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Hydrogen Shift Reactions of Rhenium Hydrido Carbyne Complexes

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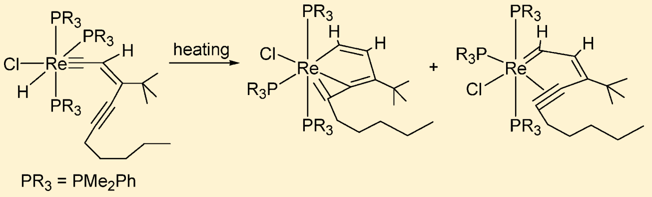
Supporting Information



ABSTRACT: Rhenium hydrido carbyne complexes Re(≡CCH=C(CMe$_3$)C≡CR)HCl(PMe$_2$Ph)$_3$ (R = H, *n*-pentyl) undergo 1,2-hydrogen shift reactions from the metal to the carbyne carbon atom to give complexes Re(HCCHC(CMe$_3$)CCR)HCl(PMe$_2$Ph)$_3$, which have two isomeric forms, namely, a metallabicyclo[3.1.0]hexatriene complex, in which the chloride is cis to the metal-bonded CH, and an alkyne−carbene complex, in which the chloride is trans to the metal-bonded CH. In contrast, a similar transformation does not occur for the analogous complex Re(≡CCH=C(CMe$_3$)C≡CSiMe$_3$)HCl(PMe$_2$Ph)$_3$, which has a SiMe$_3$ group on the C≡C moiety. A computational study suggests that the difference in the reactivity of the hydrido carbyne complexes is related to steric effects in the corresponding hydride-shift products. Formation of Re(HCCHC(CMe$_3$)CCSiMe$_3$)HCl(PMe$_2$Ph)$_3$ is not favored, mainly due to the steric interactions of the SiMe$_3$ group with CMe$_3$ and one of the phosphine ligands in the resulting metallabicyclo[3.1.0]hexatriene complex, and of the SiMe$_3$ group with the chloride ligand in the resulting alkyne−carbene complex.

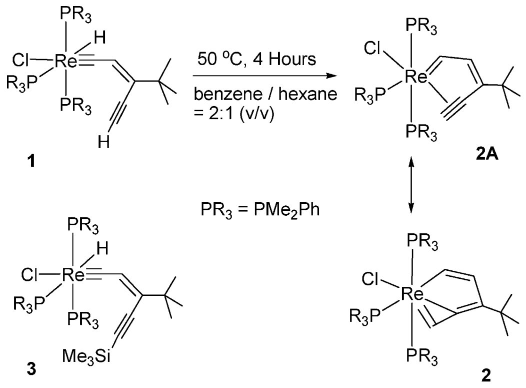
INTRODUCTION

1,2-Hydrogen shift from the metal to the carbyne carbon atom in hydrido carbyne complexes L$_n$M(H)≡CR to give carbene complexes L$_n$M=CHR is one of the important chemical properties of carbyne complexes.[1] Such a transformation is now well documented for carbyne complexes of ruthenium,[2] osmium,[3] and tungsten.[4] It has been demonstrated that the coligands can have a significant influence on the 1,2-hydrogen shift reactions. For example, the barriers for the hydrogen shift reactions of [OsH(≡CCH=CH$_2$)(CH$_3$CN)$_2$(PH$_3$)$_2$]$^{2+}$ and OsHCl$_2$(≡CCH=CH$_2$)(PH$_3$)$_2$ were calculated to be 19.4 and 26.3 kcal/mol, respectively.[3c]

Although there has been much interest in the chemistry of rhenium carbyne complexes,[5−10] and stable rhenium hydrido carbyne complexes, such as ReH(≡CCH$_3$)(η^2-CH$_2$=CH$_2$)(PNP) (PNP = N(SiMe$_2$CH$_2$PCy$_2$)$_2$),[11] [ReH$_2$(≡CCH$_2$R)(mq)(PPh$_3$)$_2$]PF$_6$, and ReH(≡CCH$_2$R)(mq)(PPh$_3$)$_2$ (mq = the anion of 2-mercaptoquinoline),[12] have been isolated; a 1,2-hydrogen shift from the metal to the carbyne carbon atom has been rarely observed for rhenium carbyne complexes.

We have recently reported that the hydrido carbyne complex Re(≡CCH=C(CMe$_3$)C≡CH)HCl(PMe$_2$Ph)$_3$ (**1**) can undergo 1,2-hydrogen shift from the metal to the carbyne carbon atom to give complex Re(HCCHC(CMe$_3$)CCH)HCl(PMe$_2$Ph)$_3$ (**2**), the structure of which can be best described as a hybrid of the resonance forms **2** (metallabicylohexatriene) and **2A** (alkyne−carbene complex) with **2** being dominant (Scheme 1).[13] In contrast, a similar transformation does not occur for the analogous complex Re(≡CCH=C(CMe$_3$)C≡CSiMe$_3$)HCl(PMe$_2$Ph)$_3$ (**3**), which has a SiMe$_3$ group on the C≡C moiety even when it was heated at 60 °C for 2 days in benzene, hexane, or THF. The results suggest that the substituent R on the C≡C moiety can have a significant effect on the 1,2-hydrogen shift reactions of hydrido carbyne complexes of the type Re(≡CCH=C(CMe$_3$)C≡CR)HCl(PMe$_2$Ph)$_3$. To further study the substituent effect on the hydrogen shift reaction, we have prepared Re(≡CCH=C(CMe$_3$)C≡C^{n}C$_5$H$_{11}$)HCl(PMe$_2$Ph)$_3$ (**7**) and found that it can also undergo hydrogen shift reaction. A computational study has been carried out to probe the origin in the different reactivities of these hydrido carbyne complexes.

