Appendix

All the calculations were of the extended Hückel[47] type with modified H_{ij}'s.[56] The basis set for the metal atoms consisted of ns, np, and $(n - 1)$d orbitals. The s and p orbitals were described by single Slater type wave functions, and d orbitals were taken as contracted linear combinations of two Slater type wave functions.

The geometries of $M(Cp)_2Me_2$ complexes were modeled after those known ($Zr(Cp)_2Me_2$,[43] $Mo(Cp)_2Bu_2$). The distances (pm) and the angles (deg) used were as follows: M-Cp = 207 (Ti), 222 (Zr), 200 (Mo); C-C(Cp) = 140; C-H(Cp) = 108; M-C = 220 (Ti), 228 (Zr), 228 (Mo); C-H(Me) = 109; Cp-M-Cp = 133 (Ti), 132.5 (Zr), 132 (Mo); C-M-C = 80 (Ti), 95.6 (Zr), 80 (Mo). A more complete study was done for the Ti derivative, in which simultaneous variation of the C-Ti-C angle and agostic deformation were tested, without major changes in the result shown for a fixed geometry. The geometries of the binuclear complexes were taken from the experimentally determined ones.

Standard parameters were used for C and H,[47] while those for the metals are listed in Table IX.

Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atomic coordinates, and bond lengths involving hydrogen (3 pages); a table of structure factors (14 pages). Ordering information is given on any masthead page.

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Steric Factors in Neutral and Anionic Alkyne Complexes of Tungsten(0)[1]

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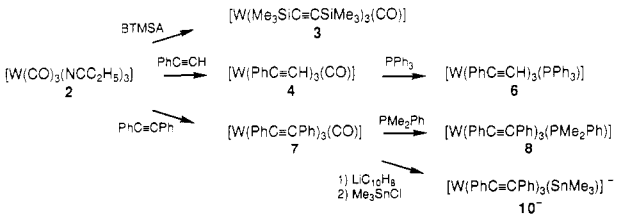
The labile W(0) source $[W(CO)_3(NCC_2H_5)_3]$ (**2**) reacts with the bulky alkyne bis(trimethylsilyl)acetylene (BTMSA) under reduced pressure to give the tris(alkyne) complex $[W(Me_3SiC{\equiv}CSiMe_3)_3(CO)]$ (**3**), which has a low barrier to alkyne rotation. The terminal alkyne PhC≡CH reacts similarly with **2** to give the tris(alkyne) complex $[W(PhC{\equiv}CH)_3(CO)]$ (**4**), isolated as an oil and derivatized by substitution with PPh_3 to give $[W(PhC{\equiv}CH)_3(PPh_3)]$ (**6**). Complex **6** is monoisomeric, with all three alkynes oriented with the acetylenic hydrogens proximal to the phosphine, while **4** exists as a mixture of isomers. ^{13}C NMR spectroscopy indicates that **4** exists in $C_6D_5CD_3$ as a mixture of $\mathbf{4}^3$ (4%), $\mathbf{4}^2$ (64%), and $\mathbf{4}^1$ (32%), with three, two, and one acetylenic hydrogen, respectively, proximal to the carbonyl. Phosphine substitution is also feasible with the more sterically crowded tris(alkyne) substrate $[W(PhC{\equiv}CPh)_3(CO)]$ (**7**), which reacts with PMe_2Ph to give $[W(PhC{\equiv}CPh)_3(PMe_2Ph)]$ (**8**), in which $\Delta G^{\ddagger}$ for alkyne rotation is 13.2 (3) kcal mol^{-1}. The importance of steric factors in determining bonding interactions and alkyne rotation barriers in $[W(RC{\equiv}CR)_3(L)]$ complexes was evaluated by comparison of the NMR characteristics of $[W(PhC{\equiv}CPh)_3(SnPh_3)]^-$ ($\mathbf{9}^-$) with those of $[W(PhC{\equiv}CPh)_3(SnMe_3)]^-$ ($\mathbf{10}^-$), prepared by naphthalenide reduction of **7** and addition of Me_3SnCl. The alkyne rotation barrier in $\mathbf{10}^-$ ($\Delta G^{\ddagger}$ = 12.7 (2) kcal mol^{-1}) is similar to that in $\mathbf{9}^-$ ($\Delta G^{\ddagger}$ = 13.1 kcal mol^{-1}), implying that steric factors are not dominant. NMR parameters involving ^{119}Sn suggest that $\mathbf{9}^-$ and $\mathbf{10}^-$ are best thought of as complexes of "$[W(PhC{\equiv}CPh)_3]$" with R_3Sn^- anions.

Introduction

It has been known for many years that the reaction of alkynes with $[W(CO)_3(NCCH_3)_3]$, a labile W(0) source, leads to the formation of tetrahedral tris(alkyne) complexes of the type $[W(RC{\equiv}CR')_3(CO)]$,[2] and the study of these complexes has been important in the development of our understanding of the bonding interactions between alkynes and transition-metal centers, particularly in the ability, unique amongst η^2 ligands, to act as four-electron donors.[2-6]

The original syntheses of tris(alkyne) complexes of W(0) included diphenylacetylene, methylphenylacetylene, and 3-hexyne ligands, and variations have subsequently led to complexes containing hexafluorobutyne ligands[7] and a crown ether alkyne ligand.[8] Reduction of $[WCl_4(PMe_3)_2]$ by sodium amalgam in the presence of PhC≡CH has also been used to prepare the tris(phenylacetylene) complex $[W(PhC{\equiv}CH)_3(PMe_3)]$[9]—the success of this complementary route confirms that the $[W(RC{\equiv}CR')_3(L)]$ stoichiometry is particularly stable.

Scheme I



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We recently established that the reaction of $[Cr(CO)_3(NCC_2H_5)_3]$ with the bulky alkyne bis(trimethylsilyl)acetylene ($Me_3SiC{\equiv}CSiMe_3$, BTMSA) leads to a bis(alkyne) complex $[Cr(CO)_2(BTMSA)_2]$[10a] (1) instead of a tris(alkyne) complex,[10b] and we have confirmed crystallographically that 1 has an approximately tetrahedral structure as would be anticipated.[10b] The synthesis and structural characterization of $[Cr(PhC{\equiv}CPh)_3(CO)]$ has established that there is no intrinsic problem in preparing tris(alkyne) complexes of Cr(0),[11] and the most obvious interpretation of the formation of the bis(alkyne) complex 1 from BTMSA and a Cr(0) source (rather than a tris(alkyne) complex) is that this reflects the bulk of the BTMSA ligand and the relatively small size of the Cr atom. This raised the possibility that the tungsten system might also be sterically congested and led us to explore, as summarized in Scheme I, some new synthetic chemistry of the tungsten tris(alkyne) system in an attempt to evaluate the importance of steric factors within this system.

