

The solution and refinement of the structure were carried out on a PDP-11 computer using local modifications of programs supplied by the Enraf-Nonius Corp.³⁸ The iridium atom was located by using an origin-removed Patterson synthesis. The positions of the remaining non-hydrogen atoms were obtained by the usual combination of structure factor and Fourier synthesis calculations and full-matrix least-squares refinements. In the least-squares refinements, the function minimized was $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are, respectively, the observed and calculated structure amplitudes and where $w = 1/\sigma^2(F_o)$. The atomic scattering factors were taken from the compilations of Cromer and Waber.^{39a} Anomalous dispersion terms used were those of Cromer.^{39b} After convergence of refinements containing the non-hydrogen atoms, a difference Fourier synthesis revealed residual electron density arising from disorder of the oxygen atom, the "equatorial" fluorine atoms F(2-5), and the carbon atoms about P(2). In a series of refinements, the populations of the minor positions were found to be approximately 0.20. This value was fixed in subsequent refinements to convergence in which atoms occupying both major and minor positions were included. The atoms occupying the major positions were allowed to vibrate anisotropically while those at the minor positions were included as isotropic bodies. The positions of the majority of hydrogen atoms were then determined in a difference Fourier synthesis. The positions of the major carbon-bound hydrogen atoms were then idealized with a C-H distance of 0.95 Å, and these atoms included as fixed contributions ($B_H = 4.0$).⁴⁰ The hydroxy hydrogen atom was not located. Although a peak corresponding

to the hydrido hydrogen atom was located in the expected area, attempted refinement of this atom was unsuccessful and no contribution from this atom was included. The hydrogen atoms associated with the minor C and O positions were not included. Least-squares refinement converged to values of $R = 0.029$ and $R_w = 0.031$, where $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|]^2$. A number of peaks on the order of 1.0 e/Å⁻³ remain in a final difference Fourier synthesis and are associated with the metal atom.

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Registry No. 4a, 79568-57-3; 4b, 83435-10-3; 6, 83380-24-9; 6-Cl, 83380-23-8; 6-I, 83380-25-0; 7, 83380-16-9; 8, 83380-17-0; 9, 83380-19-2; 13, 83380-20-5; 14, 83380-22-7; [Ir(PMe₃)₄]Cl, 60314-48-9; ICH₂OSiMe₃, 83380-15-8; NaPF₆, 21324-39-0; HBF₄, 16872-11-0; [Ir(PMe₃)₄][PF₆], 75593-00-9; IrH(CHO)I(PMe₃)₃, 83380-26-1; [Ir(PMe₃)₄]I, 83380-27-2; paraformaldehyde, 30525-89-4; iodotrimethylsilane, 16029-98-4; ammonium bifluoride, 1341-49-7; Potassium *tert*-butoxide, 865-47-4.

Supplementary Material Available: Tables of non-hydrogen atom thermal parameters (Table III) and the idealized hydrogen atom positions (Table IV), a listing of the observed and calculated structure amplitudes, views of the disordered cation and anion (Figures 2 and 3), and a stereodrawing of the unit cell (Figure 4) (26 pages). Ordering information is given on any current masthead page.

(38) Frenz, B. A. "The Enraf-Nonius CAD4 SDP--A Realtime System for Concurrent X-ray Data Collection and Crystal Structure Determinations", in "Computing in Crystallography"; Schenk, H., Olthof-Hazelkamp, R., Van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64-71.

(39) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) Table 2.2B; (b) Table 2.3.1.

(40) See paragraph at end of paper regarding supplementary material.

Formation and Cleavage of Carbon-Carbon and Tungsten-Carbon Bonds Involving Bis(η -cyclopentadienyl)tungsten Compounds[†]

