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Formation and Reactivity of a Cationic Alkylidene–Aryl Complex of Tungsten

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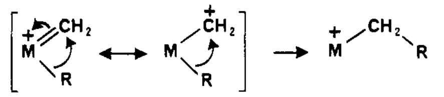
Reaction of $[W(\eta\text{-}C_5H_5)_2(CH_3)_2]$ with NH_4I in THF allows convenient access to the valuable synthetic intermediate $[W(\eta\text{-}C_5H_5)_2(CH_3)I]$ (**1**). Treatment of **1** with PhMgBr gives $[W(\eta\text{-}C_5H_5)_2(CH_3)Ph]$ (**2**), which can be oxidized to $[W(\eta\text{-}C_5H_5)_2(CH_3)Ph]PF_6$ (**3**) with ferrocenium hexafluorophosphate. The 17-electron cation in **3** can be reduced back to **2**. Treatment of **3** with the trityl radical in acetonitrile generates $[W(\eta\text{-}C_5H_5)_2(CH_2Ph)(NCCH_3)]PF_6$ (**4**), in a reaction proposed to involve initial hydrogen atom abstraction from **3** to give $[W(\eta\text{-}C_5H_5)_2(CH_2)Ph]^+$. Migratory insertion within this cationic methylidene–aryl complex then generates a 16-electron benzyl complex, which forms a stable solvent adduct. Adduct **4** can also be prepared by solvolysis of $[W(\eta\text{-}C_5H_5)_2(C_2H_4)(CH_2Ph)]PF_6$. The reaction of **3** with trityl radical in CH_2Cl_2 gives the paramagnetic compound $[W(\eta\text{-}C_5H_5)_2(CH_2Ph)Cl]PF_6$ (**5**). The cation in **5** can be reduced to $[W(\eta\text{-}C_5H_5)_2(CH_2Ph)Cl]$ (**6**), which can be reoxidized to **5**. It is proposed that the CH_2Cl_2 in an intermediate solvato–benzyl complex analogous to **4** is activated toward further reaction with the trityl radical. The intermediate methylidene complex can also be formed by hydride abstraction from **2**, as demonstrated by the isolation of **4** when **2** is treated with the trityl cation in CH_3CN. The reaction of **2** with the trityl cation in CH_2Cl_2 gives a 1:1 mixture of **3** and **5** at room temperature and **3** at −78 °C, consistent with an electron transfer/hydrogen atom abstraction mechanism for the hydride abstraction.

Introduction

We[1] and others[2] have recently established that alkylidene ligands in cationic alkylidene–alkyl complexes can readily insert into cis metal–alkyl bonds to give complexes of homologous alkyl ligands (eq 1).



(1)

Obvious analogies exist between alkylidene–alkyl insertion and two other well-known reactions: the metallacarbonium ion representation of a cationic alkylidene complex leads to a description of the insertion as a 1,2-alkyl shift comparable to Wagner–Meerwein rearrangement of a carbonium ion,[3] while the acceleration of the reaction in a complex containing an alkylidene ligand rendered electrophilic by a positive charge on the metal center[4] (or by an electron-withdrawing zirconoxy substituent in neutral niobium carbene complexes[5]) suggests a parallel with the migratory insertion of a carbonyl ligand into a metal–alkyl bond, since the acceleration is consistent with the alkyl group migrating on to the unsaturated carbon with its bonding electron pair.

The Wagner–Meerwein model suggests that aryl groups should migrate to electrophilic alkylidene ligands at least as readily as alkyl groups, since in carbonium ions aryl groups migrate in preference to alkyl groups as a consequence of the ability of the aromatic p orbital on the ipso carbon to interact simultaneously with the carbons at both termini of the migration. The carbonyl–alkyl insertion model, however, does not predict that alkylidene–aryl insertion is necessarily facile, since carbonyl–aryl insertion is slower than carbonyl–alkyl insertion, possibly as a result of the greater strength of metal–aryl bonds.[6]

Alkylidene–aryl insertion was not observed in systematic studies of the neutral niobium carbene system, and Bercaw concluded that insertion into a metal–aryl bond either did not occur or was readily reversible and thermodynamically unfavorable.[5] The metallacarbonium ion model does not, however, apply to this system, and the relevance of the results to a cationic alkylidene–aryl complex is unclear. We therefore decided to investigate the feasibility of alkylidene–aryl insertion in the cationic tungstenocene system in which we had observed alkylidene–alkyl insertion; we now wish to report that insertion to give benzyl–solvato complexes is facile within the transient complex $[W(\eta\text{-}C_5H_5)_2(CH_2)Ph]^+$ in the polar solvents acetonitrile and dichloromethane but that the course of the reaction in CH_2Cl_2 is complicated by a subsequent radical reaction to give the 17-electron cation $[W(\eta\text{-}C_5H_5)_2(CH_2Ph)Cl]^{+\cdot}$. The results obtained are summarized in Scheme I.[7]

Experimental Section

General Data. All manipulations were conducted under a nitrogen or argon atmosphere using standard Schlenk-tube techniques or a Vacuum atmospheres Dri-lab glovebox. Glassware was oven dried or flamed under vacuum before use. Diethyl ether and tetrahydrofuran (THF) were freshly distilled from Na/benzophenone ketyl, pentane from $LiAlH_4$, and methylene chloride from CaH_2. Ligroin was dried over sodium wire. AR grade acetone, benzene, and spectrophotometric grade dimethylformamide (DMF) were used without further purification. AR grade acetonitrile was used without further purification, except that the acetonitrile used for reactions involving Ph_3CPF_6 was triply distilled: from CaH_2, P_2O_5, and then CaH_2 again. ^1H NMR spectra were recorded on a Varian FT 80 at 80 MHz. Solution

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[†] Fellow of the Alfred P. Sloan Foundation, 1982–1985.