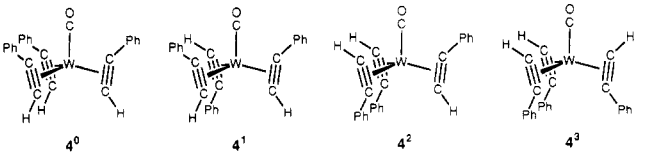
Experimental Section

General Considerations. All manipulations and reactions were performed under an atmosphere of dry nitrogen or argon, using standard Schlenk techniques,[12] or in a Vacuum Atmospheres Dry Lab except where stated otherwise. Microanalyses were performed as indicated by Schwarzkopf Microanalytical Labs, Woodside, NY, or Galbraith Laboratories, Knoxville, TN. Reactions carried out under reduced pressure were carried out in a vessel fitted with a condensor and connected to a three-way stopcock that joined the vessel to a vacuum manifold on one side and a needle valve through which nitrogen was admitted on the other. Pressures were monitored with a manometer between the stopcock and the nitrogen inlet.

Solvents and Reagents. Solvents were freshly distilled from drying agents before use as follows: CaH_2 for propionitrile, toluene, and methylene chloride; $LiAlH_4$ for pentane and heptane; sodium/benzophenone ketyl for tetrahydrofuran (THF) and diethyl ether (ether); K_2CO_3 for acetone. Absolute ethanol was used as supplied and stored under nitrogen. Tungsten hexacarbonyl (Pressure), PMe_2Ph (Strem), PPh_3 (Aldrich), diphenylacetylene (Aldrich), Me_3SnCl (Aldrich), and NEt_4Cl (Aldrich) were used as supplied. Bis(trimethylsilyl)acetylene was either used as supplied by Petrarch Chemical Co. or had been recycled by a procedure in which crystallization of a 1:1 solvate from ethanol at −25 °C was followed by distillation from molecular sieves (70 °C, 70 mmHg). Naphthalenide solutions were prepared and standardized as described previously.[13,14] $[W(CO)_3(NCC_2H_5)_3]$[15] and $[W(PhC{\equiv}CPh)_3(CO)]$[2] were prepared as described in the literature.

Spectroscopy. NMR spectra were recorded on a Bruker WM-300 or AM-300 spectrometer at 300 (^1H), 75.453 (^{13}C), or 121.513 MHz (^{31}P). ^1H and ^{13}C spectra were calibrated by using solvent resonances as follows. ^1H: CD_2HCOCD_3, δ 2.05; $C_6D_5CHD_2$, δ 2.28; C_6D_5H, δ 7.25. ^{13}C: carbonyl of $(CD_3)_2CO$, δ 206.0; ipso carbon of $C_6D_5CD_3$, δ 137.5; C_6D_6, δ 128.0. ^{31}P spectra are referenced to idealized external H_3PO_4 by using the SR parameter of the Bruker program (SR = −13351 for acetone-d_6, SR = −13800 for C_6D_6). Chemical shifts of ^{119}Sn absorptions are reported in terms of the absolute frequency Ξ[16a] and calculated related to $\Xi(Me_4Sn)$ = 37.290665 MHz.[16b] Temperature calibrations were based on the separation of the CH_3 and OH resonances of CH_3OH.[17] Exchange rates were calculated from coalescence temperatures by menas of the approximate relationship[18] $2\pi\tau(\Delta\nu) = 2^{1/2}$. Values for the free energy of activation at the coalescence temperature were obtained from the exchange rate by application of the Eyring equation.[19] The transmission coefficient K was assumed to equal unity, as is usual in dynamic NMR studies.[20] IR spectra were recorded on a Perkin-Elmer 683 spectrometer and were calibrated with the 1601-cm^{-1} band of polystyrene. Solution spectra were recorded in 0.1-mm cells with NaCl windows and Teflon spacers.

Chart I



$[W(Me_3SiC{\equiv}CSiMe_3)_3(CO)]$ (3). A suspension of $[W(CO)_3(NCC_2H_5)_3]$ (1.51 g, 3.49 mmol) in BTMSA (20 mL, 88 mmol) was heated at reflux under a reduced pressure of N_2 (25 mmHg). After 18 h, only traces of yellow crystalline $[W(CO)_3(CNC_2H_5)_3]$ remained suspended in a deep red solution. The solvent was removed in vacuo to leave a semicrystalline red paste which was washed with ethanol to give spectroscopically pure orange microcrystalline $[W(Me_3SiC{\equiv}CSiMe_3)_3(CO)]$ (0.327 g, 0.45 mmol ≡ 13%). Analytically pure material was obtained by low-temperature recrystallization from acetone. ^1H NMR (C_6D_6) δ 0.51 (s, $Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR (C_6D_6, 297 K) δ 237.3 (s, satellites $^1J_{W-C}$ = 108 Hz, CO), 200.7 (s, satellites $^1J_{W-C}$ = 34 Hz, C≡C), 1.8 (s, CH_3); IR (KBr) 2975 m, 2900 m, 1990 ms, 1945 w, 1925 vw, 1610 sh m, 1575 ms, 1555 sh m, 1450 w, 1400 mw, 1380 w, 1260–1240 br ms, 1100 br mw, 1020 w, 910 ms, 860–810 ms, 755 ms, 690 m, 655 ms, 625 m, 490 m, 475 w, 465 w, 430 m, 355 m, 325 m. Anal. Calcd for $WC_{25}H_{54}Si_6O$: C, 41.53; H, 7.52. Found (Schwarzkopf): C, 41.52; H, 7.45.

$[W(PhC{\equiv}CH)_3(CO)]$ (4). A 100-mL flask charged with $[W(CO)_3(NCC_2H_5)_3]$ (2.0 g, 4.6 mmol) was attached to the reduced pressure manifold. Phenylacetylene (20 mL, 150 mmol) was added and the pressure over the magnetically stirred solution carefully reduced to 70 mmHg. After a brief period of vigorous gas evolution (accompanied by a color change to deep red), the mixture was heated at a gentle reflux for 4 h. The homogeneous red solution was diluted with an equal volume of toluene and transferred via a cannula to a Schlenk flask. The solvent was removed, and the viscous red oil was dissolved in 25 mL of toluene and decanted onto ca. 20 g of silica gel (activity III). The solvent was removed and the product extracted with 4 × 20-mL portions of 3:1 pentane:CH_2Cl_2 to give a clear red solution, free of many of the polymeric byproducts. This solution was concentrated under reduced pressure to give a red oil, which was extracted with pentane (4 × 20 and 4 × 10 mL), until the extract showed little activity in the IR (2060-cm^{-1} band). After concentration to 30 mL, the pentane solution was decanted onto 10 g of silica gel and the remaining solvent was removed. The silica was slurried in pentane and added under nitrogen to the top of a silica chromatography column (20 × 1 cm) prepared under N_2. The product was eluted with 1:3 CH_2Cl_2:pentane. The eluant was monitored by thin-layer chromatography (TLC). Removal of solvent gave $[W(PhC{\equiv}CH)_3(CO)]$ as a spectroscopically pure yellow/red oil

