Facile Synthesis of Cationic Tungsten(VI) Alkylidene Complexes

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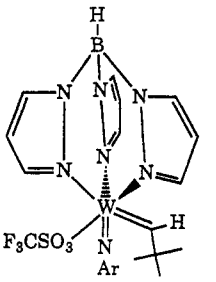
The synthesis of a series of oxygen- and moisture-stable tungsten(VI) alkylidene complexes containing the hydridotris(pyrazolyl)borate (Tp) ligand is described. The complexes, TpW(CHCMe$_2$R)(CH$_2$CMe$_2$R)(NAr) [R = Me, Ar = Ph; R = Ph, Ar = Ph; R = Ph, Ar = 2,6-i-Pr$_2$C$_6$H$_5$), **5–7**, are formed in the reaction between KTp and W(CH$_2$CMe$_2$R)$_3$(NAr)Cl. Complexes **5–7** are protonated by the noncoordinating Bronsted acid [H(OEt$_2$)$_2$]{B[(3,5-CF$_3$)$_2$C$_6$H$_3$]$_4$} giving the cationic alkylidene complexes [TpW(NPh)(CHCMe$_3$)(S)][BAr*$_4$] (S = Et$_2$O, i-Pr$_2$O, CH$_3$CN, Ar* = (3,5-CF$_3$)$_2$C$_6$H$_3$), **8–10**. The cationic amido oxo alkyl complex [TpW(NHPh)(O)(CH$_2$CMe$_2$Ph)][BF$_4$], **12**, is formed when **6** is protonated with HBF$_4$ in the presence of 1 equiv of H$_2$O. Compounds **5–7** function as catalyst precursors for the ring-opening polymerization of cyclooctene and are activated by Lewis acid cocatalysts such as AlCl$_3$.

Introduction

The chemistry of high oxidation state alkylidene complexes has historically shown a progression toward more facile modes of synthesis[1-3] and products exhibiting increasingly greater stability.[2-4] The development of metal alkylidene based catalysts for ring-opening metathesis polymerization (ROMP) has been directed by a demand for greater activity[5] in conjunction with tolerance of an ever greater array of functional groups.[6] Recent advances in acyclic diene metathesis (ADMET) polymerization have demonstrated the need for metathesis catalysts which can also function at elevated temperatures.[7]

Previous communications from this group have described the function of hydridotris(pyrazolyl)borate (Tp) ligands in the stabilization of tungsten(VI) alkylidene complexes.[3,8] Compounds like **1** and **2** have displayed remarkable air and thermal stability. In the presence of Lewis acids such as AlCl$_3$, these compounds are converted into ROMP catalysts and ADMET oligomerization catalysts.[3,8]



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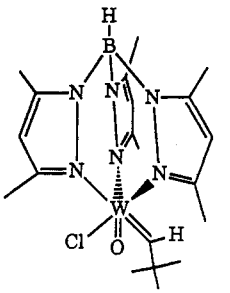

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We now report a three-step synthesis of air and thermally robust tungsten imido alkyl alkylidene complexes of the type TpW(CHCMe$_2$R)(CH$_2$CMe$_2$R)(NAr) [R = Me, Ar = Ph; R = Ph, Ar = Ph; R = Ph, Ar = 2,6-i-Pr$_2$C$_6$H$_5$). When combined with AlCl$_3$, these compounds as well as the TpW(CHCMe$_3$)(NPh)Cl derivative form active metathesis catalysts. Protonation of these complexes results in net loss of the alkyl group and, in the absence of a coordinative counterion, formation of the air stable cationic solvent complexes [TpW(NPh)(CHCMe$_3$)(S)][BAr*$_4$] (S = Et$_2$O, i-Pr$_2$O, CH$_3$CN), **8–10**. These cationic d^0 alkylidene complexes are examples of a very small group of molecules[9] whose chemistry is essentially unexplored. Protonation of **6** in the presence of water leads to the formation of the cationic oxo alkyl amido complex, [TpW(CH$_2$CMe$_2$Ph)(NHPh)(O)][BF$_4$]. The complete syntheses and characterization of these compounds are described.

Experimental Section

Materials and Methods. All syntheses were performed under dry argon atmosphere using standard Schlenk techniques. Tetrahydrofuran (THF), diethyl ether (Et$_2$O), diisopropyl ether (i-Pr$_2$O), toluene, and pentane were distilled from sodium benzophenone ketyl; dichloromethane (CH$_2$Cl$_2$) was distilled from P$_2$O$_5$. WCl$_4$(NPh)(OEt$_2$)[9] (**3**), WCl$_4$(NAr)[10] (**4**; Ar = 2,6-i-Pr$_2$C$_6$H$_3$), ClMgCH$_2$CMe$_3$,[11] ClMgCH$_2$CMe$_2$Ph,[5a] HBAr*$_4$·2OEt$_2$[12]

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(Ar* = 3,5-$C_6H_3(CF_3)_2$), and potassium hydrotris(1-pyrazolyl)-borate (KTp)[13] were prepared according to literature methods. ^1H and ^{13}C NMR spectra were recorded on a Varian VXR-300 (300 MHz), or a General Electric QE-300 (300 MHz) spectrometer. Elemental analyses are by University of Florida Analytical Services and Atlantic Microlab, Inc., Norcross, GA. IR spectra were recorded on a Perkin-Elmer 1200 series spectrometer from Nujol mulls which were prepared in air.