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Cocondensation of spiro[2,4]hepta-4,6-diene with tungsten atoms gives $[\overline{W}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2)_2]$, 1. One-electron oxidation of 1 with AgPF₆ gives $[\overline{W}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2)_2]\text{PF}_6$ which readily reduces to 1. Treatment of 1 with [Ph₃C]PF₆ or of $[\overline{W}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2)_2]\text{PF}_6$ with Ph₃C gives $[\overline{W}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{-trans-}\eta\text{-CH=CHCH}_2\text{-}\eta\text{-C}_5\text{H}_4)\text{H}]\text{PF}_6$ via a carbon-carbon bond formation reaction. $[\overline{W}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{-trans-}\eta\text{-CH=CHCH}_2\text{-}\eta\text{-C}_5\text{H}_4)\text{H}]\text{PF}_6$ is readily deprotonated with aqueous base forming $[\overline{W}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{-trans-}\eta\text{-CH=CHCH}_2\text{-}\eta\text{-C}_5\text{H}_4)]$. Treatment of $[\overline{W}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2)_2]$ with PhICl₂ cleaves both tungsten-carbon bonds forming the tetrachloro derivative $[\overline{W}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{Cl})_2\text{Cl}_2]$. This is readily reduced back to $[\overline{W}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2)_2]$ by sodium amalgam. 1 reacts with 1 equiv of benzoic acid forming $[\overline{W}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2)(\eta\text{-EtC}_5\text{H}_4)\text{OCOPh}]$ which upon treatment with trimethylsilyl silane gives $[\overline{W}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2)(\eta\text{-EtC}_5\text{H}_4)\text{I}]$. This compound reacts with PMe₃ in acetone giving first $[\overline{W}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH-}(\text{PMe}_3)(\eta\text{-EtC}_5\text{H}_4)\text{H})\text{PF}_6]$ and then $[\overline{W}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2)(\eta\text{-EtC}_5\text{H}_4)\text{PMe}_3]\text{PF}_6$. A mechanism involving a 1,2-hydrogen shift equilibrium is proposed to account for this sequence of reactions.

Introduction

The bis(η -cyclopentadienyl)tungsten moiety has proved to be a versatile system for the study of the role of a transition-metal center in basic reactions with simple hy-

drocarbon systems. For example, the study of bis(η -cyclopentadienyl)tungsten derivatives has led to the acceptance of reversible 1,2-hydrogen shifts in metal alkyls as a general phenomenon.¹ Tungstenocene is one of the

[†] Dedicated to Rolly Pettit.

(1) Cooper, N. J.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* 1979, 1121.

best characterized examples of a molecule which can undergo intermolecular activation of carbon-hydrogen bonds,^{2,3} and the ability of cis dihydrides of transition metals to undergo a photoinduced elimination of dihydrogen was first demonstrated by using dihydrido-tungstenocene.⁴

Recently, we have shown that the compound $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2)_2]$ is formed by cocondensation of spiro[2,4]hepta-4,6-diene with molybdenum atoms and that this compound reacts with iodine giving the ring-functionalized tetraiodo derivative $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2)_2\text{I}_4]$.⁵ It was clearly to be anticipated that the tungsten analogues of these compounds could be synthesized. And, if so, they would provide a means to further explore basic reactions between a reactive transition-metal center and simple hydrocarbon systems, as described below.

Experimental Section

All operations were performed in vacuo or in an inert atmosphere. All solvents were rigorously dried before use by standard procedures. Infrared spectra were determined on mulls by using a Pye Unicam SP 2000 spectrophotometer and were calibrated with polystyrene. ¹H and ¹³C NMR spectra were determined on a Bruker 3000-MHz instrument. Microanalyses were performed by the microanalytical laboratory of this department. Spiro[2,4]hepta-4,6-diene was prepared by a modification of the published method,⁶ as described elsewhere.⁷ PhICl_2 ⁸ and Me_3SiI ⁹ were prepared as described.

cyclo-Bis(2-(η -cyclopentadienyl)ethyl)tungsten, 1. Tungsten atoms (6.0 g, 32.6 mmol) were cocondensed with spiro[2,4]hepta-4,6-diene (150 cm³, 1.6 mol) over a period of 4 h by using the apparatus previously described.¹⁰ The reaction mixture was allowed to warm to room temperature and was washed from the reaction vessel with tetrahydrofuran. The extract was filtered through Celite, and the volatile components of the filtrate were removed under reduced pressure. The red oily residue was extracted with petroleum ether (40–60 °C) (2 × 250 cm³), and the extract was filtered and concentrated to ca. 30 cm³. Cooling to –20 °C and then to –78 °C gave large red crystals which were collected, washed with cold petroleum ether (30–40 °C), and dried in vacuo, yield 2 g, 5.4 mmol (15%).

Bis(η -2-chloroethyl)cyclopentadienyl)dichlorotungsten, 2. The compound $[\text{W}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2)_2]$ (0.3 g, 0.81 mmol) in tetrahydrofuran (50 cm³) was treated with PhICl_2 (0.45 g, 1.62 mmol) in tetrahydrofuran (20 cm³). The mixture was warmed to 50 °C, and the initially orange solution turned dark green. After 3 h the solvent was removed under reduced pressure and the green residue was recrystallized from tetrahydrofuran/ethanol mixture as green cubic crystals. These were collected and washed with petroleum ether (30–40 °C) and dried in vacuo, yield 0.31 g, 0.61 mmol (75%).