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(1.54 g, 3.0 mmol ≡ 64%). The material obtained as a yellow precipitate from cold pentane without chromatography was sufficiently pure for use in further syntheses. ^{1}H NMR (C_6D_6, 297 K) δ 12.35, 11.99, 9.93, 8.28, 8.26 (s, ≡CH), 7.89–7.33 (m, C_6H_5); ^{13}C NMR ($C_6D_5CD_3$, 230 K, see Chart I for key to isomer assignments) 221.7 (d, 4^1, CO), 220.3 (t, $^3J_{C-H}$ = 6 Hz, 4^2, CO), 196.1 (s, 4^1, PhC≡), 195.6 (s, 4^3, PhC≡), 194.8 (s, 4^2, PhC≡), 183.7 (d, $^1J_{C-H}$ = 195 Hz, 4^1, ≡CH), 183.4 (d, $^1J_{C-H}$ = 199 Hz, 4^2, ≡CH), 179.8 (s, 4^1, PhC≡), 176.2 (s, 4^2, PhC≡), 160.5 (d, $^1J_{C-H}$ = 201 Hz, 4^3, ≡CH), 157.7 (d, $^1J_{C-H}$ = 204 Hz, 4^2, ≡CH), 155.6 (d, $^1J_{C-H}$ = 203 Hz, 4^1, ≡CH), 143–124 (m, C_6H_5).

[W(PhC≡CH)$_3$(PPh$_3$)] (6). A 100-mL flask was charged with PPh_3 (0.5 g, 1.9 mmol) and [W(PhC≡CH)$_3$(CO)] (5.0 mL of a 0.20 M solution = 1.0 mmol) in THF. The THF was removed under reduced pressure, and heptane (20 mL) was added. The solution was heated at reflux for 3 h, until the IR spectrum of an aliquot showed no bands above 2000 cm^{-1}. After removal of the heptane under vacuum, the brown solids were extracted with acetone (3 × 20 mL), filtered, concentrated to 30 mL, and slowly cooled to −40 °C to give spectroscopically pure, tan, microcrystalline [W(C_6H_5C≡CH)$_3$(PPh_3)] (0.342 g, 0.45 mmol ≡ 45%). Colorless needles for elemental analysis were grown from hot heptane. ^{1}H NMR (C_6D_6) δ 9.64 (3 H, d, $^2J_{P-H}$ = 14 Hz, HC≡), 8.22–7.45 (30 H, m, Ph); ^{31}P NMR (C_6D_6) δ 46.5 (s, satellites $^1J_{W-P}$ = 127 Hz, PPh_3); ^{13}C{^{1}H} NMR (C_6D_6) δ 199.7 (d, $^2J_{P-H}$ = 4 Hz, satellites $^1J_{W-C}$ = 43 Hz, PhC≡), 167.1 (d, $^2J_{P-H}$ = 18 Hz, satellites $^1J_{W-C}$ = 41 Hz, $^1J_{C-H}$ = 189 Hz in gated spectra, ≡CH), 142.9 (s, ipso-C, ≡CC_6H_5), 134.9 (d, $^2J_{P-C}$ = 10 Hz, ipso-C, PC_6H_5), 131–125 (m, ≡CC_6H_5 + PC_6H_5); IR (Nujol mull) 3050 w, 1940 w, 1880 vw, 1615 vw, 1600 vw, 1590 vw, 1570 vw, 1310 vw, 1260 w, 1185 vw, 1165 w, 1090 m, 1070 mw, 1030 w, 1000 mw, 985 mw, 920 vw, 820 mw, 800 mw, 760 m, 755 ms, 745 ms, 725 w, 700 s, 680 w, 645 w. Anal. Calcd for $WC_{42}H_{33}P$: C, 67.03; H, 4.42. Found (Galbraith): C, 66.35; H, 4.33.

[W(PhC≡CPh)$_3$(PMe$_2$Ph)] (8). A mixture of [W(PhC≡CPh)$_3$(CO)] (0.752 g, 0.99 mmol) and PMe_2Ph (0.3 mL, 1.7 mmol) in THF (25 mL) was heated at reflux for 3.5 h. The clear red solution was transferred to a Schlenk flask, and ethanol (40 mL) was added. The solution was concentrated under reduced pressure until a beige, microcrystalline precipitate appeared, and the solution was then cooled slowly to −70 °C to give spectroscopically pure beige, microcrystalline [W(PhC≡CPh)$_3$(PMe_2Ph)] (0.484 g, 0.56 mmol ≡ 56%). Analytical samples were prepared by recrystallization from acetone. ^{1}H NMR (C_6D_6, 297 K) δ 8.01–6.92 (35 H, m, Ph), 1.92 (6 H, d, $^2J_{P-H}$ = 8.1 Hz, $P(CH_3)_2$); ^{31}P NMR (C_6D_6, 297 K) δ 4.28 (s, satellites $^1J_{W-P}$ = 137 Hz); ^{13}C{^{1}H} NMR (C_6D_6, 295 K) δ 197.7 (d, $^2J_{P-C}$ = 4 Hz, satellites $^1J_{W-C}$ = 38 Hz, C≡), 180.4 (d, $^2J_{P-C}$ = 18 Hz, satellites $^1J_{W-C}$ = 58 Hz, ≡C), 146.9 (s, ipso-C of PhC≡), 142.5 (s, ipso-C of ≡CPh), 137.1 (d, $^1J_{P-C}$ = 39 Hz, ipso-C of PPh), 132.6–125.5 (m, o, of PPh and ≡CPh), 17.6 (d, $^1J_{P-C}$ = 26 Hz, $P(CH_3)_2$); IR (Nujol mull) 3050 w, 1950 vw, 1805 vw, 1750 vw, 1670 sh w, 1655 br m, 1590 m, 1570 mw, 1485 m, 1475 ms, 1415 vw, 1305 vw, 1295 vw, 1280 w, 1265 mw, 1175 w, 1170 w, 1155 mw, 1100 w, 1095 vw, 1070 m, 1025 m, 1000 vw, 990 vw, 960 vw, 945 m, 940 m, 910 ms, 860 vw, 835 w, 800 vw, 780 ms, 770 ms, 765 mw, 755 m, 745 ms, 735 w, 710 sh m, 700 sh ms, 695 s, 675 mw, 665 mw, 630 w. Anal. Calcd for $WC_{50}H_{37}P$: C, 70.43; H, 4.37. Found (Galbraith): C, 69.99; H, 4.74.