TpW(CHCMe$_3$)(NPh)(CH$_2$CMe$_3$) (5). The alkylation of $WCl_4(NPh)(OEt_2)$ (3) is a variation of a previously reported method.[9a] To a cold (0 °C) stirring solution of 3 (6.21 g, 12.6 mmol) in 150 mL of Et_2O was added 20.5 mL of a 1.84 M solution of Me_3CCH_2MgCl in Et_2O (37.7 mmol). The solution rapidly became brown, and yellow salts precipitated. After 30 min the reaction mixture was allowed to warm to room temperature. After being stirred for 24 h, the solution was filtered and solvent was removed under reduced pressure. The resulting oil was redissolved in pentane and filtered through Celite. Following pentane removal, the crude material was redissolved in 20 mL of THF and cooled to 0 °C, and a 40-mL THF solution of KTp (3.20 g, 12.7 mmol) was added with stirring. After 30 min the cooling bath was removed and the solution was stirred for 18 h. Following solvent removal, the product was extracted with Et_2O, reduced in volume, and placed on a Florisil column. A yellow band was eluted with Et_2O/hexanes. Solvent removal followed by trituration with pentane gave the product as a yellow solid in 22% yield. ^1H NMR data (C_6D_6): δ 10.33 (s, 1 H, C*H*CMe$_3$), 8.45, 7.80, 7.75, 7.27, 7.24 (each a d, 1:1:1:2:1 H, Tp ring H's, 3,5-positions), 7.10 (d, 2 H, *o*-Ph), 6.96 (t, 2 H, *m*-Ph), 6.82 (t, 1 H, *p*-Ph), 5.85, 5.79, 5.74 (t, 1 H each, Tp ring H's, 4-position), 2.32, 1.66 (AB_q, 1 H each, $^2J_{HH}$ = 14 Hz, $^2J_{WH}$ = 6 Hz, C*H*$_2$CMe$_3$), 1.54, 1.48 (each a s, 9 H each, CMe$_3$). ^{13}C NMR data (C_6D_6): δ 283.3 ($^1J_{CW}$ = 153 Hz, $^1J_{CH}$ = 112 Hz, *C*HCMe$_3$), 156.2 (ipso-Ph), 146.0, 143.2, 142.9, 134.9, 134.7, 134.3 ($^1J_{CH}$ = 187 Hz, Tp ring C's, 3,5-positions), 128.6, 126.3, 124.9 ($^1J_{CH}$ = 160 Hz, Ph), 106.0, 105.8 (2:1, $^1J_{CH}$ = 178 Hz, Tp ring C's, 4-position), 67.8 ($^1J_{CW}$ = 97 Hz, $^1J_{CH}$ = 115 Hz, *C*H$_2$CMe$_3$), 46.8, 34.9 (*C*Me$_3$), 35.3, 34.4 (C*Me*$_3$). Mp: 203–204 °C dec. Anal. Calcd for $C_{25}H_{36}BN_7W$: C, 47.71; H, 5.77; N, 15.58. Found: C, 47.33; H, 5.73; N, 15.52.

TpW(CHCMe$_2$Ph)(NPh)(CH$_2$CMe$_2$Ph) (6). The alkylation of 3 is a variation of a previously reported method.[14] To a cold (−78 °C) stirring solution of 3 (5.00 g, 10.2 mmol) in 150 mL of Et_2O was added 28.0 mL of a 1.11 M solution of $PhMe_2CCH_2MgCl$ in Et_2O (31.1 mmol). The solution rapidly became brown, and yellow salts precipitated. After 30 min the reaction mixture was allowed to warm to room temperature. After being stirred for 48 h, the solution was filtered and solvent was removed under reduced pressure. The product was redissolved in pentane and filtered through Celite. Following pentane removal, the crude material was redissolved in 20 mL of THF, and a 40-mL THF solution of KTp (1.50 g, 5.95 mmol) was added with stirring. The solution was warmed to reflux for 24 h. Following solvent removal, the product was extracted with Et_2O, reduced in volume, and placed on a Florisil column. A yellow band was eluted with Et_2O/hexanes. Solvent removal followed by trituration with pentane gave the product as a yellow solid in 38% yield. ^1H NMR data ($CDCl_3$): δ 10.45 (s, 1 H, C*H*CMe$_2$Ph), 8.30–6.95 (m, 21 H, Ph, Tp ring H's, 3,5-positions), 6.33, 6.14, 6.06 (t, 1 H each, Tp ring H's, 4-position), 2.32, 1.72 (AB_q, 1 H each, $^2J_{HH}$ = 14 Hz, $^2J_{WH}$ = 10 Hz, C*H*$_2$(CH$_3$)$_2$Ph), 1.86, 1.83, 1.57, 1.47 (each a s, 3 H each, C*Me*$_2$Ph). ^{13}C NMR data ($CDCl_3$): δ 281.0 ($^1J_{CW}$ = 154 Hz, $^1J_{CH}$ = 113 Hz, *C*HCMe$_2$Ph), 157.0, 155.7, 153.1 (ipso-Ph), 145.6, 142.8, 142.7, 135.0, 134.9, 134.4 ($^1J_{CH}$ = 187 Hz, Tp ring C's, 3,5-positions), 128.4–124.4 (Ph), 105.7, 105.5, 105.4 ($^1J_{CH}$ = 177 Hz, Tp ring C's, 4-position), 67.7 ($^1J_{CW}$ = 98 Hz, $^1J_{CH}$ = 118 Hz, *C*H$_2$CMe$_2$Ph), 52.2, 41.0 (*C*Me$_2$Ph), 33.7, 33.3, 32.9, 32.9 ($^1J_{CH}$ = 124 Hz, C*Me*$_2$Ph). Mp: 144–146 °C dec. Anal. Calcd for $C_{35}H_{40}BN_7W$: C, 55.79; H, 5.35; N, 13.02. Found: C, 55.84; H, 5.37; N, 12.91.