Reduction of $[\text{W}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2)_2\text{Cl}_2]$ to $[\text{W}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2)_2]$. The compound $[\text{W}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2)_2\text{Cl}_2]$ (0.3 g, 0.39 mmol) in tetrahydrofuran (25 cm³) was treated with Na/Hg (20 g of a 3% Na in Hg), and the mixture was stirred at room temperature for 3 h. The initially green solution turned orange. This was separated from the excess amalgam, and the solvent was removed under reduced pressure. The orange residue was crystallized from petroleum ether (40–60 °C), giving pure $[\text{W}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2)_2]$ in 70% yield. The product was identified by comparison of the hydrogen-1 NMR spectrum with that of an authentic sample.

cyclo-Bis(2-(η -cyclopentadienyl)ethyl)tungsten Hexafluorophosphate, 3. Silver hexafluorophosphate (0.34 g, 1.35 mmol) in tetrahydrofuran (10 cm³) was added to $[\text{W}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2)_2]$ (0.5 g, 1.35 mmol) in tetrahydrofuran (50 cm³). Immediately a black precipitate of silver metal separated, giving a dark red solution. After being stirred at room temperature for 3 h, the mixture was filtered through Celite and ethanol (10 cm³) was added to the filtrate. The solution was concentrated under reduced pressure (ca. 20 cm³) and cooled to –78 °C. Dark red crystals separated which were collected, washed with ethanol, and dried in vacuo, yield 0.59 g, 1.15 mmol (85%).

Reduction of $[\text{W}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2)_2]\text{PF}_6$. The compound of $[\text{W}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2)_2]\text{PF}_6$ (0.20 g, 0.39 mmol) in tetrahydrofuran was stirred over Na/Hg for 3 h. The initially dark red solution turned orange. The solution was decanted from the amalgam, and the solvent was removed under reduced pressure. The red residue was crystallized from petroleum ether (40–60 °C) at –78 °C, giving crystals of $[\text{W}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2)_2]$, which were identified by comparison of the IR and hydrogen-1 NMR spectra with those of the authentic compound, yield >95%.

Bis(η -ethylcyclopentadienyl)dichlorotungsten, 4. The compound $[\text{W}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2)_2]$ (0.5 g, 1.4 mmol) in petroleum ether (40–60 °C) (100 cm³) was treated with hydrogen chloride at room temperature for 5 min. A green-black precipitate appeared instantly, and after 5 min the solvent was removed under reduced pressure. The green residue was recrystallized from dichloromethane/petroleum ether (60–80 °C) mixture, giving dark green crystals. These were collected, washed with petroleum ether (30–40 °C), and dried in vacuo, yield 0.54 g (>90%).

cyclo-(2-(η -Cyclopentadienyl)ethyl)(η -ethylcyclopentadienyl)iodotungsten, 5. The compound $[\text{W}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2)(\eta\text{-EtC}_5\text{H}_4)\text{OCOPh}]$ (3.6 g, 7.4 mmol) in tetrahydrofuran (50 cm³) was treated with trimethyliodosilane (1.5 cm³, 10.5 mmol). The solution became dark green (dark red by transmitted light). After the mixture was stirred for 1 h, the solvent was removed under reduced pressure and the residue was recrystallized from ethanol/diethyl ether at –20 °C, giving dark green crystals which were collected and dried in vacuo, yield 2.8 g (76%).

cyclo-(2-(η -Cyclopentadienyl)ethyl)(η -ethylcyclopentadienyl)(benzoato)tungsten, 16. The compound $[\text{W}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2)_2]$ (0.3 g, 8.2 mmol) in tetrahydrofuran was treated with benzoic acid (1.0 g, 8.2 mmol) in tetrahydrofuran (30 cm³). The mixture was warmed to 50 °C for 3 h. The solvent was removed under reduced pressure, and the red residue was recrystallized from toluene/petroleum ether (40–60 °C) mixture, giving red crystals, yield 3.6 g, 7.4 mmol (90%).