NEt$_4$[W(PhC≡CPh)$_3$(SnMe$_3$)] (10-NEt$_4$). A solution of [W(PhC≡CPh)$_3$(CO)] (0.57 g, 0.76 mmol) in THF (10 mL) was cooled in a dry ice/2-propanol bath. Dropwise addition of a 0.081 M THF solution of lithium naphthalenide (19.0 mL, 1.52 mmol) produced a quick color change from yellow to deep red. Me_3SnCl (0.18 g, 0.90 mmol) in THF (5 mL) was then added, and the mixture, which had become a lighter red, was allowed to warm to room temperature overnight. The solvent was removed under reduced pressure, and the red solids were washed with toluene (20 + 15 mL). The tan solid was collected by filtration and dried under vacuum before it was dissolved in ethanol (5 mL), and a solution of Et_4NCl in ethanol (0.25 g, 1.2 mmol, 5 mL) was added. A fluffy yellow precipitate of NEt_4[W(PhC≡CPh)$_3$($SnMe_3$)] formed immediately; the solvent was removed by filtration, and the spectroscopically pure (^{1}H NMR) solids (0.195 g, 0.19 mmol ≡ 25%) were rinsed with ethanol (5 mL). Analytical samples were recrystallized as yellow cubes by slow diffusion of diethyl ether into an acetone solution. ^{1}H NMR (acetone-d_6, 297 K) δ 7.25–7.0 (30 H, m, C_6H_5); 3.45 (8 H, q, $^3J_{H-H}$ = 7.3 Hz, NCH_2), 1.35 (12 H, t of t, $^3J_{H-H}$ = 7.3 Hz, $^3J_{N-H}$ = 1.9 Hz, NCH_2CH_3), −0.22 (9 H, s, satellites $^2J_{Sn-H}$ = 25.3 Hz, $Sn(CH_3)_3$); ^{119}Sn NMR (acetone-d_6, 297 K) Ξ 37.293 49 MHz ($^1J_{W-Sn}$ = 719 Hz, $^2J_{Sn-H}$ = 25.8 Hz); ^{13}C{^{1}H} NMR (acetone-d_6, 320 K) δ 192.9 (s, C≡C), 149.1 (s, ipso-C of Ph), 128–125.6 (m, o-, m-, and p-C of Ph), 53.7 (s, NCH_2), 8.11 (s, NCH_2CH_3), −1.6 (s, satellites $^1J_{Sn-C}$ = 52 Hz, $Sn(CH_3)_3$); ^{13}C{^{1}H} NMR (acetone-d_6, 240 K) δ 196.1 (s, satellites $^1J_{W-C}$ = 42 Hz, $^2J_{Sn-C}$ = 23 Hz, C≡), 186.9 (s, satellites $^1J_{W-C}$ = 36 Hz, $^2J_{Sn-C}$ = 104 Hz, ≡C), 149.8 (s, ipso-C of Ph), 145.2 (s, ipso-C of Ph), 138.9–124.6 (m, o-, m-, and p-C of Ph), 52.1 (s, NCH_2), 7.3 (s, NCH_2CH_3), −2.33 (s, satellites, $^1J_{Sn-C}$ = 51 Hz, $Sn(CH_3)_3$); IR (Nujol mull) 3050 w, 1950 vw, 1750 vw, 1650 m, 1590 m, 1570 mw, 1470 sh ms, 1440 m, 1305 w, 1275 vw, 1260 w, 1180 w, 1170 vw, 1155 vw, 1145 vw, 1135 vw, 1180 w, 1170 w, 1155 w, 1145 w, 1135 w, 1070 mw, 1025 mw, 1005 mw, 960 vw, 925 w, 915 w, 840 vw, 790 sh m, 780 ms, 760 m, 750 ms, 725 mw, 700 s, 665 w, 625 vw. Anal. Calcd for $WC_{53}H_{59}NSn$: C, 62.87; H, 5.87. Found (Galbraith): C, 62.70; H, 5.80.

Results and Discussion

Synthesis of [W(Me$_3$SiC≡CSiMe$_3$)$_3$(CO)] (3), a Complex of W(0) with a Bulky Alkyne. The most obvious interpretation of the observation that the reaction of [Cr(CO)$_3$(NCC_2H_5)$_3$] with BTMSA leads to the formation of the bis(alkyne) complex **1** is that steric congestion prevents the coordination of three bulky BTMSA ligands to the Cr atom. If this is the correct explanation (as opposed to an interpretation based on some unique electronic property of BTMSA), it should be feasible to prepare a tris(BTMSA) complex of tungsten, and we therefore began by examining the reaction of the labile W(0) source [W(CO)$_3$(NCC_2H_5)$_3$][15] (**2**) with BTMSA.

We soon determined that **2** reacts with BTMSA in the absence of solvent at reflux under a reduced pressure of nitrogen (70 mmHg) to produce low yields (after purification) of orange-red crystals, formulated as [W(Me$_3$C≡CSiMe$_3$)$_3$(CO)] (**3**, Scheme I). The product is indefinitely stable at room temperature and is stable to air and moisture in the solid state. The infrared spectrum of **3** in benzene includes a band at 1980 cm^{-1} assigned to $\nu_{C\equiv O}$ and a weaker, broader band at 1580–1610 cm^{-1} assigned to $\nu_{C\equiv C}$, consistent with the proposed formulation.

A tetrahedral geometry with the alkynes parallel to the W—C≡O group should lead to chemically inequivalent alkyne carbons in **3**, but there is only one resonance for the trimethylsilyl groups in the ^{1}H NMR spectra, even at 210 K. The ^{13}C NMR spectrum at room temperature also exhibits a single sharp resonance for the alkyne carbons and for the methyl carbons, suggesting that the alkyne is fluxional with facile alkyne rotation. At least one other tris(alkyne) complex has a relatively low barrier to alkyne rotation ($\Delta G^{\ddagger}$ = 13.1 kcal mol^{-1} for [W(PhC≡CPh)$_3$($SnPh_3$)]$^-$ at room temperature[13]), and the failure to observe inequivalent ends for the alkynes in **3** is not, therefore, unreasonable. One possible explanation for a low barrier to alkyne rotation in **3** (see below) could be that the steric crowding caused by the bulky alkyne destabilizes the ground state (with parallel alkynes) more than a transition state for alkyne rotation with one alkyne perpendicular to the W—C≡O axis.[21]

Synthesis and ^{13}C NMR Analysis of [W(PhC≡CH)$_3$(CO)] (4), a Terminal Alkyne Complex That Exhibits Geometrical Isomerism. One approach to the study of the importance of steric factors in the chemistry of [W(alkyne)$_3$(CO)] complexes involves the preparation

(21) It could be suggested that steric crowding has led to an alternate ground-state structure with symmetric alkynes. There is, however, no obvious alternative geometry that would allow the alkyne carbons to become equivalent without a dynamic process.