TpW(CHCMe$_3$)(NAr)(CH$_2$CMe$_3$) (7). The alkylation of 4 is a variation of a previously reported method.[9] To a cold (−78 °C) stirring solution of 4 (2.00 g, 3.99 mmol) in 100 mL of Et_2O was added 7.0 mL of a 1.84 M solution of Me_3CCH_2MgCl in Et_2O (12.9 mmol). The solution rapidly became yellow-brown, and yellow salts precipitated. After 30 min the reaction mixture was allowed to warm to room temperature. After being stirred for 24 h, the solution was filtered and solvent was removed under reduced pressure. The product was redissolved in pentane and filtered through Celite. Following pentane removal, the crude material was redissolved in 20 mL of THF, and a 40-mL THF solution of KTp (3.20 g, 12.7 mmol) was added with stirring. The solution was warmed to reflux for 24 h, followed by solvent removal. The product was extracted with Et_2O, reduced in volume, and placed on a Florisil column. A yellow band was eluted with Et_2O/hexanes. Solvent removal followed by recrystallization from cold Et_2O gave the product as a yellow solid in 30% yield. ^1H NMR data (C_6D_6): δ 10.60 (s, 1 H, C*H*CMe$_3$), 8.56, 7.98, 7.77, 7.34, 7.24, 7.19 (each a d, 1 H each, Tp ring H's, 3,5-positions), 7.05–6.80 (m, 3 H, Ar), 5.77, 5.69, 5.63 (t, 1 H each, Tp ring H's, 4-position), 3.75 (br s, 2 H C*H*Me$_2$); 2.73, 1.13 (AB_q, 1 H each, $^2J_{HH}$ = 14 Hz, $^2J_{WH}$ = 12 Hz, C*H*$_2$CMe$_3$), 1.50, 1.35 (each a s, 9 H each, CMe$_3$), 1.17, 0.75 (br s, 6 H each, CHC*Me*$_2$). ^{13}C NMR data (C_6D_6): δ 287.4 ($^1J_{CW}$ = 160 Hz, $^1J_{CH}$ = 111 Hz, *C*HCMe$_3$), 150.7–123.6 (Tp, Ar), 106.4, 105.6 104.7 ($^1J_{CH}$ = 177 Hz, Tp ring C's, 4-position), 62.9 ($^1J_{CW}$ = 98 Hz, $^1J_{CH}$ = 115 Hz, *C*H$_2$CMe$_3$), 46.4, 34.4 (*C*Me$_3$), 35.5, 34.6 ($^1J_{CH}$ = 125 Hz, C*Me*$_3$), 27.0 ($^1J_{CH}$ = 129 Hz, CHMe$_2$), 25.6, 23.7 ($^1J_{CH}$ = 125 Hz, CH*Me*$_2$). Mp: 212–214 °C dec. Anal. Calcd for $C_{31}H_{48}BN_7W$: C, 52.19; H, 6.78; N, 13.75. Found: C, 52.02; H, 6.91; N, 13.53.

[TpW(CHCMe$_3$)(NPh)(Et$_2$O)][BAr*$_4$] (8). A solution of HBAr*$_4$·2OEt$_2$ (0.32 g, 0.32 mmol) in 10 mL of Et_2O was added to a stirring solution of 5 (0.20 g, 0.32 mmol) in 30 mL of Et_2O. The mixture became slightly darker over a 12-h period. Filtration followed by solvent removal gave the crude product as a gold solid in 72% yield. The product can be recrystallized from Et_2O/pentane. The product was obtained as a 4:1 mixture of isomers due to rotation of the alkylidene ligand. ^1H NMR data for the major rotamer (CD_2Cl_2): δ 11.04 (s, 1 H, C*H*CMe$_3$), 8.30, 8.00, 7.92, 7.85, 7.64, 7.62 (each a d, 1 H each, Tp ring H's, 3,5-positions), 7.75 (s, 8 H, *o*-Ar*), 7.58 (s, 4 H, *p*-Ar*), 7.42 (t, 2 H, *m*-Ph), 7.28 (t, 1 H, *p*-Ph), 6.97 (d, 2 H, *o*-Ph), 6.61, 6.38, 6.34 (t, 1 H each, Tp ring H's, 4-position), 4.11 (qAB_q, 4 H, $^2J_{HH}$ = 12 Hz, $^3J_{HH}$ = 7 Hz, O(C*H*$_2$CH$_3$)$_2$), 1.36 (s, 9 H, CMe$_3$), 1.33 (t, 6H, $^3J_{HH}$ = 7 Hz, O(CH$_2$C*H*$_3$)$_2$). ^{13}C NMR data for the major rotamer (CD_2Cl_2): δ 304.6 ($^1J_{CW}$ = 154 Hz, $^1J_{CH}$ = 118 Hz, *C*HCMe$_3$), 162.2 ($^1J_{BC}$ = 50 Hz, ipso-Ar*), 153.0–107.0 (Ph, Ar*, Tp), 125.1 ($^1J_{FC}$ = 270 Hz, CF_3), 78.9 ($^1J_{CH}$ = 151 Hz, O(*C*H$_2$CH$_3$)$_2$), 48.2 (*C*Me$_3$), 34.2 ($^1J_{CH}$ = 125 Hz, C*Me*$_3$), 13.3 ($^1J_{CH}$ = 127 Hz, O(CH$_2$*C*H$_3$)$_2$). ^1H NMR data for the minor rotamer (CD_2Cl_2): δ 11.18 (s, 1 H, C*H*CMe$_3$), 8.03, 7.96, 7.93, 7.83, 7.78, 7.71 (each a d, 1 H each, Tp ring H's, 3,5-positions), 7.75 (s, 8 H, *o*-Ar*), 7.58 (s, 4 H, *p*-Ar*), 7.50 (t, 2 H, *m*-Ph), 7.30 (t, 1 H, *p*-Ph), 7.16 (d, 2 H, *o*-Ph), 6.56, 6.43, 6.32 (t, 1 H each, Tp ring H's, 4-position), 4.34 (qAB_q, 4 H, $^2J_{HH}$ = 14 Hz, $^3J_{HH}$ = 7 Hz, O(C*H*$_2$CH$_3$)$_2$), 1.43 (t, 6H, $^3J_{HH}$ = 7 Hz, O(CH$_2$C*H*$_3$)$_2$), 0.83 (s, 9 H, CMe$_3$). ^{13}C NMR data for the minor rotamer (CD_2Cl_2): δ 301.3 ($^1J_{CH}$ = 124 Hz, *C*HCMe$_3$), 162.2 ($^1J_{BC}$ = 50 Hz, ipso-Ar*), 153.0–107.0 (Ph, Ar*, Tp), 125.1 ($^1J_{FC}$ = 270 Hz, CF_3), 80.9 ($^1J_{CH}$ = 151 Hz, O(*C*H$_2$CH$_3$)$_2$), 46.0 (*C*Me$_3$), 33.6 ($^1J_{CH}$ = 124 Hz, C*Me*$_3$), 13.9 ($^1J_{CH}$ = 126 Hz, O(CH$_2$*C*H$_3$)$_2$). An NOE study was conducted on the major rotamer of 8. CHC*Me*$_3$ (Irr.): *o*-Ph, 7.1%; C*H*CMe$_3$, 19.8%. C*H*CMe$_3$ (Irr.): CHC*Me*$_3$, 1.3%. Mp: 165–168 °C dec. Anal. Calcd for $C_{56}H_{47}B_2F_{24}N_7OW$: C, 44.97; H, 3.17; N, 6.56. Found: C, 44.82; H, 3.25; N, 6.50.