Scheme 1



RESULTS AND DISCUSSION

The precursor complex Re(≡CCH=C(CMe$_3$)C≡C^{n}C$_5$H$_{11}$)HCl(PMe$_2$Ph)$_3$ (**7**) was prepared by a procedure similar to that

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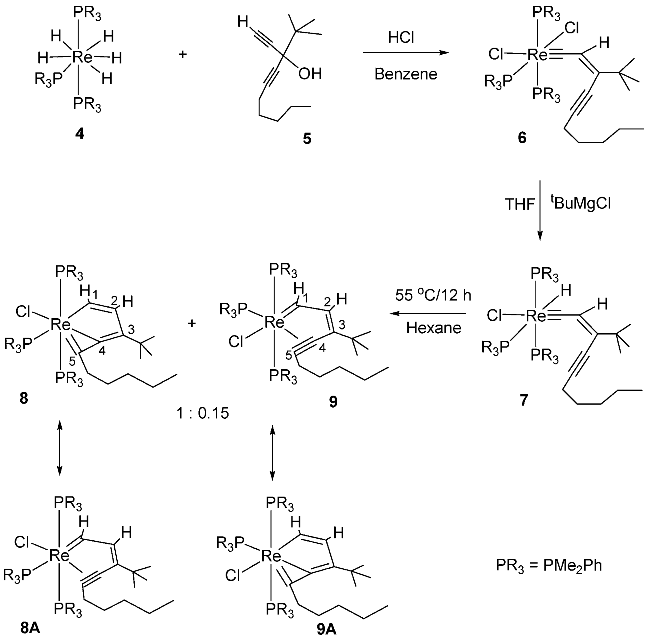
used for the preparation of **3**.[13] Treatment of $ReH_5(PMe_2Ph)_3$ (**4**) with $HC{\equiv}CC(OH)(CMe_3)C{\equiv}C^nC_5H_{11}$ (**5**) in the presence of HCl produced $Re({\equiv}CCH{=}C(CMe_3)C{\equiv}C^nC_5H_{11})Cl_2(PMe_2Ph)_3$ (**6**), which was isolated as a blue solid. Reaction of **6** with Me_3CMgCl in THF gave the hydrido carbyne complex $Re({\equiv}CCH{=}C(CMe_3)C{\equiv}C^nC_5H_{11})HCl(PMe_2Ph)_3$ (**7**), which was isolated as a purple solid in 83% yield (Scheme 2).

Scheme 2



The new carbyne complex **6** has been characterized by NMR, elemental analysis, and X-ray diffraction. The molecular structure of **6** is shown in Figure 1. The complex contains three meridionally bound PMe_2Ph ligands, two mutually cis chloride ligands, and a carbyne ligand trans to one of the chloride ligands. The Re≡C bond distance is 1.767(2) Å, and the Re−C(1)−C(2) angle is 172.3(2)°. The structural parameters related to the metal−carbon bond are similar to those of reported carbyne complexes, such as $ReCl_2({\equiv}CCH{=}CPh_2)(PMe_2Ph)_3$,[14] $[ReCl({\equiv}CC_6H_2Me_3\text{-}2,4,6)(o\text{-}(PPh_2)_2C_6H_4)]ClO_4$,[5a] and $((Me_3C)_2PCH_2SiMe_2)_2N)ReH({\equiv}CCH_2CMe_3)$.[11e]

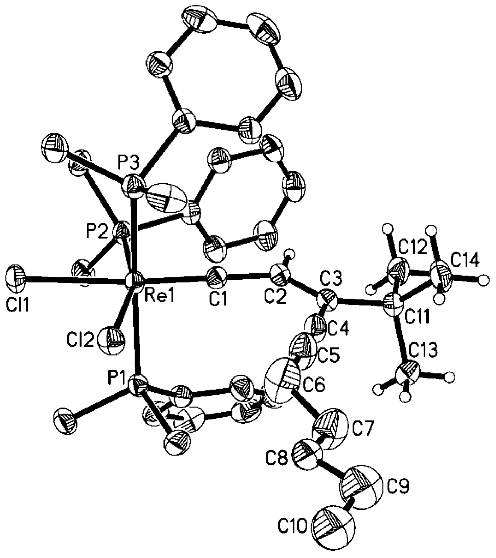


Figure 1. ORTEP drawing of **6** with thermal ellipsoids at the 35% probability level. The hydrogen atoms on PMe_2Ph ligands and the *n*-pentyl group are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Re(1)−C(1) 1.767(2), C(1)−C(2) 1.427(3); C(2)−C(1)−Re(1) 172.3(2), C(2)−C(3)−C(4) 118.5(2).

Consistent with the solid-state structure, the ^1H NMR spectrum showed a characteristic Re≡CC*H* signal at 4.04 ppm. The $^{13}C\{^1H\}$ NMR spectrum showed signals at 261.4 (Re≡*C*), 138.4 (Re≡C*C*H), 140.4 (Re≡CCH=*C*(CMe_3)), 101.2 ($C{\equiv}C^nC_5H_{11}$), and 79.7 ($C{\equiv}C^nC_5H_{11}$) ppm. The $^{31}P\{^1H\}$ NMR spectrum showed a doublet at −17.8 ppm and a triplet at −26.0 ppm with a coupling constant of 12.6 Hz.

The structure of **7** can be assigned on the basis of the NMR data. In particular, the $^{31}P\{^1H\}$ NMR spectrum showed a doublet at −17.8 ppm and a triplet at −25.6 ppm with a *J*(PP) coupling of 14.1 Hz, suggesting that complex **7** has three meridionally bound PMe_2Ph ligands. The ^1H NMR spectrum showed a characteristic Re≡CC*H* signal at 4.40 ppm. The hydride signal is overlapped with those of CH_2 in the region of 1.58−1.78 ppm. For comparison, the hydride signal of **3** was observed at 1.69 ppm. The $^{13}C\{^1H\}$ NMR spectrum of **7** showed signals at 255.7 (Re≡*C*, dt, *J*(PC) = 14.1 and 10.8 Hz), 139.9 (Re≡C*C*H), 135.9 (Re≡CCH=*C*(CMe_3)), 98.1 ($C{\equiv}C^nC_5H_{11}$), and 81.3 ppm ($C{\equiv}C^nC_5H_{11}$). The pattern of the Re≡*C* signal clearly indicates that the carbyne carbon is cis to all the three phosphorus atoms.

When complex **7** in hexane was heated at 55 °C for 12 h or a benzene solution of **7** stood at room temperature for 7 days, two new complexes were produced in a molar ratio of 1:0.15, as indicated by ^1H NMR. The ratio of the two compounds does not change with refluxing time. The major product was identified as complex **8** and the minor one as **9** (Scheme 2).