(1) (a) Hayes, J. C.; Pearson, G. D. N.; Cooper, N. J. *J. Am. Chem. Soc.* **1981**, *103*, 4648. (b) Hayes, J. C.; Cooper, N. J. *J. Am. Chem. Soc.* **1982**, *104*, 5570. (c) Hayes, J. C.; Cooper, N. J. "Organometallic Compounds: Synthesis, Structure, Theory"; Texas A&M University Press: College Station, TX, 1983, p 353. (d) Hayes, J. C.; Jernakoff, P.; Miller, G. M.; Cooper, N. J. *Pure Appl. Chem.* **1984**, *56*, 25.

(2) (a) Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 5984. (b) Kleitzein, H.; Werner, H.; Serhadli, P; Zeigler, M. L. *Angew. Chem., Int. Ed. Engl.* **1982**, *22*, 46.

(3) Kirmse, W. *Top. Curr. Chem.* **1979**, *80*, 125.

(4) The first reported example of alkylidene–alkyl insertion involved the neutral tantalum complex $[Ta(\eta\text{-}C_5H_5)_2(CHCH_3)CH_3]$, but the reaction was not as facile and required that the complex be heated for 24 h at 75 °C: Sharp, P. R.; Schrock, R. R. *J. Organomet. Chem.* **1979**, *171*, 43.

(5) Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 2650.

(6) Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299.

(7) A preliminary account of some of this work has been published: Jernakoff, P.; Cooper, N. J. *J. Am. Chem. Soc.* **1984**, *106*, 3026.

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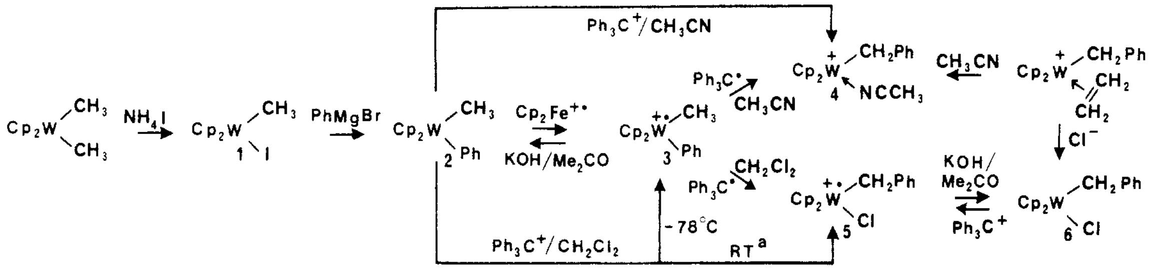
Scheme I. Formation and Reactivity of $[W(\eta\text{-}C_5H_5)_2(CH_3)Ph]PF_6$, a Potential Precursor of the Methylidene–Phenyl Complex $[W(\eta\text{-}C_5H_5)_2(CH_2)Ph]^+$ (Cp = $\eta\text{-}C_5H_5$)



[a] A comparable quantity of $[W(\eta\text{-}C_5H_5)_2(CH_3)Ph]PF_6$ is also formed in this reaction at room temperature.

EPR spectra were recorded in a 60 × 10 × 0.25 mm quartz flat cell to minimize dielectric problems on a Varian E-109 spectrometer and were calibrated against the $\langle g \rangle$ = 2.0036 resonance of 2,2-diphenyl-1-picrylhydrazyl.[8] IR spectra were obtained as KBr pellets on a Perkin-Elmer 683 spectrometer, and mass spectra were recorded with a Kratos MS-9 spectrometer. Microanalyses were performed as indicated by Schwarzkopf Microanalytical Laboratory, Woodside, NY (Sch); Galbraith Laboratories, Knoxville, TN (Gal); or Canadian Microanalytical, Vancouver, British Columbia (Can). Phenylmagnesium bromide was prepared by a literature procedure. Triphenylmethylium hexafluorophosphate (trityl hexafluorophosphate) was purchased from Alfa and recrystallized twice from acetonitrile (freshly distilled from CaH_2) at -40 °C. The recrystallized salt was stored at -40 °C in a nitrogen-filled glovebox. The dimer of the trityl radical (4-(triphenylmethyl)-1-(diphenylmethylidene)-2,5-cyclohexadiene), was prepared by a literature procedure.[9]

Bis(cyclopentadienyl)iodomethyltungsten. A dark red solution of $[W(\eta\text{-}C_5H_5)_2(CH_3)_2]$[10] (1.83 g, 5.33 mmol) and NH_4I (2.58 g, 17.8 mmol) in THF (35 mL) was stirred at 50 °C for 19 h to give an intense dark green solution. The solvent was removed under reduced pressure and the product extracted with benzene (20 mL and then 3 × 10 mL) to give a dark green solution which was filtered through a 2-cm pad of Celite 545 on a 3-cm filter frit. Ligroin (50 mL; boiling range 90–120 °C) was added and the solution concentrated under reduced pressure over 20 min to ca. 5 mL. The dark green crystals were collected by decantation and washed with ligroin (2 × 10 mL). The vacuum-dried crystals were shown to be pure $[W(\eta\text{-}C_5H_5)_2(CH_3)I]$ (2.14 g, 4.69 mmol; 88%) by comparison with an authentic sample[11] (^{1}H NMR and mass spectrum).