cyclo-(2-(η -Cyclopentadienyl)-2-(trimethylphosphonio)ethyl)(η -ethylcyclopentadienyl)hydridotungsten Tetrafluoroborate, 7. The compound $[\text{W}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2)(\eta\text{-EtC}_5\text{H}_4)\text{I}]$ (0.30 g, 0.6 mmol) in acetone (20 cm³) was treated with thallium tetrafluoroborate (0.18 g, 0.61 mmol) suspended in acetone (20 cm³). Immediately trimethylphosphine (1 g, 13.0 mmol) in acetone (20 cm³) was added. The mixture was stirred at room temperature for 12 h and a yellow precipitate separated. The mixture was filtered through Celite, and the solvent was removed from the red filtrate under reduced pressure. The red residue was recrystallized from ethanol/diethyl ether mixture,

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giving an orange powder, yield 0.71 g, 0.32 mmol (53%).

cyclo-(2-(η -Cyclopentadienyl)ethyl)(η -ethylcyclopentadienyl)(trimethylphosphine)tungsten Hexafluorophosphate, 8. The compound $[\overline{W(\eta-C_5H_4CH_2CH_2)}(\eta-EtC_5H_4)]$ (0.3 g, 0.6 mmol) in acetone (50 cm³) was treated with trimethylphosphine (1.0 g, 13 mmol), and the mixture was heated at 50 °C for 3 days. The initially dark green solution slowly turned red. The solvent was removed under reduced pressure, and the residue was extracted with water (2 × 30 cm³). The extracts were filtered, and aqueous ammonium hexafluorophosphate was added to the filtrate, giving a pink precipitate. This was collected and recrystallized from acetone/water mixture, giving large pink crystals, yield 0.21 g, 0.36 mmol (59%).

[1,4-Bis(η -cyclopentadienyl)- η -trans-2-butene]hydrido-tungsten Hexafluorophosphate, 9. Method A. The compound $[\overline{W(\eta-C_5H_4CH_2CH_2)}]$ (0.30 g, 0.81 mmol) in dichloromethane was treated with triphenylmethyl hexafluorophosphate (0.34 g, 0.81 mmol). After the mixture was stirred at room temperature for 1 week, the solvent was removed under reduced pressure, and the purple residue was recrystallized from acetone/ethanol mixture, giving purple crystals which were collected and dried in vacuo, yield 70%.

Method B. The compound $[\overline{W(\eta-C_5H_4CH_2CH_2)}]PF_6$ (0.5 g, 0.97 mmol) in tetrahydrofuran (50 cm³) was treated with an excess of triphenylmethyl radical (3 mmol) in tetrahydrofuran (30 cm³). The mixture was warmed to 50 °C for 4 h, giving a red-blue solution. The solvent was removed under reduced pressure, and the purple residue was recrystallized from acetone/ethanol mixture, giving purple crystals, yield 0.35 g, 0.68 mmol (70%).

[1,4-Bis(η -cyclopentadienyl)- η -trans-2-butene]tungsten, 10. The compound $[\overline{W(\eta-C_5H_4CH_2-trans-\eta-CH=CHCH_2-\eta-C_5H_4)H}]PF_6$ (0.20 g, 0.39 mmol) in acetone (10 cm³) was treated with aqueous sodium hydroxide (10 cm³ of a 1 M solution). The initially purple solution turned orange. The mixture was extracted with toluene (2 × 30 cm³), the toluene layer was separated, and solvent was then removed under reduced pressure. The residue was recrystallized from toluene/petroleum ether (40–60 °C) at –20 °C, giving an orange powder, yield 0.11 g, 0.3 mmol (77%).

Results

Cocondensation of tungsten atoms with spiro[2,4]hepta-4,6-diene forms the yellow-brown crystalline compound $[\overline{W(\eta-C_5H_4CH_2CH_2)}]$ (1). The yield of 1 based on tungsten atoms arriving in the cocondensate was only about 15% compared to 40% for the analogous reaction of molybdenum atoms with spiro[2,4]hepta-4,6-diene. Also, there was a substantial amount of polymerized diene in the reaction mixture. We do not know whether it is the high-temperature conditions required for the generation of the tungsten atoms (ca. 3600 °C), with the concomitant increase of radiation of photons and possibly electrons or ions, which is the cause of the poor yield, or if the tungsten atoms being intrinsically more reactive than molybdenum atoms undergo more complex reactions with the spiro[2,4]hepta-4,6-diene. The compound 1 sublimes at ca. 100 °C and is soluble in nonpolar hydrocarbon solvents. Solutions in air show evidence for decomposition within a few minutes.

Treatment of 1 with $PhICl_2$ causes cleavage of both tungsten–carbon bonds the desired tetrachloro derivative $[\overline{W(\eta-C_5H_4CH_2CH_2Cl)_2}]Cl_2$ (2) in 75% yield.