The structure of complex **8** has been confirmed by an X-ray diffraction study. As shown in Figure 2, it contains an essentially planar bicyclic metallacycle. The maximum deviation from the least-squares plane through Re1 and C1−C5 is 0.011 Å for C2. The C1−C2, C2−C3, C3−C4, and C4−C5 bond distances are 1.355(7), 1.454(7), 1.361(7), and 1.325(7) Å, respectively. The Re−C5 bond length (1.991(5) Å) is within those reported for typical $Re{=}CR_2$(carbene, R = H or alkyl) bonds (1.850−2.153 Å)[15,16] and shorter than those reported for Re−C bonds of rhenium−η^2-alkyne (2e donor) complexes (2.118−2.247 Å).[17] The Re−C1 bond length of 2.160(5) Å is within the range of those reported for typical Re−CH(vinyl) bonds (1.996−2.305 Å)[15,18] and longer than those reported for typical Re=CHR(carbene) bonds.[15,16]

Scheme 2 shows two resonance forms contributing to the overall structure of the metallacycle of complex **8**: metallabicyclo[3.1.0]hexatriene complex (**8**) and alkyne−carbene complex (**8A**). In view of the fact that the Re−C5 bond is significantly shorter than the Re−C1 bond, we consider that resonance form **8** is the dominant one. DFT calculations further support that resonance form **8** makes a greater contribution to the overall structure of **8**. As shown in Figure 3, the optimized structure reproduces well the structural feature of **8** described above. The calculated Wiberg bond indices (which are a measure of bond strength) of Re−C1, Re−C4, and Re−C5 are 0.664, 0.638, and 1.034, respectively. The data

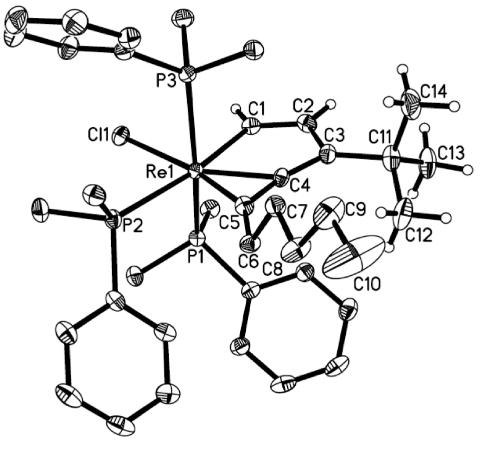


Figure 2. ORTEP drawing of **8** with thermal ellipsoids at the 35% probability level. The hydrogen atoms on PMe_2Ph ligands and the *n*-pentyl group are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Re(1)−C(1) 2.160(5), Re(1)−C(4) 2.085(4), Re(1)−C(5) 1.991(5), C(1)−C(2) 1.355(7), C(2)−C(3) 1.454(7), C(3)−C(4) 1.361(7), C(4)−C(5) 1.325(7), C(5)−C(6) 1.504(7); C(1)−C(2)−C(3) 113.9(4), C(2)−C(1)−Re(1) 120.9(3), C(3)−C(4)−Re(1) 126.9(4), C(4)−Re(1)−C(1) 69.88(18), C(4)−C(3)−C(2) 108.3(4), C(4)−C(5)−Re(1) 74.9(3), C(5)−Re(1)−C(1) 107.74(19), C(5)−Re(1)−C(4) 37.86(19), C(5)−C(4)−Re(1) 67.2(3), C(5)−C(4)−C(3) 165.9(5).

suggest that Re−C1 and Re−C4 bonds can be considered as Re−C single bonds while Re−C5 as a Re═C bond.

Consistent with the solid-state structure, the $^{31}P\{^1H\}$ NMR of **8** in C_6D_6 showed a doublet at −29.9 ppm and a triplet at −31.1 ppm with a *J*(PP) coupling constant of 13.3 Hz. The ^1H NMR in C_6D_6 showed the ReCH═CH signals at 9.67 (ReC*H*═CH) ppm and 8.95 (ReCH═C*H*) ppm. The $^{13}C\{^1H\}$ NMR spectrum in C_6D_6 showed signals at δ 221.8 (C5), 172.1 (C1), 153.5 (C4), 146.6 (C2), and 133.6 (C3). The ^{13}C NMR data clearly indicate that C5 has carbene character. The NMR as well as the structural data suggest that complex **8** can be best described as a metallabicyclohexatriene complex.

The structure of **9** can be assigned on the basis of the NMR data. The $^{31}P\{^1H\}$ NMR spectrum of **9** in C_6D_6 showed a doublet at −29.7 ppm and a triplet at −30.4 ppm with a *J*(PP) coupling constant of 13.3 Hz, indicating that the three phosphine ligands are meridionally bound to rhenium. The ^1H NMR spectrum in C_6D_6 showed a ReC*H*CH signal at 13.92 ppm and a ReCHC*H* signal at 8.68 ppm, indicating that the rhenium-bound CH group has carbene character. Consistent with the carbene character of the rhenium-bound CH group, the $^{13}C\{^1H\}$ NMR spectrum in C_6D_6 showed a signal of ReCH at 236.8 ppm (dt, *J*(PC) ≈ 12.4 Hz, 9.8 Hz). The magnitude of the *J*(PC) couplings for the Re═CH signal implies that the CH is cis to all the phosphorus atoms. In contrast, the corresponding ReCH signal of **8** appears at 172.1 ppm. The coupling (39.8 Hz) between this carbon and the unique P is significantly larger as expected. The ^{13}C signals associated with the C≡C moiety in **9** were observed at 148.5 ($C{\equiv}C^nC_5H_{11}$) and 118.1 ($C{\equiv}C^nC_5H_{11}$) ppm. For comparison, the ^{13}C signals of η^2-PhC≡CH in $Re(Br)(H)(NO)(PCy_3)_2(\eta^2\text{-}HC{\equiv}CPh)$ were observed at 106.9 (s, ≡CPh) and 106.8 (s, HC≡) ppm[16a] and those of η^2-PhC≡CPh in $Re(CO)(NO)(PMe_3)_2(\eta^2\text{-}PhC{\equiv}CPh)$ were observed at 137.6 and 144.9 ppm.[19] The NMR data suggest that the structure of **9** has contributions from the resonance forms **9** (alkyne−carbene complex) and **9A** (metallabicylohexatriene) with **9** being dominant.

While we have not been able to get crystals of **9** suitable for X-ray diffraction analysis, further information on the structure of **9** comes from the DFT study, which supports the description mentioned above. In the optimized structure of **9** (Figure 4), the C1−C2, C2−C3, C3−C4, and C4−C5 bond distances are 1.450, 1.367, 1.423, and 1.277 Å, respectively. The Re−C5 bond length (2.184 Å) is within those reported for Re−C bonds of rhenium−η^2-alkyne (2e donor) complexes (2.118−2.247 Å)[17] and longer than those reported for typical Re═CR_2(carbene, R = H, alkyl) bonds (1.850−2.153 Å).[15,16] The Re−C1 bond length (1.956 Å) is within the range of those reported for typical Re═CR_2(carbene, R = H, alkyl) bonds (1.850−2.153 Å)[15,16] and shorter than those reported for typical Re−CH(vinyl) bonds (1.996−2.305 Å).[15,18] Furthermore, the calculated Wiberg bond indices of Re−C1, Re−C4, and Re−C5 are 1.183, 0.463, and 0.495, respectively, suggesting that Re−C1 can be considered as a double bond, while Re−C5 and Re−C4 as a single bond. The calculated structural parameters, NBO analysis, and NMR data support that the resonance form **9** has a greater contribution. Thus, it can be best described as an alkyne−carbene complex.