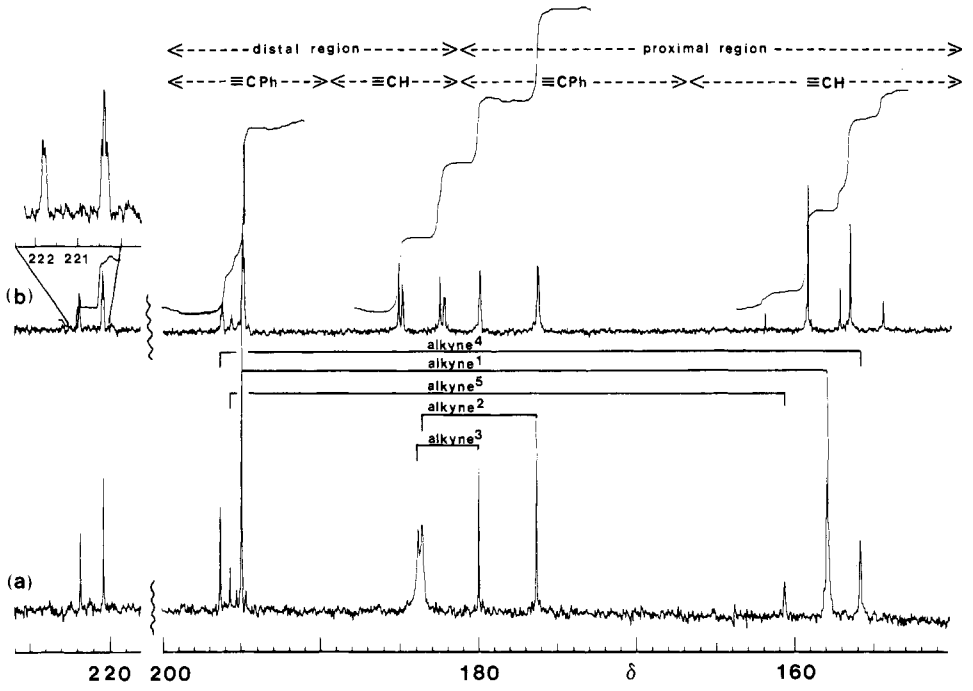

Figure 1. Carbon-13 NMR spectra of $[W(PhC{\equiv}CH)_3(CO)]$ in the carbonyl and alkyne regions at 230 K: (a) with broad band proton decoupling; (b) fully coupled.

of complexes of asymmetric alkynes in which the ends of the alkyne differ markedly in bulk, and simple examples of such complexes could include complexes of terminal alkynes. Previous attempts to prepare tris(alkyne) complexes of W(0) by reaction of terminal alkynes with $[W(CO)_3(NCCH_3)_3]$ were unsuccessful and gave "brown polymeric residues",[2] but we have now been able to prepare a tris(alkyne) complex of phenylacetylene by reacting $[W(CO)_3(NCC_2H_5)_3]$ with neat PhC≡CH at reflux under reduced pressure to minimize product thermolysis.

The reaction of $[W(CO)_3(NCC_2H_5)_3]$ with PhC≡CH is accompanied by extensive polymerization of the alkyne, but a spectroscopically pure tris(alkyne) product can be obtained in good yield after a series of extractions followed by chromatography on silica. The complex can be isolated as a solid from cold (−50 °C) pentane, but it melts at ca. −30 °C to give a waxy oil which was unsuitable for combustion analysis. Spectroscopic studies and the preparation of an analytically pure derivative have, however, allowed us to unambiguously characterize the product as a mixture of three isomers of $[W(PhC{\equiv}CH)_3(CO)]$ (**4**).

The IR spectrum of **4** exhibits a single band in the carbonyl region, at 2060 cm^{-1}, consistent with the proposed formulation, but ^1H NMR and ^{13}C NMR spectra are much more complex than we initially anticipated. The $^{13}C\{^1H\}$ NMR spectrum in the carbonyl and alkyne regions (Figure 1a), for example, has 2 absorptions in the carbonyl region, and no less than 10 resonances in the alkyne region. Comparison with the ^1H-coupled spectrum (Figure 1b) establishes that five of these alkyne resonances can be assigned to alkyne carbons carrying hydrogens, implying that the remaining alkyne carbons carry phenyl groups.

The complex ^{13}C spectrum of **4** suggests that the compound exists as a mixture of isomers, which most probably involve different orientations of the alkynes in the pseudotetrahedral environment around tungsten. The CO ligand defines an apical position, and there are four possible isomers that differ with respect to the orientations of the alkyne ligands relative to the apical CO. These four isomers, designated 4^0, 4^1, 4^2, and 4^3 (Chart I), have, respectively, 0, 1, 2, or 3 acetylenic hydrogens in the proximal positions and, conversely, 3, 2, 1, or 0 phenyl groups in the proximal positions (Table I). Several examples have been reported previously in which bis(alkyne) complexes exhibit isomerism because they have several accessible alkyne orientations,[22] but, to the best of our knowledge, **4** provides the first example of a tris(alkyne) complex that exhibits orientational isomerism.

Table I. Number of Acetylene Hydrogens and Phenyl Groups in Proximal and Distal Positions in Isomers of 4

	4^0	4^1	4^2	4^3
proximal ≡CH	0	1	2	3
distal ≡CH	3	2	1	0
proximal ≡CPh	3	2	1	0
distal ≡CPh	0	1	2	3

The spectra in Figure 1 can be readily assigned on the basis of data reported by Wilkinson for $[W(PhC{\equiv}CH)_3(PMe_3)]$ (**5**),[9] the synthesis of which was mentioned above. This molecule has been established crystallographically to have all three acetylenic hydrogens proximal in the solid state, and has a ^{13}C spectrum in which the distal acetylenic carbons carrying phenyls resonate at δ 201.4 and the proximal carbons carrying hydrogens resonate at δ 164.2.[9]

Assuming that the alkyne orientations in **5** are the same in solution as in the solid state, the cluster of resonances in Figure 1 around δ 195 can then be assigned to distal ≡CPh groups, and the cluster between δ 155 and 161 to proximal ≡CH groups. This in turn suggests that the resonances with single-bond C–H couplings around δ 184 correspond to distal ≡CH groups, while those without such couplings between δ 175 and 180 can be assigned to proximal ≡CPh groups. The soundness of these assignments is confirmed by the observation that the 10 resonances form 5 ≡CPh, ≡CH pairs in which each component has similar intensity as indicated by braces in Figure 1 labeled alkyne^1, alkyne^2, etc., in order of decreasing in-