Compound 2 forms deep green crystals which are soluble in the more polar solvents such as dichloromethane and tetrahydrofuran. Solutions are moderately stable in air.

Treatment of 2 with sodium amalgam in tetrahydrofuran results in a rapid reduction, giving 1 in essentially quantitative yield.

Compound 1 readily undergoes a one-electron oxidation when treated with silver hexafluorophosphate, giving the

compound $[\overline{W(\eta-C_5H_4CH_2CH_2)}]PF_6$ (3). This may be readily reduced back to 1 with sodium amalgam.

As would be expected, the tungsten–carbon bonds of 1 are readily cleaved with proton acids, and 1 reacts with hydrogen chloride to give $[\overline{W(\eta-C_5H_4Et)_2}Cl_2]$ (4) instantly in a quantitative reaction.

It was decided to attempt to synthesize the compound $[\overline{W(\eta-C_5H_4CH_2CH_2)}(\eta-EtC_5H_4)I]$ (5) in order to compare its reactivity with that of $[\overline{W(\eta-C_5H_5)_2}MeI]$.¹²

Addition of 1 mol of benzoic acid to $[\overline{W(\eta-C_5H_4CH_2CH_2)}]$ results in the cleavage of only one tungsten–carbon bond, giving the compound $[\overline{W(\eta-C_5H_4CH_2CH_2)}(\eta-EtC_5H_4)OCOPh]$ (6). Treatment of this with trimethylsilyl silane results in the clean metathetical exchange reaction, giving $[\overline{W(\eta-C_5H_4CH_2CH_2)}(\eta-EtC_5H_4)I]$ (5) in high yield.

Solutions of 5 in acetone were treated with a slight excess of trimethylphosphine at 50 °C, and the ensuing reaction was monitored by ¹H NMR spectroscopy. This showed that there was a steady reduction of the initial spectrum of 5 and new bands assignable to $[\overline{W(\eta-C_5H_4CH_2CH(PMe_3)(\eta-EtC_5H_4)H)}]PF_6$ (7) appeared. After 3 days a second group of bands appeared which are assignable to the compound $[\overline{W(\eta-C_5H_4CH_2CH_2)}(\eta-EtC_5H_4)PMe_3]PF_6$ (8). Compound 7 was separately prepared from tetrahydrofuran solutions of 5 with thallium tetrafluoroborate at room temperature in the presence of trimethylphosphine. Similarly, 8 was prepared from 5 and an excess of trimethylphosphine at 50 °C for 3 days.

The reaction between 5 and phenyldimethylphosphine at 50 °C was also monitored by hydrogen-1 NMR spectroscopy over a period of 1 week. The spectra show the formation of bands assignable to the compound $[\overline{W(\eta-C_5H_4CH_2CH(PPhMe_2)(\eta-EtC_5H_4)H)}]I$.

The abstraction of a hydride ion from the β -carbon of transition-metal alkyls, giving a olefin-metal cation is a general and normally facile reaction. However, when $[\overline{W(\eta-C_5H_4CH_2CH_2)}]$ was treated with triphenylmethyl tetrafluoroborate, then there is a very slow reaction, and after 1 week the ethylene-hydride cation $[\overline{W(\eta-C_5H_4CH_2-trans-\eta-CH=CHCH_2-\eta-C_5H_4)H}]PF_6$ (9) could be isolated.

The structure proposed for the cation in 9 is clearly indicated by the ¹H NMR spectrum. The spectrum of 9 in deuterioacetone after a few minutes shows a decrease in the intensity of the band assignable to the W hydrogen, and this may be understood in terms of deuterium–hydrogen exchange with the solvent.

Evidence that the W hydrogen in 9 is labile is shown by the reaction with aqueous base which causes rapid deprotonation forming the neutral olefin derivative $[\overline{W(\eta-C_5H_4CH_2-trans-\eta-CH=CHCH_2-\eta-C_5H_4)}]$ (10).

Compound 9 was formed in a rapid reaction between $[\overline{W(\eta-C_5H_4CH_2CH_2)}]PF_6$ (3) and the triphenylmethyl radical.