Alkyne−carbene complexes, complexes containing both carbene and alkyne ligands, are interesting as they have been suggested as reaction intermediates in many organometallic and catalytic reactions, for example, benzannulation reactions of Fischer chromium carbene complexes with alkynes to give substituted phenols,[20] alkyne polymerization,[21] and enyne metathesis[22] catalyzed by carbene complexes. Well-characterized alkyne−carbene complexes have been previously reported for metals, such as chromium, molybdenum, tungsten, and ruthenium.[23] Complex **9** represents a rare example of rhenium alkyne−carbene complexes.

It is interesting to note that complexes **1** and **7** can undergo hydrogen shift reactions upon heating, whereas complex **3** is

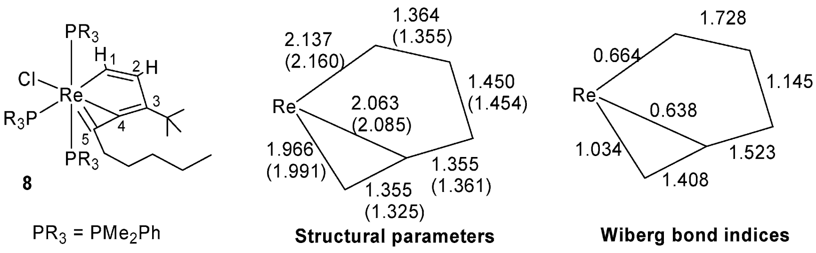


Figure 3. Comparison of selected calculated and experimental (in parentheses) structural parameters (bond length in anstroms) and calculated Wiberg bond indices of complex **8**.

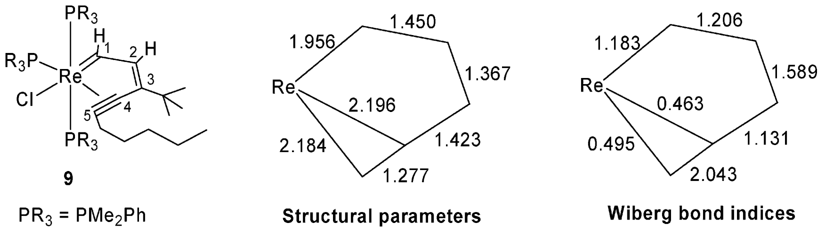


Figure 4. Selected calculated structural parameters (bond length in angstroms) and Wiberg bond indices of complex **9**.

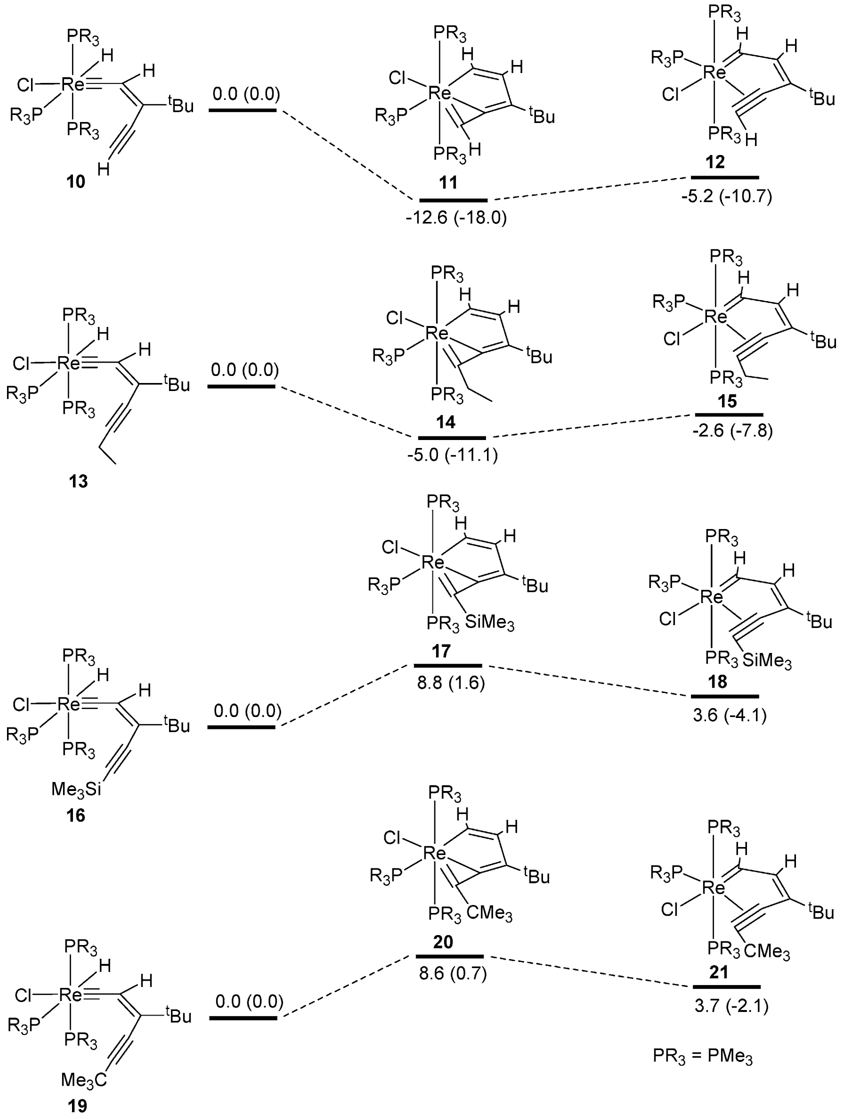


Figure 5. Energy profiles calculated for the hydrogen shift reactions of **10**, **13**, **16**, and **19**. The relative electronic energies and Gibbs free energies (in parentheses) at 298 K are given in kcal/mol.

stable under similar conditions. To understand the observations, we have performed the DFT study of the thermodynamics for the hydrogen shift reactions of **10**, **13**, and **16** (the model complexes of **1**, **7**, and **3**, respectively). The results are summarized in Figure 5. Clearly, the calculated results are in agreement with the experimental results. The hydrogen shift reactions involving **10** and **13** are thermodynamically favorable, whereas that involving **16** is not.