[TpW(CHCMe$_3$)(NPh)(i-Pr$_2$O)][BAr*$_4$] (9). HBAr*$_4$·2OEt$_2$ (0.65 g, 0.64 mmol) was dissolved in 20 mL of i-Pr$_2$O, followed by solvent removal and drying under reduced pressure for 2 h. The acid was redissolved in 20 mL of i-Pr$_2$O and added to a stirring solution of 5 (0.50 g, 0.80 mmol) in 20 mL of i-Pr$_2$O. The mixture became slightly darker after addition and was allowed

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to stir for 1 h. The solution was filtered and reduced in volume by half, and 50 mL of pentane was added, resulting in precipitation of a gold microcrystalline solid in 82% yield. The product can be recrystallized from i-Pr_2O/pentane. ^1H NMR data (CD_2Cl_2; 0 °C): δ 10.98 (s, 1 H, C*H*CMe$_3$), 8.38, 8.00, 7.90, 7.79, 7.64, 7.59 (each a d, 1 H each, Tp ring H's, 3,5-positions), 7.73 (s, 8 H, *o*-Ar*), 7.57 (s, 4 H, *p*-Ar*), 7.35 (t, 2 H, *m*-Ph), 7.22 (t, 1 H, *p*-Ph), 6.82 (d, 2 H, *o*-Ph), 6.58, 6.31, 6.29 (t, 1 H each, Tp ring H's, 4-position), 4.30 (br sept, 2 H, O(C*H*Me$_2$)$_2$), 1.48, 1.22 (each a d, 6 H each, O(CH*Me*$_2$)$_2$), 1.34 (s, 9 H, CMe$_3$). ^{13}C NMR data (CD_2Cl_2; 0 °C): δ 303.8 ($^1J_{CW}$ = 155 Hz, $^1J_{CH}$ = 115 Hz, *C*HCMe$_3$), 162.0 ($^1J_{BC}$ = 50 Hz, ipso-Ar*), 152.8–107.1 (Ph, Ar*, Tp), 125.1 ($^1J_{FC}$ = 271 Hz, CF_3), 80.7 (O(*C*HMe$_2$)$_2$), 48.8 (*C*Me$_3$), 34.1 ($^1J_{CH}$ = 125 Hz, C*Me*$_3$), 23.1, 20.5 ($^1J_{CH}$ = 126 Hz, O(CH*Me*$_2$)$_2$). Mp: 130–135 °C dec. Anal. Calcd for $C_{58}H_{51}B_2F_{24}N_7OW$: C, 45.72; H, 3.37; N, 6.43. Found: C, 45.68; H, 3.33; N, 6.19.

[TpW(CHCMe$_3$)(NPh)(NCMe)][BAr*$_4$] (10). A solution of **9** (0.30 g, 1.97 mmol) in 20 mL of CH_3CN was prepared and stirred for 6 h. Solvent removal gave the product as a gold solid in 87% yield. The product was obtained as a 6:1 mixture of isomers due to rotation of the alkylidene ligand. ^1H NMR data for the major rotamer ($CDCl_3$): δ 11.67 (s, 1 H, C*H*CMe$_3$), 8.09, 7.85, 7.82, 7.78, 7.74, 7.55 (each a d, 1 H each, Tp ring H's, 3,5-positions), 7.72 (s, 8 H, *o*-Ar*), 7.53 (s, 4 H, *p*-Ar*), 7.47–7.02 (m, 5 H, Ph), 6.42, 6.39, 6.24 (t, 1 H each, Tp ring H's, 4-position), 2.45 (s, 3 H, NCMe), 1.37 (s, 9 H, CMe$_3$). ^{13}C NMR data for the major rotamer ($CDCl_3$): δ 314.8 ($^1J_{CW}$ = 143 Hz, $^1J_{CH}$ = 112 Hz, *C*HCMe$_3$), 161.7 ($^1J_{BC}$ = 50 Hz, ipso-Ar*), 153.0–106.9 (Ph, Ar*, Tp, N*C*Me), 124.5 ($^1J_{FC}$ = 271 Hz, CF_3), 48.5 (*C*Me$_3$), 33.3 ($^1J_{CH}$ = 126 Hz, C*Me*$_3$), 3.6 ($^1J_{CH}$ = 139 Hz, NC*Me*). ^1H NMR data for the minor rotamer ($CDCl_3$): δ 11.81 (s, 1 H, $^2J_{HW}$ = 10 Hz, C*H*CMe$_3$), 7.93–7.02 (m, 23 H, Tp ring H's, 3,5-positions, Ar*, Ph), 6.46, 6.40, 6.37 (t, 1 H each, Tp ring H's, 4-position), 2.48 (s, 3H, NCMe), 0.78 (s, 9 H, CMe$_3$). ^{13}C NMR data for the minor rotamer ($CDCl_3$): δ 307.7 (*C*HCMe$_3$), 161.7 ($^1J_{BC}$ = 50 Hz, ipso-Ar*), 153.0–106.9 (Ph, Ar*, Tp, NCMe), 124.5 ($^1J_{FC}$ = 271 Hz, CF_3), 46.6 (*C*Me$_3$), 32.1 ($^1J_{CH}$ = 126 Hz, C*Me*$_3$), 3.7 ($^1J_{CH}$ = 139 Hz, NC*Me*). Mp: 135–140 °C dec. Anal. Calcd for $C_{54}H_{40}B_2F_{24}N_8W$: C, 44.35; H, 2.76; N, 7.66. Found: C, 44.53; H, 2.81; N, 7.39.