Bis(cyclopentadienyl)methylphenyltungsten. A solution of $[W(\eta\text{-}C_5H_5)_2(CH_3)I]$ (2.14 g, 4.69 mmol) in diethyl ether (25 mL) was treated with 20 mL of a 1.15 M solution of C_6H_5MgBr in diethyl ether (23.0 mmol). After 19 h at 45 °C the stirred mixture had changed from dark green to dark red. The solvent was removed under reduced pressure and ethanol (30 mL) slowly added at 0 °C. The ethanol was removed under reduced pressure, and water (75 mL) and toluene (150 mL) added. Vigorous shaking (20 min) gave a bright red toluene layer and a cloudy white aqueous layer. The mixture was filtered through a 3-cm pad of Celite 545 on a 5-cm filter frit and the pad washed with toluene (3 × 100 mL). The organic phase was concentrated to ca. 15 mL and then placed on a 20 × 2.7 cm column of deactivated alumina in pentane. Elution with pentane gave a dark orange band which was collected and concentrated under reduced pressure to give a bright orange powder. The biphenyl side product was removed by sublimation (3 h, 50 °C) to yield spectroscopically pure $[W(\eta\text{-}C_5H_5)_2(CH_3)Ph]$ (1.41 g, 3.47 mmol; 74%). Recrystallization from pentane at -60 °C gave analytically pure material as orange-red plates (55% recovery). Anal. Calcd for $C_{17}H_{18}W$: C, 50.26; H, 4.48. Found (Gal): C, 50.29; H, 4.17. ^{1}H NMR (80 MHz, acetone-d_6): δ 7.65–6.70 (d, 5, C_6H_5), 4.63 (s, 10, $2C_5H_5$), 0.07 (s, satellites, J_{W-H} = 5.6 Hz, 3, WCH_3). IR: 3130 w, 3125 w, 3085 w, 3055 mw, 3033 mw, 2962 mw, 2930 mw, 2890 mw, 2820 mw, 1560 m br, 1471 m, 1422 ms, 1367 mw, 1201 m, 1190 mw, 1107 s, 1068 s, 1014 vs, 994 vs, 950 m, 938 m, 899 m, 867 s br, 837 vs, 823 s, 805 s, 799 s, 779 s, 731 vs, 702 vs, 639 m, 590 m, 473 mw br, 396 m, 373 m, 343 mw br cm^{-1}. Mass spectrum (parent ion, ^{184}W): *m/e* 406.

Bis(cyclopentadienyl)methylphenyltungsten Hexafluorophosphate. This complex is sensitive to typical labortory light levels and should be handled in vessels wrapped in Al foil. A 0.014 M solution of ferrocenium hexafluorophosphate in CH_2Cl_2 (35 mL, 0.49 mmol) at -78 °C was added to an orange solution of $[W(\eta\text{-}C_5H_5)_2(CH_3)Ph]$ (0.20 g, 0.49 mmol) in CH_2Cl_2 (10 mL) at -78 °C to give an instantaneous color change to a clear dark red solution. After 2 h at -78 °C, the stirred solution was warmed to -45 °C and the solvent removed under reduced pressure (4 h). The solid was washed with 3 × 20 mL portions of toluene to give spectroscopically pure $[W(\eta\text{-}C_5H_5)_2(CH_3)Ph]PF_6$ (IR and EPR) as a brick-red powder (0.23 g, 0.42 mmol; 86%). Analytically pure material was obtained as red needles in 43% overall yield by careful concentration over ca. 30 min of a CH_3Cl_2 solution of the salt at room temperature. Anal. Calcd for $C_{17}H_{18}F_6PW$: C, 37.04; H, 3.30. Found (Gal): C, 37.07; H, 3.34. EPR (CH_2Cl_2, 25 °C, 9.439 GHz): $\langle g \rangle$ = 2.049. IR: 3133 s, 3068 w, 3052 mw, 2970 w br, 2902 w, 1571 m, 1560 w, 1438 s br, 1420 ms, 1385 m, 1337 w, 1316 w, 1304 w, 1245 w, 1211 w, 1128 w, 1070 mw, 1025 m sh, 1019 ms, 1000 m, 969 mw br, 850 vs br, 741 s, 703 ms, 552 s, 490 w, 365 mw br cm^{-1}.

Reduction of Bis(cyclopentadienyl)methylphenyltungsten Hexafluorophosphate. A dark red solution of $[W(\eta\text{-}C_5H_5)_2(CH_3)Ph]PF_6$ (0.14 g, 0.25 mmol) in acetone (15 mL) was vigorously stirred with a solution of saturated aqueous KOH (35 mL) for 0.5 h. The red-orange acetone layer was decanted off and the solvent removed under reduced pressure to give a brick-red solid. The solid was extracted with pentane (2 × 30 mL) to give a bright orange solution. Removal of the solvent from the filtered solution under reduced pressure gave an oily orange powder which was shown to be $[W(\eta\text{-}C_5H_5)_2(CH_3)Ph]$ (0.06 g, 0.15 mmol; 60 %) by comparison (^{1}H NMR) with an authentic sample.