The different behaviors of **10**, **13**, and **16** could be rationalized in term of steric effects. In the calculated structure of the hypothetic product **17** (one of the assumed products from **16**), the $SiMe_3$ group is in close contact with the CMe_3 group on the metallacycle with r(H···H) = 2.104 Å. The $SiMe_3$ group is also in close contact with one of the PMe_3 ligands with r(H···H) = 2.118 Å. These H···H distances are significantly shorter than the sum (2.40 Å) of van der Waals radii (1.20 Å)[24] of two hydrogen atoms, suggesting the presence of strong repulsive steric interaction in **17**. As reflected by the structural parameters, the repulsive steric interaction is reduced in the analogous complexes **11** (one of the products from **10**) and **14** (one of the products from **13**). In the calculated structure of **11**, the close H···H contacts involving CH=CHC(CMe_3)-

CCH are longer than 2.30 Å; in the calculated structure of **14**, only one H···H contact (involving CH═CHC(CMe_3)CCEt) with a H···H distance of less than 2.2 Å is present. Thus, due to steric effects, the formation of **17** from **16** is less favored than the formation of **11** and **14** from **10** and **13**, respectively. For comparison, it is noted that the eclipsed conformer of ethane has a H···H contact of 2.36 Å and that the staggered conformer of ethane has a H···H contact of 2.54 Å. The eclipsed conformer of ethane is less stable than the staggered conformer by 2.9 kcal/mol.[25]

Examination of the structural parameters (Figure 6) of alkyne−carbene complexes **12**, **15**, and **18** reveals that steric interaction resulting from short H···H contacts involving CH═CHC(CMe_3)CCR may not be the dominant factor determining the relative stability of these complexes. On the other hand, it is noted that the Re−C(η^2-alkyne) bond distances (2.311 and 2.205 Å) in complex **18** are appreciable longer than those in complexes **15** (2.180 and 2.205 Å) and **12** (2.114 and 2.190 Å). The longer Re−C(η^2-alkyne) bond distances in **18** can be related to the repulsive steric interaction between the $SiMe_3$ group and the Cl ligand. In complex **18**, one of the H atoms of the $SiMe_3$ group is in close contact with the Cl ligands with r(Cl···H) = 2.826 Å. The Cl···H distance is shorter than the sum (2.95 Å) of the van der Waals radii of one hydrogen atom (1.20 Å) and one chlorine atom (1.75 Å),[24] suggesting the presence of repulsive steric interaction in **18**. As expected, when the alkyne carbons are moved 0.1 Å closer to the Re center, the Cl···H distance is also shortened by ca. 0.1 Å, raising the energy from **18** by 1.1 kcal/mol. The repulsive steric interaction involving Cl···H contact in complexes **12** and **15** should be insignificant as the Cl···H distances are longer than 2.9 Å. As a result of the repulsive steric interaction involving Cl···H contact in complex **18**, the alkyne ligand cannot interact efficiently with the rhenium center to form a strong Re−alkyne bond as those in **12** and **15**. Therefore, the formation of **18** from **16** is less favored than the formation of **12** and **15** from **10** and **13**, respectively.

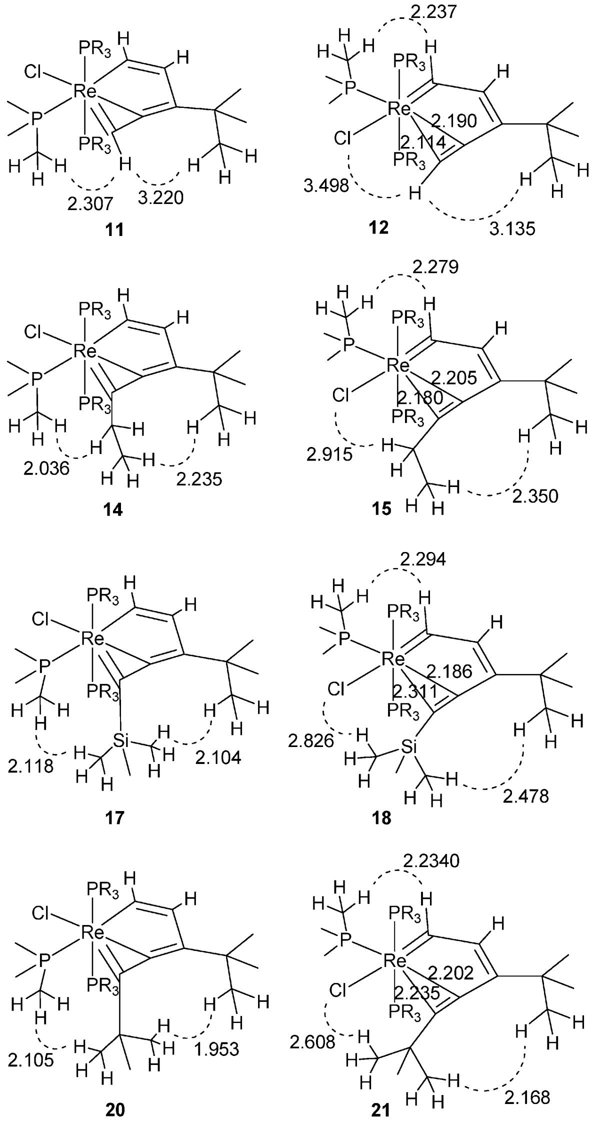


Figure 6. Short H···H and H···Cl contacts (in angstroms) in the optimized structures of **11**, **12**, **14**, **15**, **17**, **18**, **20**, and **21**. R = Me.

To further support the above proposition, we have calculated thermodynamics for the hydrogen shift reaction of the model complex **19** with a CMe_3 group attached to C≡C. On the basis of the arguments above, it is expected that the hydrogen shift reaction of **19** to give complexes **20** and **21** should be thermodynamically not favorable. The expectation was confirmed by the calculation results (Figure 5). The results are consistent with the structural parameters of **20** and **21**. In the calculated structure of **20**, the terminal CMe_3 group is in close contact with the CMe_3 group on the metallacycle with r(H···H) = 1.953 Å, and with one of the PMe_3 ligands with r(H···H) = 2.105 Å, indicating the presence of strong repulsive steric interaction. In complex **21**, one of the H atoms of the CMe_3 group is in close contact with the Cl ligand with r(Cl···H) = 2.608 Å, again indicating the presence of strong repulsive steric interaction.

■ SUMMARY

Rhenium hydrido carbyne complexes Re(≡CCH═C(CMe_3)-C≡CR)HCl(PMe_2Ph)$_3$ (R = H, n-pentyl) undergo 1,2-hydrogen shift reactions from the metal to the carbyne carbon atom to give complexes Re(HCCHC(CMe_3)CCR)HCl-(PMe_2Ph)$_3$. In contrast, a similar transformation does not occur for the analogous complex Re(≡CCH═C(CMe_3)C≡CSiMe$_3$)HCl(PMe_2Ph)$_3$, which has a $SiMe_3$ group on the C≡C moiety. A computational study suggests that the difference in the reactivity of the hydrido carbyne complexes is related to steric effects in the corresponding hydride-shift product.