TpW(CHCMe$_3$)(NPh)(Cl) (11). To a solution of **5** (0.40 g, 0.64 mmol) in 50 mL of Et_2O was added 0.64 mL of a 1 M solution of HCl in Et_2O. The mixture was stirred for 4 h, during which time a yellow precipitate formed. After solvent removal the product was redissolved in CH_2Cl_2 and filtered. Solvent removal gave the product as a yellow solid in 76% yield. The product can be recrystallized from CH_2Cl_2/Et_2O. ^1H NMR data (CD_2Cl_2): δ 10.62 (s, 1 H, C*H*CMe$_3$), 8.35, 7.92, 7.83, 7.77, 7.73 (each a d, 1:1:2:1:1 H, Tp ring H's, 3,5-positions), 7.32 (t, 2 H, *m*-Ph), 7.16 (t, 1 H, *p*-Ph), 7.14 (d, 2 H, *o*-Ph), 6.38, 6.36, 6.21 (t, 1 H each, Tp ring H's, 4-position), 1.37 (s, 9 H, CMe$_3$). ^{13}C NMR data (CD_2Cl_2): δ 298.7 ($^1J_{CW}$ = 149 Hz, $^1J_{CH}$ = 117 Hz, *C*HCMe$_3$), 155.2 (ipso-Ph), 147.2, 143.7, 142.8, 136.6, 135.5, 135.0 ($^1J_{CH}$ = 188 Hz, Tp ring C's, 3,5-positions), 128.6, 126.5, 126.0 ($^1J_{CH}$ = 161 Hz, Ph), 106.9, 106.1, 106.0 ($^1J_{CH}$ = 179 Hz, Tp ring C's, 4-position), 46.6 (*C*Me$_3$), 34.3 ($^1J_{CH}$ = 125 Hz, C*Me*$_3$). Anal. Calcd for $C_{20}H_{25}BClN_7W$: C, 40.47; H, 4.24; N, 16.52. Found: C, 40.24; H, 4.19; N, 16.27.

[TpW(CH$_2$CMe$_2$Ph)(NHPh)(O)][BF$_4$] (12). A mixture of 0.02 mL of water (0.02 g, 1.1 mmol) and 2.25 mL of a 0.67 M Et_2O solution of HBF_4 (1.5 mmol) in 10 mL of Et_2O was prepared and added to a solution of **6** (0.88 g, 1.2 mmol) in 40 mL of Et_2O. The resulting mixture was stirred for 12 h, during which time a yellow precipitate formed. After solvent removal the product was redissolved in CH_2Cl_2 and filtered. Solvent removal and trituration with pentane and Et_2O gave the product as a greenish-yellow solid in 80% yield. ^1H NMR data (CD_2Cl_2): δ 8.17, 7.83, 7.82, 7.81, 7.78, 7.71 (each a d, 1 H each, Tp ring H's, 3,5-positions), 7.50–7.00 (m, 10 H, Ph), 6.42, 6.35, 6.25 (t, 1 H each, Tp ring H's, 4-position), 3.07, 2.85 (AB$_q$, 1 H each, $^2J_{HH}$ = 14 Hz, $^2J_{WH}$ = 11 Hz, C*H*$_2$(CH$_3$)$_2$Ph), 1.72, 1.60 (each a s, 3 H each, C*Me*$_2$Ph). ^{13}C NMR data (CD_2Cl_2): δ 153.0, 152.3 (ipso-Ph), 145.9, 144.8, 137.8, 135.3 (1:2:1:2, Tp ring C's, 3,5-positions), 130.5, 130.3, 128.7, 128.3, 126.6, 125.9 (Ph), 107.4, 107.3, 107.2 (Tp ring C's, 4-position), 86.1 ($^1J_{CW}$ = 92 Hz, *C*H$_2$CMe$_2$Ph), 44.3 (*C*Me$_2$Ph), 34.4, 31.3 (C*Me*$_2$Ph). ^{19}F NMR (CD_2Cl_2; $CFCl_3$): δ −148.8 (BF_4). MS: M$^+$ = 638 for TpW(CH$_2$CMe$_2$Ph)(NHPh)(O)$^+$. IR (Nujol) ν_{NH} = 3122.5 cm^{-1}, ν_{BH} = 2535.4 cm^{-1}, ν_{WO} = 880 cm^{-1} (br). Anal. Calcd for $C_{25}H_{29}B_2F_4N_7OW \cdot 0.5C_4H_{10}O$: C, 42.55; H, 4.50; N, 12.87. Found: C, 42.90; H, 4.45; N, 13.17.

TpW(CH$_2$CMe$_2$Ph)(NPh)(O) (13). To a stirring solution of **12** (0.28 g, 0.39 mmol) in 20 mL of CH_2Cl_2 was added NEt_3 (0.73 g, 0.72 mmol), resulting in a color change to bright yellow. The solution was stirred for 30 min, followed by solvent removal. The residue was extracted with pentane, which was removed under reduced pressure, giving the product as a yellow solid in 81% yield. ^1H NMR data ($CDCl_3$): δ 8.01, 7.94, 7.88, 7.73, 7.69, 7.66 (each a d, 1 H each, Tp ring H's, 3,5-positions), 7.55–6.97 (m, 10 H, Ph), 6.29, 6.23, 6.22 (t, 1 H each, Tp ring H's, 4-position), 2.67, 2.22 (AB$_q$, 1 H each, $^2J_{HH}$ = 14 Hz, $^2J_{WH}$ = 9 Hz, C*H*$_2$(CH$_3$)$_2$Ph), 1.74, 1.69 (each a s, 3 H each, C*Me*$_2$Ph). ^{13}C NMR data ($CDCl_3$): δ 155.3, 154.2 (ipso-Ph), 144.6, 144.5, 143.9, 136.2, 134.8, 134.6 (Tp ring C's, 3,5-positions), 128.1, 127.7, 126.2, 125.7, 125.4, 124.9 (Ph), 106.3, 106.0, 105.9 (Tp ring C's, 4-position), 72.2 ($^1J_{CW}$ = 111 Hz, *C*H$_2$CMe$_2$Ph), 42.5 (*C*Me$_2$Ph), 33.2, 32.0 (C*Me*$_2$Ph). IR (Nujol) ν_{BH} = 2484.2 cm^{-1}; $\nu_{W=O}$ = 911.8 cm^{-1}. Anal. Calcd for $C_{35}H_{40}BN_7W$: C, 47.12; H, 4.43; N, 15.39. Found: C, 47.07; H, 4.44; N, 15.39.