Bis(cyclopentadienyl)(acetonitrile)benzyltungsten Hexafluorophosphate. A dark red solution of $[W(\eta\text{-}C_5H_5)_2(CH_3)Ph]PF_6$ (0.12 g, 0.22 mmol) in acetonitrile (20 mL) was added to a yellow slurry of trityl dimer[9] (0.28 g, 0.58 mmol) in acetonitrile (40 mL). The mixture was stirred at room temperature for 2.5 h to give a bright orange slurry. The orange-yellow oily solid obtained when the solvent was removed under reduced pressure was washed with diethyl ether (4 × 20 mL) to give spectroscopically (^{1}H NMR) pure $[W(\eta\text{-}C_5H_5)_2(CH_2C_6H_5)(NCCH_3)]PF_6$ as a tan powder (0.12 g, 0.20 mmol; 91%) which was dried in vacuo. Analytically pure material was obtained as brown-orange plates and rods after slow concentration of a saturated CH_2Cl_2 solution under reduced pressure (60% recovery). Anal. Calcd for $C_{19}H_{20}NF_6PW$: C, 38.60; H, 3.42. Found (Sch): C, 38.33; H, 3.52. ^{1}H NMR (80 MHz, acetone-d_6): δ 7.20–7.00 (c, 5 H, C_6H_5), 5.43 (s, 10, $2C_5H_5$), 2.81 (s, 3, CH_3CN), 2.65 (s, satellites, J_{W-H} = 8.1 Hz, 2, WCH_2). IR 3245 vw, 3125 vs, 3050 w, 3015 m, 2935 m, 2325 vw, 2286 vw, 2235 vw, 1588 s, 1565 w, 1485 s, 1440 s br, 1412 s br, 1384 ms, 1258 mw br, 1208 m, 1182 m, 1156 m, 1128, mw sh, 1116 m, 1068 m, 1018 s, 993 s, 958 m, 840 vs br, 763 vs, 738 ms, 709 vs, 558 vs cm^{-1}.

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[8] Hutchinson, C. A.; Pastor, R. L. *Phys. Rev.* **1951**, *81*, 282.

[9] (a) Copenhauer, J. W.; Roy, M. F.; Marvel, C. S. *J. Am. Chem. Soc.* **1935**, *57*, 1311. (b) McBride, J. M. *Tetrahedron* **1974**, *30*, 2009 and references therein.

[10] Benfield, F. W. S.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1974**, 1324.

[11] Cooper, N. J.; Green, M. L. H. *Chem. Soc., Dalton Trans.* **1979**, 1121.

Solvolysis of Bis(cyclopentadienyl)benzyl(ethylene)tungsten Hexafluorophosphate. A pale orange solution of $[W(\eta\text{-}C_5H_5)_2(CH_2C_6H_5)(C_2H_4)]PF_6$[12] (89 mg, 0.15 mmol) in acetonitrile (20 mL) was stirred for 48 h at 45 °C to give a darker orange solution. The solution was filtered and the solvent removed under reduced pressure to give a glassy orange solid which was shown to be $[W(\eta\text{-}C_5H_5)_2(CH_2C_6H_5)(NCCH_3)]PF_6$ (67 mg, 0.11 mmol; 73 %) by comparison with an authentic sample (^{1}H NMR and IR).

Bis(cyclopentadienyl)benzylchlorotungsten Hexafluorophosphate. A yellow solution of trityl dimer[9] (0.18 g, 0.37 mmol) in CH_2Cl_2 (15 mL) was carefully layered onto a dark red solution of $[W(\eta\text{-}C_5H_5)_2(CH_3)Ph]PF_6$ (0.11 g, 0.20 mmol) in CH_2Cl_2 (40 mL). Mixing of the layers resulted within 10 min in the deposition of black crystalline $[W(\eta\text{-}C_5H_5)_2(CH_2C_6H_5)Cl]PF_6$. The crystals were collected by decantation after 15 h, washed with CH_2Cl_2 (3 × 25 mL), and dried in vacuo (0.08 g, 0.14 mmol; 70%). Anal. Calcd for $C_{17}H_{17}ClF_6PW$: C, 34.86; H, 2.93. Found (Gal): C, 34.95; H, 2.94. EPR (acetone, 25 °C, 9.422 GHz): $\langle g \rangle = 2.006$ (t, $a_H = 4.5$ G). IR: 3138 s, 3078 vw, 2960 br vw, 2925 br vw, 1598 mw, 1489 m, 1454 m, 1444 s, 1429 s, 1387 m, 1207 w, 1187 w, 1126 m, 1080 m, 1066 w, 1030 ms, 1010 m, 921 ms, 904 ms, 879 vs br, 771 s, 740 m, 710 s, 562 vs, 365 w br, 325 w, 309 ms cm^{-1}.