■ EXPERIMENTAL SECTION

All manipulations were carried out under a nitrogen atmosphere using standard Schlenck techniques unless otherwise stated. Solvents were distilled under nitrogen from sodium benzophenone (hexane, benzene, THF). The starting material $ReH_5(PMe_2Ph)_3$ was prepared following the procedure described in the literature.[26] 3-*tert*-Butyldeca-1,4-diyn-3-ol was prepared from ethynylmagnesium bromide and 2,2-dimethyldec-4-yn-3-one.[27] All other reagents were used as purchased from Aldrich Chemical Co. or Strem Chemical Co.

Microanalyses were performed by M-H-W Laboratories (Phoenix, AZ). ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ spectra were collected on a Bruker ARX-400 spectrometer (400 MHz). ^1H and ^{13}C NMR shifts are relative to TMS and ^{31}P chemical shifts relative to 85% H_3PO_4.

Re(≡C-CH═C(CMe_3)(C≡C^nC_5H_{11}))Cl_2(PMe_2Ph)$_3$ (6). To a solution of $ReH_5(PMe_2Ph)_3$ (2.251 g, 3.72 mmol) and 3-*tert*-butyldeca-1,4-diyn-3-ol (910 mg, 4.41 mmol) in benzene (40 mL) was slowly added hydrogen chloride in diethyl ether (1.0 M, 6.2 mL, 6.2 mmol). After the mixture was stirred at room temperature for 8 h, another portion of hydrogen chloride (1.0 M in diethyl ether, 3.0 mL, 3.0 mmol) was slowly added again, and the reaction mixture was stirred for a further 12 h to give a green solution with a brownish yellow precipitate. The reaction mixture was filtered through a filter paper to remove the brownish yellow precipitate, which was identified as the known paramagnetic complex *fac*-$ReCl_3(PMe_2Ph)_3$. Yield: 912 mg, 34.7%. The solvent of the green filtrate was removed under vacuum, and the residue was washed with methanol (3 mL × 3) with the help of sonication to give a blue precipitate, which was collected by filtration and dried under vacuum. Yield: 730 mg, 22.8%. $^{31}P\{^1H\}$ NMR (161.98 MHz, CD_2Cl_2): δ −17.8 (d, *J*(PP) = 12.6 Hz), −26.0 (t, *J*(PP) = 12.5 Hz). ^1H NMR (400.13 MHz, CD_2Cl_2): δ 0.90 (t, *J*(HH) = 7.0 Hz, 3H, $CH_2CH_2CH_2CH_2CH_3$), 0.98 (s, 9H, *t-Bu*), 1.25−1.47 (m, 4 H, $CH_2CH_2CH_2CH_2CH_3$), 1.53 (d, *J*(PH) = 9.6 Hz, 6H, PMe_2Ph), 1.58−1.68 (m, 2H, $CH_2CH_2CH_2CH_2CH_3$), 1.89 (t, *J*(PH) = 3.2 Hz, 6H, PMe_2Ph), 2.07 (t, *J*(PH) = 3.4 Hz, 6H, PMe_2Ph), 2.45 (t, *J*(HH) = 7.0 Hz, 2H, $CH_2CH_2CH_2CH_2CH_3$), 4.04 (br s, 1H, Re≡C-C*H*=C), 6.16 (t, *J*(PH) = 8.7 Hz, 2H, *Ph*), 6.93 (t, *J*(HH) = 7.2 Hz, 2H, *Ph*), 7.10 (t, *J*(HH) = 7.2 Hz, 1H, *Ph*), 7.33−7.55 (m, 10H, *Ph*). $^{13}C\{^1H\}$ NMR (100.62 MHz, CD_2Cl_2): δ 261.4 (dt, *J*(PC) = 15.4 Hz, 15.0 Hz, Re≡C), 141.8 (t, *J*(PC) = 19.6 Hz, *Ph*), 140.6 (d, *J*(PC) = 47.5 Hz, *Ph*), 140.4 (q, *J*(PC) = 3.5 Hz, Re≡C-CH=*C*), 138.4 (q, *J*(PC) = 3.2 Hz, Re≡C-CH=C), 129.8 (t, *J*(PC) = 4.4 Hz, *Ph*), 128.6 (d, *J*(PC) = 8.6 Hz, *Ph*), 128.2 (s, *Ph*), 127.5 (s, *Ph*), 127.5 (t, *J*(PC) = 3.8 Hz, *Ph*), 126.6 (d, *J*(PC) = 9.0 Hz, *Ph*), 101.2 (s, C≡*C*-*n*-C_5H_{11}), 79.7 (s, *C*≡C-*n*-C_5H_{11}), 35.6 (s, *C*$(CH_3)_3$), 30.6 (s, $CH_2CH_2CH_2CH_2CH_3$), 27.5 (s, $C(CH_3)_3$), 27.2 (s, $CH_2CH_2CH_2CH_2CH_3$), 21.5 (s, $CH_2CH_2CH_2CH_2CH_3$), 19.9 (s, $CH_2CH_2CH_2CH_2CH_3$), 18.9 (d, *J*(PC) = 35.2 Hz, PMe_2Ph), 18.1 (t, *J*(PC) = 18.0 Hz, PMe_2Ph), 13.1 (s, $CH_2CH_2CH_2CH_2CH_3$), 10.7 (t, *J*(PC) = 14.7 Hz, PMe_2Ph). Anal. Calcd. for $C_{38}H_{54}Cl_2P_3Re$: C, 53.02; H, 6.32. Found: C, 53.09; H, 6.37.