Deuteration Studies of 5 and 6. A solution of **5** (0.10 g, 0.16 mmol) in 10 mL of Et_2O was cooled to −78 °C, and 0.26 mL of a 0.62 M Et_2O solution of CF_3COOD was added with stirring. The cooling bath was removed, and the reaction mixture was warmed to ambient temperature. After 30 min, the solvent was removed in vacuo, yielding a yellow solid. ^1H NMR indicated a 6.1:1 ratio of proton to deuterium substitution on the alkylidene.

A similar deuteration experiment was performed on compound **6**. ^1H NMR indicated a 6.5:1 ratio of proton to deuterium substitution on the alkylidene.

Polymerization Studies. Compounds **5**, **6**, **7**, and **11** catalyzed the ROMP of cyclooctene when combined with $AlCl_3$. In a typical reaction, $AlCl_3$ (0.008 g, 0.06 mmol) was added to a neat stirring solution of cyclooctene (1.69 g, 15.3 mmol) and catalyst **5** (0.019 g, 0.03 mmol) at ambient temperature. The solution became viscous, and stirring ceased within 5 min. After 24 h, the sample was dissolved in 20 mL of toluene, precipitated in methanol, filtered, and dried in vacuo, giving 1.47 g of polyoctenomer (87% yield, 70% trans). In general the polymer yields varied between 70 and 87%.

Results and Discussion

Alkylation of the tungsten(VI) imido complexes, W(NAr)(Et$_2$O)Cl$_4$ (**3**, Ar = Ph; **2**, Ar = 2,6-i-$Pr_2C_6H_3$),[9a,14] followed by addition of the anionic tris-chelating ligand hydridotris(1-pyrazolyl)borate (Tp), yields air- and thermally-stable alkyl alkylidene imido complexes of the type TpW(CHCMe$_2$R)(CH$_2$CMe$_2$R)(NAr) [**5**, R = Me, Ar = Ph; **6**, R = Ph, Ar = Ph; **7**, R = Ph, Ar = 2,6-i-$Pr_2C_6H_5$; eq 1]. A related product was reported for the addition of

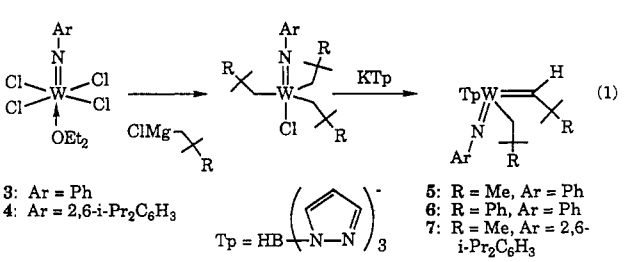

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Table I. Alkylidene ^1H and ^{13}C NMR Data for Compounds 5–9

	δ_H	δ_C	J_{CH}	J_{CW}
5	10.33	283.3	112	153
6	10.45	281.0	113	154
7	10.60	287.4	111	160
8 major	11.04	304.6	118	154
minor	11.18	301.3	124	
9	10.98	303.8	115	155
10 major	11.67	314.8	112	143
minor	11.81	307.7		
11	10.62	298.7	117	149

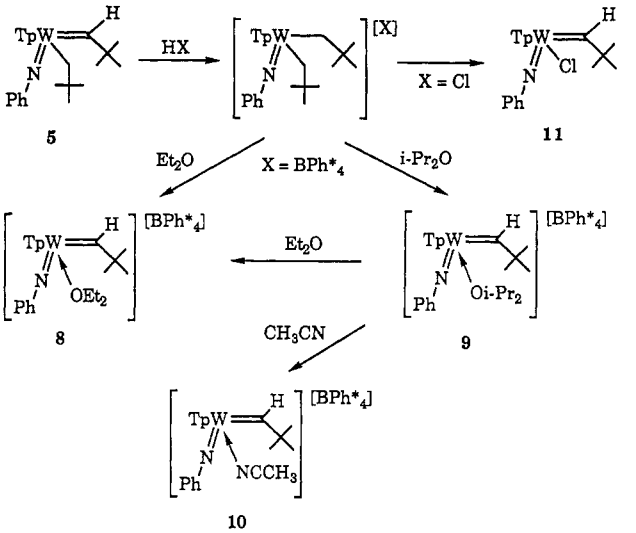
NaCp to $W(NPh)(CH_2CMe_3)_3Cl$.[9] The reaction is believed to proceed via ligand coordination and concomitant α-hydrogen abstraction to give the product shown and 1 equiv of either neopentane or *tert*-butylbenzene. The syntheses of the intermediate trisalkyl imido complexes have also been reported.[9,14] Though these intermediate complexes are isolable, it was found that addition of KTp to the crude alkylation product did not adversely affect the overall yield. Thus the reaction in eq 1 represents a facile (esssentially one-pot) procedure for the synthesis of compounds **5–7** in moderate yields.

As stated, each of these alkyl alkylidene complexes is air stable indefinitely in solution and as a solid, mirroring the stability of other high oxidation state tungsten alkylidene complexes reported by this group.[3,8] This enhanced stability relative to the preponderance of other reported high oxidation state alkylidene complexes[16] is due to the fact that they are coordinatively and electronically saturated (assuming donation of the lone electron pair on the imido nitrogen to tungsten). In this regard, they display the enhanced stability associated with other six coordinate, 18 e^- alkylidene complexes.[9b] Furthermore, additional stability is attributable to the rigid octahedral geometry demanded by the Tp ligand.[15]

The characterization of compounds **5–7** by ^1H and ^{13}C NMR is in accord with results reported previously for tungsten(VI) alkylidene complexes[16] (see Table I). Signals for the alkylidene protons range from 10.33 to 10.60 ppm, with alkylidene carbon chemical shift values varying from 281.0 to 287.4 ppm ($^1J_{CH}$ = 111–113 Hz). Considering that these complexes are formed via α-hydrogen abstraction, it is conceivable that further α-hydrogen exchange might lead to loss of a second equivalent of alkane to give an alkylidyne complex.[17] Alternatively, rapid hydrogen exchange at elevated temperatures would result in equilibration of the α-hydrogens of the alkyl and alkylidene groups.[18] However, warming a sample of **5** in C_6D_5Br to 160 °C demonstrated no evidence of reaction, decomposition, or broadening of signals by ^1H NMR.