Bis(cyclopentadienyl)benzylchlorotungsten. A pale orange slurry of $[W(\eta\text{-}C_5H_5)_2(CH_2C_6H_5)(C_2H_4)]PF_6$[12] (0.26 g, 0.45 mmol) and NMe_4Cl (1.10 g, 10.0 mmol) in DMF (20 mL) was stirred at 72 °C for 15 h to give a dark red solution. The solution was filtered, and diethyl ether (50 mL) and water (30 mL) were added. Vigorous shaking (10 min) produced a dark orange ether layer and a pale orange water/DMF layer. The ether layer was collected, washed with water (2 × 30 mL), filtered, and evaporated to dryness under reduced pressure to yield spectroscopically pure (^{1}H NMR) $[W(\eta\text{-}C_5H_5)_2(CH_2C_6H_5)Cl]$ as a brown crystalline solid (0.11 g, 0.25 mmol; 56%). Analytically pure material was obtained as brown plates via slow concentration of a saturated ether solution (ca. 65% recovery). Anal. Calcd for $C_{17}H_{17}ClW$: C, 46.33; H, 3.90. Found: (Can): C, 46.58; H, 3.90. ^{1}H NMR (80 MHz, acetone-d_6): δ 7.15–6.75 (c, 5, C_6H_5), 5.02 (s, 10, $2C_5H_5$), 2.49 (s, satellites, $J_{W-H} = 8.3$ Hz, 2, WCH_2). IR 3141 m, 3128 m, 3106 m, 3073 mw, 3011 mw, 2980 w, 2935 mw br, 1592 s, 1487 s, 1429 s, 1385 w, 1365 mw, 1346 w, 1207 s, 1180 m, 1155 m, 1112 ms, 1078 m, 1060 w, 1040 w, 1000 s br, 935 m br, 890 ms, 840 ms, 832 vs, 800 s, 759 vs, 704 vs, 595 m, 559 s cm^{-1}. Mass spectrum (parent ion ^{184}W): *m/e* 440.

Reduction of Bis(cyclopentadienyl)benzylchlorotungsten Hexafluorophosphate. A dark red-purple solution of $[W(\eta\text{-}C_5H_5)_2(CH_2C_6H_5)Cl]PF_6$ (84 mg, 0.14 mmol) in acetone (20 mL) was vigorously stirred with a saturated solution of aqueous KOH (10 mL) at room temperature for 0.5 h. The red-orange organic layer was decanted off and the solvent removed under reduced pressure to give a red-brown glassy solid. Extraction with CH_2Cl_2 (50 mL) gave an orange solution which was filtered and concentrated under reduced pressure to yield brown crystalline flakes shown to be $[W(\eta\text{-}C_5H_5)_2(CH_2C_6H_5)Cl]$ (46 mg, 0.10 mmol; 71%) by ^{1}H NMR comparison with an authentic sample.

Oxidation of Bis(cyclopentadienyl)benzylchlorotungsten. A 0.052 M solution of trityl hexafluorophosphate in CH_2Cl_2 (1.45 mL, 0.08 mmol) was added to a stirred dark orange methylene chloride solution (15 mL) of $[W(\eta\text{-}C_5H_5)_2(CH_2C_6H_5)Cl]$ (32 mg, 0.07 mmol). An immediate reaction produced grayish black precipitate and a yellowish solution. The precipitate was collected by decantation and washed with CH_2Cl_2. The gray-black powder obtained when the precipitate was dried under vacuum was shown to be $[W(\eta\text{-}C_5H_5)_2(CH_2C_6H_5)Cl]PF_6$ (31 mg, 0.05 mmol; 71%) by comparison with an authentic sample (IR and EPR).

Reaction of Bis(cyclopentadienyl)methylphenyltungsten with Trityl Hexafluorophosphate in Acetonitrile. A 0.012 M solution of trityl hexafluorophosphate in acetonitrile (3 mL, 0.36 mmol) was added to a stirred solution of $[W(\eta\text{-}C_5H_5)_2(CH_3)Ph]$ (13 mg, 0.032 mmol) in acetonitrile (2 mL). The orange solution immediately turned bright red but lightened to an orange color after 10 min. After 1 h the solvent was removed under reduced pressure to yield a sticky orange solid which was washed with toluene (3 × 5 mL) to leave a dull orange powder. ^{1}H NMR spectra of the vacuum dried solid showed that $[W(\eta\text{-}C_5H_5)_2(CH_2C_6H_5)(NCCH_3)]PF_6$ was the only diamagnetic tungstenocene derivative present, and integration relative to 7.3 mg of added ferrocene established that the reaction proceeded in an 83% yield.

Reaction of Bis(cyclopentadienyl)methylphenyltungsten with Trityl Hexafluorophosphate in Methylene Chloride. (a) At Room Temperature. A 0.034 M solution of trityl hexafluorophosphate in methylene chloride (5.7 mL, 0.19 mmol) was added to a stirred solution of $[W(\eta\text{-}C_5H_5)_2(CH_3)Ph]$ (79 mg, 0.19 mmol) in CH_2Cl_2. The orange solution immediately turned bright red, and a black-gray precipitate formed within 2 min. The red supernatant was separated from the precipitate by filtration after 50 min. The precipitate was washed with CH_2Cl_2 (2 × 10 mL), dried under vacuum, and shown to be $[W(\eta\text{-}C_5H_5)_2(CH_2C_6H_5)Cl]PF_6$ (47 mg, 0.08 mmol; 42%) by IR comparison with an authentic sample. The combined filtrates were concentrated under reduced pressure to give an oily red-brown solid which was washed with toluene (3 × 10 mL) to leave a brick-red powder. IR comparison with an authentic sample showed that the vacuum dried solid was $[W(\eta\text{-}C_5H_5)_2(CH_3)Ph]PF_6$ (39 mg, 0.07 mmol; 37%). **(b) At −78 °C.** A 0.04 M solution of trityl hexafluorophosphate in methylene chloride at −78 °C (15 mL, 0.60 mmol) was added to a stirred solution of $[W(\eta\text{-}C_5H_5)_2(CH_3)Ph]$ (0.25 g, 0.62 mmol) in 15 mL of CH_2Cl_2 at −78 °C. The orange solution immediately turned bright red, and a dull red precipitate formed. After 10 min the stirred suspension was warmed to −45 °C and the solvent removed under reduced pressure over a period of 3 h. Trituration with toluene at −45 °C and vacuum drying left $[W(\eta\text{-}C_5H_5)_2(CH_3)Ph]PF_6$ (0.28 g, 0.51 mmol; 82%) as a dull red powder (IR and EPR).

