An identical workup gave an orange powder (0.0335 g, ca. 0.056 mmol, 55%). Composition: Chart II, entry 5.

(η^5-$C_5H_4SnPh_3$)Re(NO)(PPh_3)(C≡C$SnPh_3$) (20). Complex **1** (0.0198 g, 0.0347 mmol), THF (2 mL), hexane (2 mL), and *n*-BuLi (35 μL, 2.05 M in hexane) were combined in a procedure analogous to that for converting **1** to **12**. Then Ph_3SnCl (0.035 g, 0.091 mmol) was added. After 1.5 h, solvent was removed under oil pump vacuum. The residue was extracted with refluxing hexane (15 mL). The extract was filtered through a medium frit and cooled to −20 °C. After 2 h, the resulting yellow powder was collected by filtration and dried under oil pump vacuum to give **20** (0.021 g, 0.017 mmol, 49%), mp 92–101 °C. Anal. Calcd for $C_{61}H_{49}NOPReSn_2$: C, 57.84; H, 3.90. Found: C, 57.67; H, 4.16. Mass spectrum (positive Cs-FAB (20 kV, tetraglyme/toluene), *m*/*z* (maximum of isotope distribution, relative intensity)): 1266 (20^+, 100%), 1188 ($20^+ - C_6H_6$, 25%), 918 ($20^+ - SnPh_3$, 45%), 840 ($20^+ - SnPh_3 - C_6H_6$, 13%).

(η^5-$C_5H_4SnPh_3$)Re(NO)(PPh_3)(C≡CH) (21). Complex **1** (0.130 g, 0.229 mmol), THF (2 mL), hexane (2 mL), *n*-BuLi (230 μL, 2.05 M in hexane), and Ph_3SnCl (0.197 g, 0.511 mmol) were combined in a procedure analogous to that given for **20**. After 10 min, solvent was removed under oil pump vacuum. The residue was dissolved in a minimum of CH_2Cl_2 (ca. 1.5 mL), and hexane (15 mL) was added. The solution was eluted with hexane through a silica column that had been pretreated with $(Me_3Si)_2NH$. Solvent was removed from the orange band under oil pump vacuum to give **21** as an orange powder (0.0484 g, 0.053 mmol, 23%), mp 102–106 °C. Anal. Calcd for $C_{43}H_{35}NOPReSn$: C, 56.28; H, 3.84. Found: C, 56.43; H, 3.91.

Conversion of 2 to 17. A Schlenk flask was charged with **2** (0.0403 g, 0.063 mmol), THF (3 mL), and a stir bar and was cooled to −80 °C. Then *n*-BuLi (50 μL, 2.2 M in hexane) was added with stirring. After 1.5 h, CH_3I (40 μL, 0.64 mmol) was added, and the cooling bath was removed. After 1 h, solvent was removed under oil pump vacuum. The residue was extracted with benzene (3 × 2.5 mL), and the extract was filtered through Celite (4 cm). The solvent was removed from the filtrate under oil pump vacuum. The residue was dissolved in CH_2Cl_2 (1 mL), and hexane (10 mL) was added. The solvent was removed by rotary evaporation and then oil pump vacuum to give **17** as a red powder (0.039 g, 0.060 mmol, 95%), which was pure by ^1H and ^{31}P NMR spectroscopy.

(η^5-$C_5(CH_3)_5$)Re(NO)(PPh_3)(C≡C$Si(CH_3)_3$) (23). Complex **2** (0.0638 g, 0.100 mmol), THF (5 mL), *n*-BuLi (65 μL, 2.46 M in hexane), and $(CH_3)_3SiCl$ (20 μL, 0.16 mmol) were combined in a procedure analogous to that for converting **2** to **17**. The residue was extracted with hexanes (2 × 10 mL), and the extracts were passed through a medium-frit Kramer filter. The resulting orange solution was concentrated to ca. 2 mL and kept at −20 °C for 48 h. The supernatant was decanted from the resulting orange crystals, which were dried under oil pump vacuum to give **23** (0.0611 g, 0.086 mmol, 86%), mp 168–170 °C. Anal. Calcd for $C_{33}H_{39}NOPSiRe$: C, 55.75; H, 5.53. Found: C, 55.52; H, 5.60. Mass spectrum (positive Cs-FAB (20 kV, tetraglyme/toluene), *m*/*z* (^{187}Re, relative intensity)): 711 (23^+, 51%), 710 (23^+ − H, 100%).

(η^5-$C_5(CH_3)_5$)Re(NO)(PPh_3)(C≡C$SnPh_3$) (24). Complex **2** (0.0652 g, 0.102 mmol), THF (4.5 mL), *n*-BuLi (82 μL, 2.2 M in hexane), and Ph_3SnCl (0.100 g, 0.259 mmol) were reacted in a procedure analogous to that for converting **2** to **17**. The residue was extracted with hexane (20 mL). The extract was filtered and cooled to −80 °C. The resulting orange powder was collected by filtration (medium frit) at −80 °C and dried under oil pump vacuum to give **24** (0.0452 g, 0.046 mmol, 45%), mp 82–87 °C. Anal. Calcd for $C_{48}H_{45}NOPSnRe$: C, 58.37; H, 4.59. Found: C, 58.28; H, 4.61. Mass spectrum (positive Cs-FAB (20 kV, tetraglyme/toluene), *m*/*z* (maximum of isotope distribution, relative intensity)): 987 (24^+, 37%), 909 ($24^+ - C_6H_6$, 4%), 640 ($24^+ - SnPh_3$, 23%).

Deuterium Labeling Experiments. A. Complex **2** (0.032 g, 0.050 mmol), THF (3 mL), *n*-BuLi (32 μL, 2.46 M in hexane), and D_2O (99.9%, 15 μL, 0.75 mmol) were combined in a procedure analogous to that for converting **2** to **17**. The residue was extracted with 5:1 hexane/THF (v/v, 2 × 5 mL). The extract was filtered through an oven-dried medium frit. The solvent was removed from the filtrate under oil pump vacuum. The residue was dissolved in CH_2Cl_2 (0.5 mL), and hexane (10 mL) was added. After 14 h, the resulting orange needles were collected by filtration and dried under oil pump vacuum to give (η^5-$C_5(CH_3)_5$)Re(NO)(PPh_3)(C≡CD) (**2**-d_1, 0.028 g, 0.044 mmol, 88%). Mass spectra (EI, 17 eV; *m*/*z* (relative intensity)): 637/638/639/640/641 (13/61/39/100/31); for the reactant **2** 636/637/638/639/640 (4/60/25/100/32). The program "Matrix" (D. A. Chrisope, IBM) calculated a 86:14 **2**-d_1:**2** ratio from these data.

B. The preceding sample of **2**-d_1 was converted to **17**-d_n by a procedure analogous to that given for the unlabeled substrate above. A similar mass spectral analysis showed the **17**-d_n to be deuterated at the natural abundance level.

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