Re(≡C-CH=C(CMe$_3$)C≡C^{n}C$_5$H$_{11}$)HCl(PMe$_2$Ph)$_3$ (7). To a solution of **6** (500 mg, 0.58 mmol) in THF (15 mL) was slowly added *tert*-butylmagnesium chloride (1.0 M in THF, 2.8 mL, 2.8 mmol). After the mixture was stirred at room temperature for 40 min, the solvent of the reaction mixture was removed under vacuum and the residue was carefully treated with methanol (3 mL) to quench the excess *tert*-butylmagnesium chloride, and then all the solvents were removed under vacuum again. The residue was extracted with hexane (10 mL × 3). The solvent of the filtrate was removed under vacuum to give a purple solid, which was dried under vacuum. Yield: 397 mg, 82.7%. $^{31}P\{^1H\}$ NMR (161.98 MHz, C_6D_6): δ −17.8 (d, *J*(PP) = 14.1 Hz), −25.6 (t, *J*(PP) = 13.7 Hz). ^1H NMR (400.13 MHz, C_6D_6): δ 0.95 (t, *J*(HH) = 7.2 Hz, 3H, CH_3), 1.10 (s, 9H, $C(CH_3)_3$), 1.28−1.39 (m, 2H, CH_2), 1.39−1.49 (m, 2H, CH_2), 1.58 (d, *J*(PH) = 7.8 Hz, 6H, PMe_2Ph), 1.58−1.78 (m, 3H, Re*H* and CH_2), 2.11 (t, *J*(PH) = 3.3 Hz, 6H, PMe_2Ph), 2.29 (t, *J*(HH) = 7.1 Hz, 2H, CH_2), 2.34 (t, *J*(PH) = 3.4 Hz, 6H, PMe_2Ph), 4.40 (br, 1H, Re≡C-C*H*=C), 7.00−7.26 (m, 11H, *Ph*), 7.58−7.72 (m, 4H, *Ph*). $^{13}C\{^1H\}$ NMR (100.62 MHz, C_6D_6): δ 255.7 (dt, *J*(PC) = 10.8 Hz, 14.1 Hz, Re≡C), 144.4 (t, *J*(PC) = 16.9 Hz, *Ph*), 144.2 (d, *J*(PC) = 33.6 Hz, *Ph*), 139.9 (br, Re≡C-CH=C), 135.9 (q, *J*(PC) = 2.8 Hz, Re≡C-CH=C), 129.5 (t, *J*(PC) = 4.6 Hz, *Ph*), 129.0 (d, *J*(PC) = 9.5 Hz, *Ph*), 127.4 (s, *Ph*), 127.2 (t, *J*(PC) = 3.9 Hz, *Ph*), 126.9 (d, *J*(PC) = 7.4 Hz, *Ph*), 126.8 (s, *Ph*), 98.1 (s, C≡C), 81.3 (s, C≡C), 35.5 (s, $C(CH_3)_3$), 30.7 (s, CH_2), 28.0 (dt, *J*(PC) = 18.8 Hz, 3.0 Hz, PMe_2Ph), 27.8 (s, $C(CH_3)_3$), 27.7 (s, CH_2), 21.7 (s, CH_2), 19.8 (s, CH_2), 16.9 (d, *J*(PC) = 25.3 Hz, PMe_2Ph), 16.6 (t, *J*(PC) =15.9 Hz, PMe_2Ph), 13.3 (s, CH_3). Anal. Calcd for $C_{38}H_{55}ClP_3Re$: C, 55.23; H, 6.71. Found: C, 54.98; H, 6.52.

Re(CH=CH-C(CMe$_3$)=C-C^{n}C$_5$H$_{11}$)Cl(PMe$_2$Ph)$_3$ (8) and Re(=CH-CH=C(CMe$_3$)-C≡C^{n}C$_5$H$_{11}$))Cl(PMe$_2$Ph)$_3$ (9). A solution of **7** (397 mg, 0.58 mmol) in hexane (15 mL) was stirred at 55 °C for 12 h. The solvent of the reaction mixture was then removed under vacuum at room temperature. The residue was washed with hexane (1 mL × 3) to give a red solid, which was collected by filtration and dried under vacuum. The red solid was identified as a mixture of **8** and **9** in a ratio of 1:0.15 as indicated by ^1H NMR. Yield: 131 mg, 33.0%. Anal. Calcd for $C_{38}H_{55}ClP_3Re$: C, 55.23; H, 6.71. Found: C, 55.44; H, 6.57.

NMR data for **8**: $^{31}P\{^1H\}$ NMR (161.98 MHz, C_6D_6): δ −29.9 (d, *J*(PP) = 13.4 Hz), −31.1 (t, *J*(PP) = 13.3 Hz). ^1H NMR (400.13 MHz, C_6D_6): δ 0.86 (t, *J*(HH) = 7.2 Hz, 3H, $CH_2CH_2CH_2CH_2CH_3$), 1.05−1.14 (m, 2H, $CH_2CH_2CH_2CH_2CH_3$), 1.21−1.26 (m, 2H, $CH_2CH_2CH_2CH_2CH_3$), 1.36 (t, *J*(PH) = 4.0 Hz, 6H, PMe_2Ph), 1.38−1.45 (m, 2H, $CH_2CH_2CH_2CH_2CH_3$), 1.55 (d, *J*(PH) = 6.5 Hz, 6H, PMe_2Ph), 1.66 (t, *J*(PH) = 3.8 Hz, 6H, PMe_2Ph), 1.74 (s, 9H, $C(CH_3)_3$), 2.90 (m, 2H, $CH_2CH_2CH_2CH_2CH_3$), 7.00−7.50 (m, 15H, *Ph*), 8.95 (ddt, *J*(HH) = 7.0 Hz, *J*(PH) ≈ 3.0, 2.6 Hz, 1H, Re-CH=C*H*), 9.67 (ddt, *J*(HH) = 7.0 Hz, *J*(PH) ≈ 3.8, 3.5 Hz, 1H, Re-C*H*). $^{13}C\{^1H\}$ NMR (100.62 MHz, C_6D_6): δ 221.8 (dt, *J*(PC) = 19.5, 9.4 Hz, Re=*C*-*n*-C_5H_{11}), 172.1 (dt, *J*(PC) = 39.9 Hz, 18.0 Hz, Re-CH), 153.5 (t, *J*(PC) = 3.0 Hz, Re-C=*C*C$(CH_3)_3$), 146.6 (dt, *J*(PC) = 4.6 Hz, 3.6 Hz, Re-CH=CH), 142.0 (t, *J*(PC) = 17.6 Hz, *Ph*), 139.9 (d, *J*(PC) = 26.3 Hz, *Ph*), 133.6 (t, *J*(PC) = 6.0 Hz, Re-C=C*C*$(CH_3)_3$), 132.1 (d, *J*(PC) = 11.1 Hz, *Ph*), 129.8 (t, *J*(PC) = 4.2 Hz, *Ph*), 128.2 (s, *Ph*), 127.4 (s, *Ph*), 127.1 (d, *J*(PC) = 8.2 Hz, *Ph*), 126.9 (t, *J*(PC) = 4.0 Hz, *Ph*), 45.0 (d, *J*(PC) = 9.4 Hz, $CH_2CH_2CH_2CH_2CH_3$), 39.8 (s, $C(CH_3)_3$), 31.6 (s, $CH_2CH_2CH_2CH_2CH_3$), 30.7 (s, $C(CH_3)_3$), 25.9 (s, $CH_2CH_2CH_2CH_2CH_3$), 21.8 (s, $CH_2CH_2CH_2CH_2CH_3$), 18.4 (d, *J*(PC) = 22.4 Hz, PMe_2Ph), 13.3 (s, $CH_2CH_2CH_2CH_2CH_3$), 12.1 (t, *J*(PC) = 17.2 Hz, PMe_2Ph), 11.2 (t, *J*(PC) = 17.3 Hz, PMe_2Ph). NMR data for **9**: $^{31}P\{^1H\}$ NMR (161.98 MHz, C_6D_6): δ −29.7 (d, *J*(PP) = 13.0 Hz), −30.4 (t, *J*(PP) = 13.3 Hz). ^1H NMR (400.13 MHz, C_6D_6): δ 1.03 (t, *J*(HH) = 6.8 Hz, 3H, $CH_2CH_2CH_2CH_2CH_3$), 1.14−1.18 (m, 2H, $CH_2CH_2CH_2CH_2CH_3$), 1.18−1.26 (m, 12H, PMe_2Ph), 1.38−1.45 (m, 4H, $CH_2CH_2CH_2CH_2CH_3$), 1.65 (s, 9H, $C(CH_3)_3$), 1.88 (d, *J*(PH) = 7.2 Hz, 6H, PMe_2Ph), 2.58 (t, *J*(HH) = 8.0 Hz, 2H, $CH_2CH_2CH_2CH_2CH_3$), 7.00−7.50 (m, 15H, *Ph*), 8.68 (d, *J*(HH) = 5.0 Hz, 1H, Re=CH-C*H*), 13.92 (ddt, *J*(HH) = 5.1 Hz, *J*(PH) ≈ 18.5, 3.2 Hz, 1H, Re=C*H*). $^{13}C\{^1H\}$ NMR (100.62 MHz, C_6D_6): δ 236.8 (dt, *J*(PC) ≈ 12.4, 9.8 Hz, Re=CH), 157.4 (dt, *J*(PC) ≈ 3.7, 2.5 Hz, Re(=CH-CH=*C*C$(CH_3)_3$)), 155.2 (dt, *J*(PC) ≈ 9.0 Hz, 2.6 Hz, Re-CH=*C*H), 148.5 (dt, *J*(PC) = 15.4 Hz, 7.7 Hz, C≡C^{n}C$_5$H$_{11}$), 143.9 (d, *J*(PC) = 30.2 Hz, *Ph*), 141.5 (t, *J*(PC) = 19.1 Hz, *Ph*), 129.9 (t, *J*(PC) = 4.5 Hz, *Ph*), 129.7 (s, *Ph*), 127.3 (s, *Ph*), 127.2 (s, *Ph*), 126.7 (t, *J*(PC) = 3.9 Hz, *Ph*), 118.1 (br, *C*≡C^{n}C$_5$H$_{11}$), 38.2 (s, $C(CH_3)_3$), 34.0 (s, $CH_2CH_2CH_2CH_2CH_3$), 32.5 (s, $CH_2CH_2CH_2CH_2CH_3$), 31.5 (s, $C(CH_3)_3$), 30.5 (s, $CH_2CH_2CH_2CH_2CH_3$), 22.0 (s, $CH_2CH_2CH_2CH_2CH_3$), 17.0 (d, *J*(PC) = 26.3 Hz, PMe_2Ph), 14.4 (t, *J*(PC) = 14.1 Hz, PMe_2Ph), 13.5 (s, $CH_2CH_2CH_2CH_2CH_3$), 12.3 (t, *J*(PC) ≈ 12.1 Hz, PMe_2Ph).