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Table II. ^{13}C NMR Resonances for Carbonyl and Acetylenic Carbons of [W(PhC≡CH)$_3$(CO)]

δ	mult	J_{C-H}	integral	group	position	alkyne	isomer
221.7	d	4	9	C≡O			4^1
220.1	t	6	17	C≡O			4^2
196.1	s		11	≡CPh	distal	4	4^1
195.6	s		4	≡CPh	distal	5	4^3
194.8	s		37	≡CPh	distal	1	4^2
183.7	d	195	22	≡CH	distal	3	4^1 (or 4^2)
183.4	d	199	23	≡CH	distal	2	4^2 (or 4^1)
179.8	s		24	≡CPh	proximal	3	4^1 (or 4^2)
176.2	s		28	≡CPh	proximal	2	4^2 (or 4^1)
160.5	d	201	4	≡CH	proximal	5	4^3
157.7	d	204	43	≡CH	proximal	1	4^2
155.6	d	203	9	≡CH	proximal	4	4^1

tensity. These must correspond to five types of chemically inequivalent PhC≡CH ligands.

The carbonyl resonances at δ 220.1 and 221.7 in Figure 1b clearly exhibit long-range coupling to one and two hydrogens, respectively, and the key to the interpretation of this is Wilkinson's observation of much larger coupling between the apical ^{31}P in **5** and the proximal carbons (16 Hz) than between the apical ^{31}P and the distal carbons (5 Hz). This observation is somewhat surprising, since the proximal acetylenic C is essentially cis to the PMe_3 ligand, but similar large couplings have been previously observed between an acetylenic hydrogen and a cisoid carbonyl in [W(CO)(S_2CNR^1)$_2$(HC≡CR^2)] complexes[6] and in the present system can be interpreted in terms of asymmetry in the binding of the alkyne to the metal center. Assuming that there are similarly large proximal/apical coupling patterns in **4**, the triplet carbonyl can be assigned to 4^2 while the doublet carbonyl can be assigned to 4^1 with the two isomers present in a ca 2:1 ratio.

Assignment of the alkyne ligands of 4^2 and 4^1 follows readily. The most intense resonances (alkyne[1]) are those of an alkyne with a proximal ≡CH group, which must be the two alkynes of 4^2 with proximal ≡CH groups. Complex 4^1 should also contain an alkyne with a proximal ≡CH, which should give rise to absorptions with intensities approximately 25% those of alkyne[1]. This must be alkyne[4].

Isomers 4^2 and 4^1 should, respectively, have one and two alkynes with distal ≡CH groups, which should have approximately equally intense ^{13}C resonances given the 2:1 ratio of 4^2 and 4^1. These must be alkyne[2] and alkyne[3], but there is no obvious way (nor a pressing need) to distinguish between them.

This leaves alkyne[5] as the only unassigned alkyne—since this has a proximal ≡CH, it must indicate the presence of a small quantity of 4^3, and with full assignments in hand, we can use the integrated intensity of the proximal ≡CH groups (corrected for statistical factors) to calculate that **4** is 4% 4^3, 68% 4^2, and 28% 4^1. Similar calculations based on the distal ≡CPh groups give a composition of 4% 4^3, 60% 4^2, and 36% 4^1 and based on the carbonyls (assuming that 4% 4^3 is unobserved) give 63% 4^2 and 33% 4^1. If we average these values, the true composition is ca. 4% 4^3, 64% 4^2, and 32% 4^1.

The importance of the ^{13}C analysis of **4** (the spectral data and assignments are summarized in Table II) is that it unambiguously establishes that **4** exists as a mixture of isomers. From the relative concentrations, we can calculate that 4^3 and 4^1 are only 1.3 and 0.3 kcal mol^{-1} less stable than 4^2, respectively,[23] and we can conclude that, while the isomer ratios may well be sterically controlled, the steric environment in **4** is not so crowded that it produces large free-energy differences between various isomers.

Preparation of Monoisomeric [W(PhC≡CH)$_3$(PPh$_3$)] (6). A stable derivative of [W(PhC≡CH)$_3$(CO)] was readily prepared by substitution with PPh_3 in refluxing heptane to give [W(PhC≡CH)$_3$(PPh_3)] (**6**). Samples of the compound are indefinitely stable at room temperature and analyzed satisfactorily.

NMR spectra of **6** suggest that it exists as a single isomer in solution; two doublets are observed in the ^{13}C spectrum for the acetylenic carbons at δ 199.7 ($^2J_{P-C}$ = 4 Hz, no further splitting in a gated decoupled spectrum) and at δ 167.1 ($^2J_{P-C}$ = 18 Hz, $^1J_{C-H}$ = 189 Hz in a gated decoupled spectrum). These resonances are assigned to a distal ≡CPh and a proximal ≡CH, respectively, in accord with the chemical shift and coupling criteria established above. This indicates that **6** exists as a single stereoisomer with the phenyl groups oriented away from a bulky, apical PPh_3 group. This structure is analogous to the solid-state structure of [W(PhC≡CH)$_3$(PMe_3)][9] and suggests that increasing the bulk of the apical ligand from a carbonyl to PPh_3 produces sufficient steric differentiation to lock in a single, dominant isomer.

Preparation and Characterization of [W(PhC≡CPh)$_3$(PMe_2Ph)] (8). Despite the long history of work on [M(RC≡CR)$_3$(CO)] complexes of the group 6 metals, there is only one other report (in addition to our observation that PPh_3 replaces CO in **4**) of substitution of a donor ligand for the carbonyl ligand in one of these complexes.[8] It was not, therefore, obvious how general such thermal substitutions might be with other alkynes, particularly bulkier alkynes, and this led us to examine the reaction of the diphenylacetylene complex [W(PhC≡CPh)$_3$(CO)] (**7**) with the electronically flexible (σ-donor and π-acceptor) phosphine PMe_2Ph.

The reaction of **7** with PMe_2Ph in THF proceeded slowly at room temperature, and IR spectra indicated that most of **1** had not reacted after 48 h. Reaction was, however, more rapid at reflux in THF and was complete in 3.5 h to give moderate yields of [W(PhC≡CPh)$_3$(PMe_2Ph)] (**8**) (Scheme I). This complex is indefinitely stable in air and under vacuum, and although [W(RC≡CR)$_3$(PR_3)] complexes are probably most conveniently prepared by other routes,[9] the reaction does confirm that carbonyl substitution in [M(RC≡CR)$_3$(CO)] complexes is not limited to complexes of terminal alkynes.

The spectroscopic characteristics of the phosphine complex **8** are similar to those of **7**. The room-temperature ^{13}C NMR spectrum in C_6D_6 exhibits two alkyne carbon resonances, both doublets, at δ 197.8 ($^2J_{P-C}$ = 4 Hz) and δ 180.4 ($^2J_{P-C}$ = 19 Hz), assigned to the distal and proximal ≡CPh groups, respectively.