Complexes **5–7** do not react with olefins in the absence of a Lewis acid. However, mixtures of each of these complexes and $AlCl_3$ have been shown to catalyze the ring-opening metathesis polymerzation (ROMP) of cyclooctene. As these compounds are coordinatively saturated, an attractive mechanism for this reaction involves abstraction of the alkyl group by $AlCl_3$, thereby reducing the electron count at the metal center as well as creating a coordination site for olefin binding. Such a ligand abstraction mechanism has been postulated for other coordinatively saturated metal catalysts requiring a Lewis acid cocatalyst.[19] The results of the protonation studies described below suggest that this is probably not the mechanism of catalyst activation since compound **9** is not a ROMP catalyst.

Scheme I



The possibility that catalyst activation involving Lewis acid complexing with the lone electron pair on the imido nitrogen[20] may also be considered. A major drawback of this mechanism is the necessity of invoking a seven-coordinate intermediate. Such complexes are known though uncommon for Tp complexes of tungsten.[15,21] Attempts to isolate or identify by NMR the active catalytic species have been unsuccessful, and the mechanism of catalyst activation remains unclear.

Protonation of $TpW(NPh)(CHCMe_3)(CH_2CMe_3)$ (**5**) with hydrochloric acid results in net loss of neopentane and chloride coordination to yield $TpW(NPh)(CHCMe_3)Cl$ (**11**; Scheme I). A similar product was reported for the protonation of the analogous Cp complex.[9a] However, protonation of **5** with $HBAr^*_4{\cdot}2Et_2O$ (Ar^* = 3,5-$C_6H_3(CF_3)_2$), an acid having a weakly coordinating counterion, yields the cationic Et_2O solvento complex, $[TpW(NPh)(CHCMe_3)(Et_2O)][BAr^*_4]$ (**8**; Scheme I). The only observed product is **8**, even when the reaction is conducted in the presence of potentially coordinating ligands such as olefins and alkynes. The product is air stable as a solid and can be warmed to reflux in THF with no evidence of decomposition or THF substitution. We ascribe this unusual lack of reactivity to the extraordinary electrophilicity of the $[TpW(NPh)(CHCMe_3)]^+$ fragment.

The ^1H NMR spectrum of **8** shows a 4:1 mixture of isomers due to rotation about the tungsten–carbon double bond.[22] NOE studies of the major isomer shows enhancement (7.1%) of the ortho protons of the phenylimido group when the *tert*-butyl signal is irradiated. As no enhance-

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(21) Caffyn, A. J. M.; Feng, S. G.; Dierdorf, A.; Gamble, A. S.; Eldredge, P. A.; Vossen, M. R.; White, P. S.; Templeton, J. L. *Organometallics* **1991**, *10*, 2842.
(22) (a) Schrock, R. R.; Crowe, W. E.; Bazan, G. C.; DiMare, M.; O'Regan, M. B.; Schofield, M. H. *Organometallics* **1991**, *10*, 1832. (b) Oskam, J. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1992**, *114*, 7588.

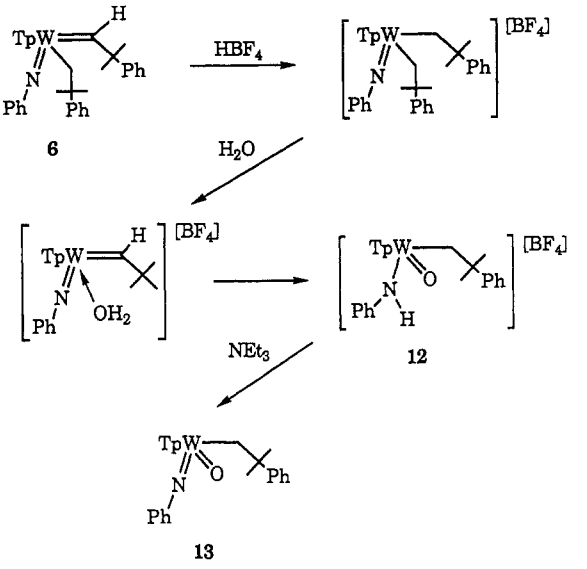
ment is observed when the alkylidene proton is irradiated, the major isomer is believed to be the syn-rotamer, which has the *tert*-butyl group proximal to the imido group. The signals for the diastereotopic methylene protons of the coordinated ether appear as a single set of AB quartets of quartets (AB portion of an ABX_3 spin system), indicating that the ether rotates freely, but does not dissociate on the NMR time scale. The corresponding neophylidene complex was observed by ^1H NMR during the protonation of **6**; however the complex was not isolable.

Protonation of **5** in diisopropyl ether solution yields the analogous i-Pr_2O adduct, [TpW(NPh)(CHCMe$_3$)(i-Pr_2O)][BAr*$_4$] (**9**; Scheme I). In contrast to the diethyl ether adduct, compound **9** shows some thermal instability in solution, decomposing within hours in CD_2Cl_2 solution at ambient temperature, though it is stable for an indefinite period as a solid. Only one alkylidene rotamer appears in the ^1H NMR spectrum, perhaps due to the increased steric constraint of the complexed i-Pr_2O versus Et_2O. However, the isopropyl methyl groups appear as a pair of doublets, indicating free rotation on the NMR time scale.