Results and Discussion

The cationic alkylidene–alkyl complexes in which we have previously observed insertion reactions were generated from 17-electron tungstenocene alkyls of the type $[W(\eta\text{-}C_5H_5)_2(CH_2R)R']^{+\cdot}$ by reaction with the triphenylmethyl (trityl) radical, as generated by in situ thermolysis of its dimer, 4-(triphenylmethyl)-1-(diphenylmethylidene)-2,5-cyclohexadiene.[1] It seemed probable that an analogous reaction with the 17-electron cation $[W(\eta\text{-}C_5H_5)_2(CH_3)Ph]^{+\cdot}$ would lead to an alkylidene–aryl complex, and a sequence in which $[W(\eta\text{-}C_5H_5)_2(CH_3)I]$ (**1**) is phenylated with PhMgBr and the $[W(\eta\text{-}C_5H_5)_2(CH_3)Ph]$ produced is then oxidized provides an obvious route to the substrate for this reaction (see Scheme I).

The original preparation of the proposed starting material **1** is, however, lengthy, and does not allow convenient access to this valuable synthetic intermediate in the tungstenocene system.[11] We therefore began by developing a new preparation of **1** from the reaction of $[W(\eta\text{-}C_5H_5)_2(CH_3)_2]$[10] with ammonium iodide in THF. The reaction uses the Brønsted acidity of the ammonium ion to cleave a tungsten–methyl bond and is analogous to the preparation of $[W(\eta\text{-}C_5H_5)_2(CH_3)CO_2Ph]$ by reaction of $[W(\eta\text{-}C_5H_5)_2(CH_3)_2]$ with benzoic acid.[13] Since the dimethyl complex is prepared directly from $[W(\eta\text{-}C_5H_5)_2Cl_2]$ and the reaction with NH_4I proceeds reliably in high yield, the reaction allows routine preparation of **1** on a multigram scale.

Phenylation of **1** to give $[W\eta\text{-}C_5H_5)_2(CH_3)Ph]$ (**2**) proceeds in good yield at room temperature in diethyl ether, and complex **2** can be conveniently oxidized to $[W(\eta\text{-}C_5H_5)_2CH_3)Ph]PF_6$ (**3**) using ferrocenium hexafluorophosphate in CH_2Cl_2. The salt is indefinitely stable in the solid state under an inert atmosphere at room temperature, but solutions of **3** are light sensitive at room temperature and should be protected from direct sunlight or prolonged

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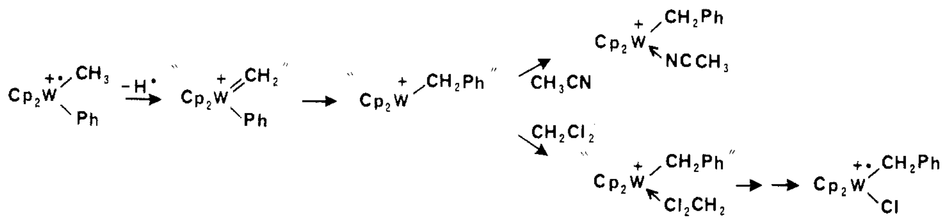
[12] Benfield, F. W. S.; Cooper, N. J.; Green, M. L. H. *J. Organomet. Chem.* **1974**, *76*, 49.

[13] Cooper, N. J.; Green, M. L. H.; Mahtab, R. *J. Chem. Soc., Dalton Trans.* **1979**, 1557.

Scheme II. Proposed Mechanisms for the Reactions Which Follow Hydrogen Atom Abstraction from $[W(\eta\text{-}C_5H_5)_2(CH_3)Ph]PF_6$ in CH_3CN and CH_2Cl_2 (Cp = $\eta\text{-}C_5H_5$)



exposure to laboratory light. Decomposition can also be minimized by handling solutions at low temperature, and crude material which had been carefully handled at −45 °C was identical by IR and EPR with recrystallized material and was typically used for subsequent experiments without further purification. Oxidation of 2 can also be effected with Ph_3CPF_6 at −78 °C or with $AgPF_6$ at room temperature, although the latter reagent in CH_2Cl_2 gives material contaminated with small quantities of $[W(\eta\text{-}C_5H_5)_2(CH_2Ph)Cl]PF_6$ (see below).