The spectra are temperature dependent, and as the temperature is raised, the resonances of the alkyne carbons reversibly broaden and approach each other. Two distinct resonances are still observed at 365 K, the highest temperature that could be safely attained, but, at this temperature, the resonances of the carbons of the associated phenyl rings have coalesced. The ipso carbons, for example (originally at δ 146.8 and 142.5, Δδ = 330 Hz at 75.45 MHz), coalesce at 355 ± 5 K, from which we can calculate a rate of exchange of k_1 = 733 s^{-1} and a barrier to rotation of $\Delta G^{\ddagger}$ = 13.2 (3) kcal mol^{-1}.

Alkyne Rotation and Tin Coordination in the Trimethylstannane Complex NEt_4[W(PhC≡CPh)$_3$($SnMe_3$)]. Although it was clear from the synthesis of **3** that bulky alkyne substituents do not impede access to

(23) This assumes that the isomers are in thermodynamic equilibrium. This seems reasonable since they can be interconverted by alkyne rotation and alkyne rotation barriers are typically only 15–20 kcal mol^{-1}.[3,13]

Table III. Selected NMR Parameters Involving ^{119}Sn for $[W(PhC{\equiv}CPh)_3(SnR_3)]^-$ Complexes

tin ligand	$\Xi(^{119}Sn)$, MHz	$\delta(^{119}Sn)$, ppm	$^1J_{Sn-C}$, Hz	$^2J_{Sn-C}$, Hz proximal	$^2J_{Sn-C}$, Hz distal	$^1J_{W-Sn}$, Hz
$SnPh_3$[23]	37.292 80	57.2	91	107	ca. 35	815
$SnMe_3$	37.293 49	75.5	51	104	23	719

$[W(RC{\equiv}CR)_3(CO)]$ complexes, a low rotation barrier as a result of steric factors still seemed a reasonable explanation for the failure to observe chemical inequivalence for the ends of the alkyne ligands in **3**. The observation that there was a relatively small energy difference between three of the four possible isomers of $[W(PhC{\equiv}CH)_3(CO)]$ did not, however, seem consistent with serious steric congestion in the $[W(RC{\equiv}CR)_3(L)]$ ligand environment, and our ability to substitute a PMe_2Ph ligand for the CO in **7** also argued against serious crowding in these environments. We therefore decided to probe further the importance of steric factors in this system by comparing alkyne rotation barriers in two electronically similar but sterically very different $[W(RC{\equiv}CR)_3(L)]$ complexes.

Our previous work on $[W(PhC{\equiv}CPh)_3(SnPh_3)]^-$ (**9**$^-$)[13] suggested that this could be approached very straightforwardly by preparing analogues of **9**$^-$ containing other trialkylstannane ligands. This was achieved as shown in Scheme I by reducing **7** with 2 equiv of lithium naphthalenide and treating the reduced solution with a slight excess of Me_3SnCl at −78 °C. After counterion exchange, this sequence gave $NEt_4[W(PhC{\equiv}CPh)_3(SnMe_3)]$ (**10**-NEt_4) as yellow needles in good yield. The compound appears to be indefinitely stable to air and moisture but was routinely handled under dry nitrogen. The spectroscopic properties of **10**$^-$ resemble those of **9**$^-$ and support the proposed formulation—^1H NMR spectra, for example, contain resonances assigned to the aromatic protons, the NEt_4^+ cation, and the $SnMe_3$ group.

The NMR parameters involving ^{119}Sn are particularly intriguing and offer some insight into the nature of the $SnMe_3$ ligand. As can be seen by inspection of Table III, these parameters clearly resemble those observed for **9**$^-$,[24] but they differ markedly from data reported for other tin compounds. The $^1J_{W-Sn}$ values, for example, are much larger than the reported value of 150 Hz for $^1J_{W-Sn}$ in $[W(\eta\text{-}C_5H_5)(CO)_2(SnMe_3)]$,[16b] while the $^1J_{Sn-C}$ values are amongst the lowest reported.[25] The conjunction of these two unusual factors would suggest that the W–Sn bond must have unusually high Sn 5s character, while the Sn–C bonds must have unusually high Sn 5p character. This should be reflected in the bond angles involved,[26,27] and the small C–Sn–C angle of 98.6° observed[13] for **9**$^-$ is certainly consistent with this interpretation (cf. 113.4° for C–S–C in Ph_3SnBr[28]).

The similarity of the NMR parameters involving ^{119}Sn for **9**$^-$ and **10**$^-$ implies that there is some unusual common parameter inducing high p character in the Sn–C bonds in both the Ph_3Sn and Me_3Sn ligands. Since the ligands are very different sterically, the common factor must be electronic, and we suggest that both **9**$^-$ and **10**$^-$ should be thought of as complexes of $[W(PhC{\equiv}CPh)_3]$ (containing W(0)) with R_3Sn^- anions—these would be isoelectronic with trialkylstibine ligands, and high Sn 5p character in the Sn–C bonds would be consistent with the established pyramidal structure of the discrete $SnCl_3^-$ ions in, for example, $[Co(Ph_2PCH_2CH_2PPh_2)_2Cl]SnCl_3$, with average Cl–Sn–Cl angles of 94.5°.[29]

Table IV. Barriers to Alkyne Rotation in $[M(RC{\equiv}CR)_3L]$ Complexes

complex	$\Delta G^{\ddagger}$, kcal mol^{-1}	ref
$[Cr(PhC{\equiv}CPh)_3(CO)]$	13.0	11
$[W(PhC{\equiv}CPh)_3(CO)]$	17.8	13
$[W(Me_3SiC{\equiv}CSiMe_3)_3(CO)]$	small	this work
$[W(PhC{\equiv}CPh)_3(PMe_2Ph)]$	13.2	this work
$[W(PhC{\equiv}CPh)_3(SnMe_3)]^-$	12.7	this work
$[W(PhC{\equiv}CPh)_3(SnPh_3)]^-$	13.1	13