Crystal Structure Analysis. The crystal of **6** was grown by slowly evaporating the solvent from its saturated solution in hexane. The crystal of **8** was grown from a benzene solution layered with hexane at 4 °C. The diffraction intensity data of **6** and **8** were collected with an Oxford Diffraction Gemini S Ultra X-ray diffractometer with monochromatized Cu Kα radiation (λ = 1.54178 Å). Lattice determination, data collection, and reduction were carried out using CrysAlisPro 171.33.46. Absorption correction was performed using the built-in SADABS program and the CrysAlisPro program suite. Structure solution and refinement for all compounds were performed using the Olex2 software[28] package (which embedded SHELXTL[29]). All the structures were solved by direct methods, expanded by difference Fourier syntheses and refined by full matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically with a riding model for the hydrogen atoms, except noted separately. Further details on crystal data, data collection, and refinements are summarized in Table 1.

Computational Study. The mPW1K (modified Perdew−Wang 1-parameter for kinetics) DFT exchange-correlation functional theory of Truhlar and co-workers[30] was used to optimize all of the structures studied in this work. This functional is based on the Perdew−Wang exchange functional[31] with Adamo and Barone's modified enhancement factor[32] and the Perdew−Wang correlation functional. Frequency calculations at the same level of theory have also been performed to identify all stationary points as minima (zero imaginary frequency) or transition states (one imaginary frequency). The LANL2DZ effective core potentials and basis sets were used to describe P, Cl, Si, and Re.[33] The standard 6-31G basis set was used for

Table 1. Crystallographic Details for Complexes 6 and 8

	6	8
empirical formula	$C_{38}H_{54}Cl_2P_3Re$	$C_{38}H_{55}ClP_3Re$
formula wt	860.82	826.38
T, K	173(2)	143(2)
wavelength, Å	1.5418	1.5418
cryst syst	monoclinic	monoclinic
space group	$P2(1)/n$	$P2(1)/n$
a, Å	19.0109(4)	9.76930(10)
b, Å	19.2536(5)	10.00020(10)
c, Å	21.9965(6)	38.8107(4)
α, deg	90	90
β, deg	98.130(3)	95.0890(10)
γ, deg	90	90
vol, $Å^3$	7970.4(3)	3776.66(7)
Z	8	4
d (calcd), Mg/m^3	1.435	1.453
θ range for data collection, deg	2.88−67.50	4.57−67.50
reflns collected	47903	22740
independent reflns	13727 [R(int) = 0.0342]	6785 [R(int) = 0.0612]
data/restraints/params	13727/16/811	6785/0/397
goodness of fit on F^2	1.024	1.013
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0227$, $wR2 = 0.0538$	$R1 = 0.03722$, $wR2 = 0.0822$
largest diff peak and hole, $e{\cdot}Å^{-3}$	0.927 and −0.399	2.133 and −0.921

optimization and the larger basis set 6-311+G* was used for single-point calculation for C and H. Polarization functionals were added for P(ζ(d) = 0.387), Cl(ζ(d) = 0.640), Si(ζ(d) = 0.284), and Re(ζ(f) = 0.869).[34] Natural bond orbital (NBO)[35] analysis is also done at the same level. All of the calculations were performed with the Gaussian 03 package.[36]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Complete ref 36, tables giving Cartesian coordinates and electronic energies for all the calculated structures, and X-ray crystallographic files (CIF) for **6** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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