Paramagnetic $[W(\eta\text{-}C_5H_5)_2(CH_3)Ph]PF_6$ was characterized by analysis, by EPR,[14] and by reduction back to 2 with aqueous KOH/acetone. The single resonance observed in the EPR spectrum has a $\langle g \rangle$ value comparable to that of other tungstenocene dialkyl cations[1,13] and slightly higher than those reported for dihalotungstenocene cations.[15] Reduction to the corresponding neutral tungstenocene dialkyl by aqueous KOH/acetone has been observed for other tungstenocene dialkyl cations.[1]

It was anticipated that hydrogen atom abstraction from $[W(\eta\text{-}C_5H_5)_2(CH_3)Ph]^+$ would lead to formation of the target methylidene complex $[W(\eta\text{-}C_5H_5)_2(CH_2)Ph]^+$, but the optimum conditions for the reaction were initially unclear. The 16-electron benzyl complex $[W(\eta\text{-}C_5H_5)_2(CH_2Ph)]^+$ which would result from methylidene insertion into the tungsten–aryl bond would lack a β-C–H, and the analogous 16-electron complexes formed by migratory insertion in alkylidene–alkyl complexes are unstable until they form 18-electron alkene hydrides by β-elimination.[1] The benzyl cation cannot β-eliminate, and it was assumed that the reaction would have to be performed in the presence of a trapping agent to obtain a stable 18-electron adduct of the benzyl cation.

In practice the benzyl cation was readily trapped in >90% crude yield as $[W(\eta\text{-}C_5H_5)_2(CH_2Ph)(NCCH_3)]PF_6$ (4) by reacting $[W(\eta\text{-}C_5H_5)_2(CH_3)Ph]PF_6$ with the trityl radical in the donor solvent acetonitrile. The proposed mechanism of formation of 4 is summarized in Scheme II, which implies that a discrete 16-electron benzyl cation is formed.[16] The experimental data do not distinguish between this possibility and a concerted mechanism, similar to that established for carbonyl–alkyl insertion,[17] in which a solvent molecule is intimately involved in the transition state for insertion.

The identity of 4 was confirmed by an alternate synthesis involving solvolysis of the benzyl complex $[W(\eta\text{-}C_5H_5)_2(C_2H_4)CH_2Ph]PF_6$[12] in acetonitrile at 45 °C.

More complex chemistry than a simple insertion reaction occurred when hydrogen atom abstraction from $[W(\eta\text{-}C_5H_5)_2(CH_3)Ph]^{+\cdot}$ was attempted in CH_2Cl_2, a solvent which we have successfully used in the past for reactions with the trityl radical.[18] The reaction gave black insoluble crystals which would only redissolve in polar solvents such as acetone and acetonitrile, suggesting that the product was ionic; this was confirmed by the presence of the characteristic absorptions of PF_6^- in the IR spectrum of the solid, but ^1H NMR provided no evidence for the presence of an organometallic cation containing cyclopentadienyl ligands. The complex instead exhibited a single resonance in its EPR spectrum with a $\langle g \rangle$ value of 2.006, intermediate between the typical values for 17-electron tungstenocene dialkyl and dihalo cations,[1,15] with triplet hyperfine coupling suggesting that it was a salt of the 17-electron tungstenocene benzyl halide $[W(\eta\text{-}C_5H_5)_2(CH_2Ph)Cl]^{+\cdot}$.

The paramagnetic product was confirmed to be $[W(\eta\text{-}C_5H_5)_2(CH_2Ph)Cl]PF_6$ (5) by reduction of the salt to the neutral 18-electron complex $[W(\eta\text{-}C_5H_5)_2(CH_2Ph)Cl]$ (6) and by the reoxidation of 6 to 5. The reduction was again conveniently effected by treating the 17-elecron cation with aqueous KOH/acetone, and the brown crystalline product was identified as 6 by comparison with an authentic sample prepared by displacement of ethylene from the benzyl complex $[W(\eta\text{-}C_5H_5)_2(C_2H_4)CH_2Ph]PF_6$ by Cl^-.

Reoxidation of 6 to 5 was accomplished by treatment with trityl hexafluorophosphate in CH_2Cl_2 at room temperature. This oxidant also generates an equivalent of the trityl radical, but there was no evidence that this subsequently abstracted a hydrogen atom from 5 to give a benzylidene complex ($[W(\eta\text{-}C_5H_5)_2(CHPh)Cl]^+$ analogous to the stable ethylidene iodide which we have recently reported.[19,20]

The formation of 5 when a hydrogen atom is abstracted from $[W(\eta\text{-}C_5H_5)_2(CH_3)Ph]PF_6$ in CH_2Cl_2 suggests that the intermediate methylidene complex $[W(\eta\text{-}C_5H_5)_2(CH_2)Ph]^+$ undergoes the expected migratory insertion reaction to generate a solvato–benzyl complex analogous to the isolated acetonitrile complex (see Scheme II) but that coordination to the metal center activates the solvent molecule toward a further reaction with trityl radical in which a chlorine atom is transferred to the metal. This interpretation is supported by optimization experiments which established that 3 equiv of the trityl radical were required to obtain the maximum yield of 73%. Experiments in which 1 or 2 equiv of the radical were employed gave lower yields of 5 (28% and 51%, respectively), together with quantities of unreacted 3 corresponding to essentially quantitative mass recovery. The high recovery of 3 not only is consistent with the need for more than one equivalent of trityl radical but also suggests that the intermediate formed after migratory insertion reacts more

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[14] ^1H NMR showed no evidence for the presence of diamagnetic tungstenocene contaminants.