Our objective in preparing **10**$^-$ was to study the influence of steric factors on alkyne rotation in these systems, and alkyne rotation in **10**$^-$ was readily monitored by using ^{13}C NMR spectroscopy. The spectrum of **10**$^-$ at room temperature contains no observable resonance that can be assigned to the alkyne carbons, but at lower temperatures, two distinct resonances are observed, at δ 196.1 ($^1J_{W-C}$ = 23 Hz, $^2J_{Sn-C}$ = 23 Hz) and δ 186.9 ($^1J_{W-C}$ = 36 Hz, $^2J_{Sn-C}$ = 104 Hz), suggesting that **10**$^-$ is fluxional and that the alkyne resonances are near coalescence at room temperature. The temperature-dependent behavior is reversible, and determination of a coalescence temperature of 290 K for the alkyne carbons permits the calculation of a barrier of $\Delta G^{\ddagger}$ = 12.7 (3) kcal mol^{-1} for alkyne rotation in **10**$^-$ (Table IV). This is very close to the value of 13.1 kcal mol^{-1} observed for the triphenylstannane complex, **9**$^-$, suggesting that steric factors certainly do not dominate the barriers to alkyne rotation in $[W(RC{\equiv}CR)_3(L)]$ complexes. It is also, however, clear from the similarity of the barrier to alkyne rotation in **8** to those in **9**$^-$ and **10**$^-$ that there is also no simple electronic interpretation of the barriers. This is in accord with a qualitative molecular orbital study[30] which demonstrates that a fully synergistic metal–alkyne bonding interaction is maintained even at the transition state for rotation, but a more detailed study of the dependence of the electronic structure of $[W(RC{\equiv}CR)_3(L)]$ complexes on both steric and electronic factors would be required to accurately interpret the observed variations in alkyne rotation barriers.

Conclusion

The observation that $[W(CO)_3(NCC_2H_5)_3]$ does give a tris(alkyne) complex $[W(BTMSA)_3(CO)]$ (**3**) when reacted with BTMSA (rather than a bis(alkyne) complex analogous to $[Cr(CO)_2(BTMSA)_2]$ (**1**)) supports the hypothesis that the formation of **1** from $[Cr(CO)_3(NCC_2H_5)_3]$ and BTMSA reflects steric problems in coordinating three bulky BTMSA ligands around Cr(0). Our other synthetic results in the tungsten system, including the small free-energy differences between the three observable isomers of $[W(PhC{\equiv}CH)_3(CO)]$ (**4**^{1}, **4**^{2}, and **4**^{3}), and the accessibility by carbonyl substitution of the tris(alkyne) phosphine complexes $[W(PhC{\equiv}CH)_3(PPh_3)]$ and $[W(PhC{\equiv}CPh)_3(PMe_2Ph)]$ suggest, however, that tris(alkyne) complexes of the larger W atom are not very sterically crowded. This is strongly supported by the observation that there are similar barriers to alkyne rotation in $[W(PhC{\equiv}CPh)_3(SnPh_3)]^-$ (**9**$^-$) and $[W(PhC{\equiv}CPh)_3(SnMe_3)]^-$ (**10**$^-$), despite the obvious difference in steric bulk between the Ph_3Sn^- and Me_3Sn^- ligands. Our NMR studies incidentally sug-

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gest that 9^- and 10^- are best thought of as complexes of "[W(PhC≡CPh)$_3$]" with R_3Sn^- anions and are therefore analogous to stibine complexes.

In addition to their implications for the evaluation of steric factors in the chemistry of these polyalkyne complexes of zero-valent group 6 metals, our results have shown that the reaction of [W(CO)$_3$(NC$_2$H$_5$)$_3$] with alkynes can provide a more general route to [W(alkyne)$_3$(CO)] complexes than was previously established—the key to preparing complexes of polymerization-prone terminal alkynes by this route has been to carry out the reaction in neat alkyne and to minimize product thermolysis by conducting the reaction at reflux under reduced pressure.

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Highly Enantioselective Hydrosilylation of Ketones with Chiral and C_2-Symmetrical Bis(oxazolinyl)pyridine–Rhodium Catalysts

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Chiral and C_2-symmetrical 2,6-bis(4′-R-oxazolin-2′-yl)pyridines (pybox, **1a–e**, R = *i*-Pr, *sec*-Bu, *t*-Bu, Et, and Ph) have been newly designed and synthesized from the corresponding optically active β-amino alcohols and pyridine-2,6-dicarboxylic acid as auxiliaries for metal-catalyzed reactions. We have found that the trivalent rhodium–pybox complexes **2a–e** can act as catalysts for asymmetric reduction of ketones with diphenylsilane. The (*S*,*S*)-ip-pybox–rhodium complex **2a** (1 mol % with respect to the ketone) with the aid of $AgBF_4$ has exhibited an extremely high level of enantioselectivity for the reduction of acetophenone derivatives, above 90% ee on the average. Under the same reaction conditions, we have attained complete selection of the prochiral face of 1-tetralone in 99% ee. Several other ketones also have relatively higher results e.g. 95% ee for ethyl levulinate, 94% ee for 1-acetylnaphthalene, and 63% ee for 2-octanone. We have examined α,β-unsaturated ketones, resulting in an exclusive 1,2-reduction for benzalacetone, β-ionone, and chalcone but in lower enantioselection. We have also examined the effect of the substituents on the pybox ligands in the reduction of acetophenone and ethyl levulinate. In the mixed-ligand experiments a facile ligand-exchange reaction between the coordinating pybox and the free pybox ligand in the reaction media was observed, resulting in complete linearity of the enantiomeric excess between the product and the catalytic system.

Chiral organic molecules for metal-catalyzed reactions have been newly designed and synthesized as auxiliaries for enantiotopic-differentiative reactions and molecular recognition.[1] Especially, nitrogen-containing organic molecules have recently attracted much attention in asymmetric reduction, alkylation, and oxidation, including biomimetic reactions.[2]

In the reduction of ketones, chiral catalysts have currently been required to attain an extremely high level of enantioselectivity.[3] Although the reported highly enantioselective reduction of ketones by hydrogenation with chiral phoshine–metal catalysts is a very attractive method, giving optically active secondary alcohols, the reduction is accessible for hetero-substituted ketones, not for simle aliphatic and aromatic ketones.

It is noteworthy that some chiral nitrogen-containing ligands and their rhodium complexes can attain excellent enantioselection in the hydrosilylative reduction of ketones,[4] in which no chiral phosphine ligand could achieve optical yields higher than 90%.[5] In terms of enantioface recognition for simple ketones, we have been interested in the design and synthesis of new chiral and C_2-symmetrical terdentate pyridine ligands and their rhodium complexes as catalysts in the asymmetric hydrosilylation of ketones.

We report here the synthesis of new chiral pyridine ligands having two chiral oxazoline rings and their trivalent rhodium complexes, which exhibit extremely high enantioselectivity in the reduction of several aromatic and aliphatic ketones.[6] From a mechanistic viewpoint, we also disclose the effects of extra addition of the ligands and the linearity in asymmetric induction with the mixed-ligand system.

Results and Discussion

Design and Synthesis of the Chiral Bis(oxazolinyl)pyridine Ligand and Its Rhodium(III) Complex. Our design for the terdentate ligand includes two chiral oxazoline rings introduced at the 2,6-positions of a pyridine skeleton: 2,6-*bis*(*ox*azolinyl)*py*ridine (*pybox*). The chi-

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