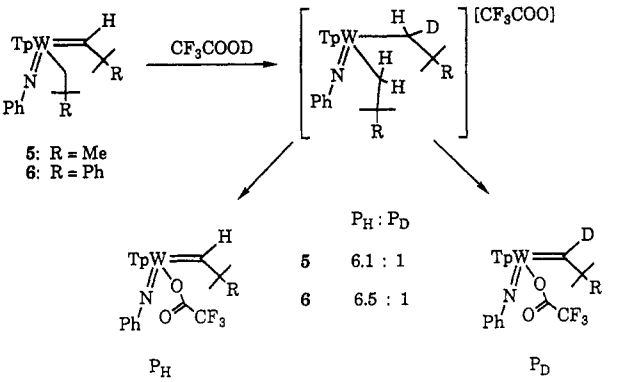
The i-Pr_2O group proved more labile than Et_2O, with compound **9** converting to **8** when stirred in Et_2O at room temperature. Dissolution of **9** in acetonitrile results in formation of the CH_3CN adduct, [TpW(NPh)(CHCMe$_3$)(CH$_3$CN)][BAr*$_4$] (**10**, Scheme I). As with **8**, the acetonitrile complex is air and thermally stable as a solid and in solution. The complex may be warmed to reflux in acetonitrile with no evidence of decomposition. Compound **10** also proved to be inert to substitution, suggesting that the lability of these relatively weak donor ligands may be closely related to their relative size. Attempts to catalyze olefin metathesis[23] with any of these cationic alkylidene complexes met with no success, a surprising result particularly in the case of the labile diisopropyl ether adduct. A tendency to decompose in solution, even in the presence of olefin, combined with poor solubility in neat monomer are stumbling blocks for the use of **9** as a metathesis catalyst. To date, protonation reactions conducted in the presence of olefins have not demonstrated any tendency toward metathesis.

Addition of HBF_4 to compound **6** in the presence of 1 equiv of H_2O results in the formation of what is characterized as a cationic amido oxo alkyl complex, [Tp(NHPh)(O)(CH$_2$CMe$_2$Ph)][BF_4] (**12**). No other products are observed. Because the amido signal in the ^1H NMR cannot be located (it is believed to resonate under the phenyl region),[24] we have relied on other spectroscopic evidence for characterization. Compound **6** shows a strong W=N stretch at 1360 cm^{-1}, which is absent in **12** and is replaced by a W=O stretch at 880 cm^{-1}. A weak NH stretch at 3122 cm^{-1} coupled with the somewhat low energy W=O stretch may indicate some intramolecular hydrogen bonding between the amido proton and the oxo group. Mass spectroscopy identifies the parent ion peak of the cation at 638 mu. ^{19}F NMR shows the presence of BF_4 anion. Further, compound **12** can be deprotonated by NEt_3 to yield the neutral oxo imido species, Tp(NPh)(O)(CH$_2$CMe$_2$Ph) (**13**; Scheme II). Attempts to obtain crystals of

Scheme II



Scheme III



12 that are suitable for a single-crystal X-ray diffraction study have been unsuccessful. This reaction sequence may be viewed as a possible pathway for hydrolytic decomposition of these cationic alkylidene complexes.[25]

One possible mechanism (Scheme II) for formation of **12** involves protonation of the alkylidene carbon followed by α-hydrogen abstraction and loss of *tert*-butylbenzene. Coordination of H_2O, followed by proton transfer, would generate compound **12**. Attack of the proton at the alkylidene carbon is postulated based on a theoretical study by Cundari and Gordon[26] which indicates the HOMO of an alkylidene imido complex resides there. A deuteration study was performed to ascertain the mechanism of protonation (Scheme III).

Addition of 1 equiv of CF_3COOD to compound **5** resulted in a 6.1:1 (P_H:P_D) mixture of proton to deuterium substitution at the alkylidene carbon. A 6.5:1 (P_H:P_D) mixture was observed for the deuteration of **6**. If deuterium attack occurred at the alkylidene carbon, a product ratio of 3:1 (P_H:P_D) would be expected in the absence of a kinetic isotope effect. A normal kinetic isotope effect would only decrease the product ratio, with a lower limit of 2:1 for no deuterium transfer ($k_H \gg k_D$).[27] The somewhat high P_H:P_D ratios may be explained by a site selectivity for protonation/deuteration in conjunction with a site selectivity for α-hydrogen/deuterium transfer or by

(23) Grubbs, et al., have reported that W(CHC$_6$H$_4$OMe)(NAr)(OCMe(CF$_3$)$_2$)$_2$(THF) polymerizes norbornene and cyclooctene, presumably via initial loss of THF (see ref 2). Muetterties and Band have shown that the diethyl ether adduct of CH_3WOCl_3 is an olefin metathesis catalyst precursor, with the proposed intermediate being CH_2WOCl_2. Muetterties, E. L.; Band, E. *J. Am. Chem. Soc.* **1980**, *102*, 6572.

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(26) Cundari, T. R.; Gordon, M. S. *Organometallics* **1992**, *11*, 55.

an inverse isotope effect. Because the metal center is chiral, is it not unreasonable to assume attack on one enantioface of the alkylidene should be preferred. Further, the α-protons on the resulting bisalkyl complex intermediate would be diastereotopic pairs which might have different proclivities toward α-H transfer. Finally, deuterium attack at the imido nitrogen would result in formation of only the product P_H. Thus the high P_H:P_D ratio could also be explained by a partitioning of the deuterium attack between the alkylidene and the imido groups.

Given the results of the deuteration experiments, we conclude that proton attack at the alkylidene carbon must be occurring at least to some extent. The only other source of deuterium incorporation into the products would be by an exchange reaction between the product P_H and excess CF_3COOD. We can rule out this possibility because P_H exchanges its alkylidene α-H atom with excess CF_3COOD much more slowly than the protonation reaction ($t_{1/2}$ = 24 h for exchange) and because the reactions were carried out with stoichiometric amounts of acid. Unfortunately, these studies give no information regarding the extent of potential competing mechanisms which involve protonation of the imido nitrogen or direct protonation of the alkyl group neither of which would result in product P_D.

(27) (a) The ratio of P_H:P_D does not directly correspond to the ratio k_H:k_D because P_D is formed by α-H abstraction while P_H is formed by either H or D abstraction. The expected isotope effect (k_H:k_D) for an α-H abstraction reaction is on the order of 6.[27b] If k_H:k_D were 6 in the reaction in scheme 3, a product ratio, P_H:P_D, of 2.16 would have been observed. (b) Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3210.

Conclusion

The kinetic stability of the complexes reported in this paper undoubtedly arises from a combination of the bulky nature of the Tp ligand, its ability to enforce an octahedral coordination sphere, and the inertness to Tp substitution demanded by the chelate effect. This stability will facilitate the further development of the chemistry of the cationic alkylidene complexes, while it may inhibit the use of compounds **5–7** as metathesis catalysts. These properties also explain why the observed chemistry is initiated by attack of reagents at the ligands rather than at the metal center. Further work is in progress exploring the use of other polydentate ligands for related chemistry.

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