[15] Lindsell, W. E. *J. Chem. Soc., Dalton Trans.* **1975**, 2548.

[16] Such a cationic, 16-electron tungstenocene alkyl might well undergo a facile α-elimination reaction to generate the 18-electron benzylidene complex $[W(\eta\text{-}C_5H_5)_2(CHPh)H]^+$.[11] We have, however, observed no evidence for the formation of this complex, and either the benzyl cation does not undergo an α-elimination reaction, or, more probably, the α-elimination is readily reversible.

[17] Wax, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 7028.

[18] Hayes, J. C.; Cooper, N. J., manuscript in preparation.

[19] Miller, G. M.; Cooper, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 709.

[20] The stability of 5 under these conditions could simply reflect its insolubility in CH_2Cl_2, but we have also established that solutions of 5 in acetone do not react with the trityl radical.

readily than **3** with the radical, in conformity with a reaction involving activation of CH_2Cl_2 by coordination to the metal center.

It is possible that tungsten–chlorine bond formation does not require an intermediate CH_2Cl_2 complex and that **5** is formed by reaction of $[W(\eta\text{-}C_5H_5)_2CH_2Ph]^+$ with a chlorine atom formed by reaction of the trityl radical with the solvent. The formation of at least a transient CH_2Cl_2 complex is more probable, however, since we have previously reacted tungstenocene dialkyl cations with the trityl radical in CH_2Cl_2 without observing solvent-derived products.[18]

Alkylidene–alkyl complexes of the type $[W(\eta\text{-}C_5H_5)_2(CHR)(CH_2R')]^+$ are formally the products of hydride ion abstraction from the corresponding dialkyls $[W(\eta\text{-}C_5H_5)_2(CH_2R)(CH_2R')]$, and we have previously established for the cases in which R = R′ = H or CH_3 and R = H, R′ = CH_3 that the cationic alkylidenes can be prepared from the dialkyls by reaction with the triphenylmethylium (trityl) cation. The reaction is not, however, a direct 2-electron hydride abstraction but instead involves initial electron transfer to generate the 17-electron dialkyl cation and an equivalent of the trityl radical, followed by hydrogen atom transfer.[1] The unprecedented nature of this two-step mechanism for hydride transfer from a transition-metal alkyl has led us to investigate the corresponding reaction of $[W(\eta\text{-}C_5H_5)_2(CH_3)Ph]$.

Evidence that $[W(\eta\text{-}C_5H_5)_2(CH_2)Ph]^+$ could indeed be generated directly from $[W(\eta\text{-}C_5H_5)_2(CH_3)Ph]$ came from reaction with the trityl cation in dry acetonitrile, which gave $[W(\eta\text{-}C_5H_5)_2(CH_2Ph)(NCCH_3)]PF_6$ in excellent yield as the only observable product.

Complementary data on the significance of an electron-transfer pathway for this reaction came from experiments in which $[W(\eta\text{-}C_5H_5)_2(CH_3)Ph]$ was reacted with trityl hexafluorophosphate in CH_2Cl_2. At room temperature this resulted in formation of an approximately 1:1 mixture of $[W(\eta\text{-}C_5H_5)_2(CH_2Ph)Cl]PF_6$ and $[W(\eta\text{-}C_5H_5)_2(CH_3)Ph]PF_6$, consistent with a two-step hydride-transfer mechanism: the initial step would be formation of **3**, and subsequent reaction of **3** with the trityl radical coproduct would result in conversion to **5** via $[W(\eta\text{-}C_5H_5)_2(CH_2)Ph]^+$ and the CH_2Cl_2 solvate of its insertion product. The low yield of **5** and the persistence of an approximately equivalent amount of **3** is consistent with the generation of a limited quantity of trityl radical. Essentially quantitative electron transfer was confirmed to be the initial step by carrying out the reaction at −78 °C to give $[W(\eta\text{-}C_5H_5)_2(CH_3)Ph]PF_6$ in good yield.

Conclusion

The results presented above establish that the cationic methylidene–aryl complex $[W(\eta\text{-}C_5H_5)_2(CH_2)Ph]^+$, generated by hydrogen abstraction from the 17-electron cation $[W(\eta\text{-}C_5H_5)_2(CH_3)Ph]^{+\cdot}$, undergoes a migratory insertion reaction in acetonitrile and in dichloromethane to form benzyl derivatives. The complexity of the reaction sequences means that the rate of the insertion reaction can not be directly determined, but the speed of formation of $[W(\eta\text{-}C_5H_5)_2(CH_2Ph)Cl]^{+\cdot}$ indicates that the insertion is rapid and strengthens the idea that the facile migratory insertion in alkylidene–alkyl complexes reflects the metallacarbonium ion character of the substrates and is analogous to Wagner–Meerwein rearrangement of carbonium ions.

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Registry No. **1**, 71531-99-2; **2**, 89710-99-6; **3**, 89711-01-3; **4**, 89711-03-5; **5**, 100113-65-3; **6**, 100113-66-4; $[W(\eta\text{-}C_5H_5)_2(CH_3)_2]$, 39333-53-4; $[W(\eta\text{-}C_5H_5)_2(CH_2Ph)(n\text{-}C_2H_4)]PF_6$, 53770-69-7.