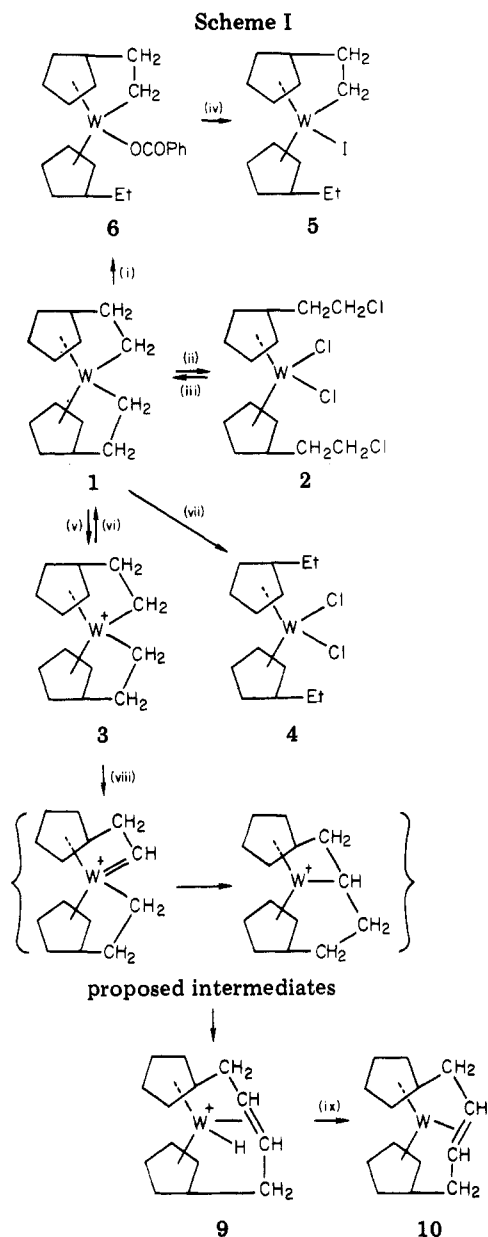
Discussion

The structures for the new compounds 1–10 are shown in the Schemes I and II and are proposed on the basis of the data given in Table I.

Table I. Analytical and Spectroscopic Data

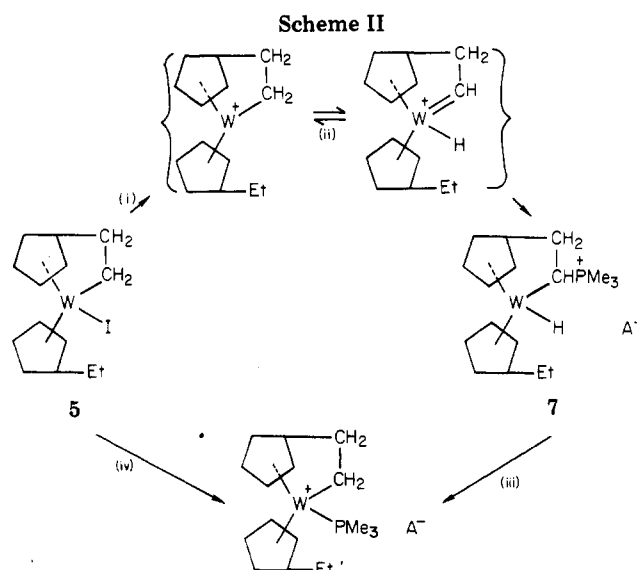
compd (color)	anal. ^b	hydrogen-1 NMR data ^a
1, [W(η -C ₅ H ₄ CH ₂ CH ₂) ₂] (red)	45.9 (45.7) 4.4 ^c (4.4)	5.37 (2, m (6 lines)), 5.62 (2, m), 5.90 (2, m), 6.05 (2, m), ^d (2 η -C ₅ H ₄), 7.12 (2, ddd, <i>J</i> = 12.6, 11.3, 3.4), 7.61 (2, ddd, <i>J</i> = 12.6, 6.6, 11.0, 2-C(ring)CH ₂), 9.96 (2, ddd, <i>J</i> = 11.3, 6.6, 6.6, <i>J</i> (¹³ W-H) = 8.0), 11.42 (2, ddd, <i>J</i> = 3.4, 11.0, 6.6, <i>J</i> (¹³ W-H) = 8.0) ^f
2, [W(η -C ₅ H ₄ CH ₂ CH ₂ Cl) ₂] (dark green)	33.4 (32.9) 3.3 ^c (3.1)	4.57 (8, c, br, 2 η -C ₅ H ₄), 6.55 (4, t, <i>J</i> = 7.0, 2 ring-CH ₂), 7.11 (4, t, <i>J</i> = 7.0, 2CH ₂ Cl) ^g
3, [W(η -C ₅ H ₄ CH ₂ CH ₂) ₂]PF ₆ (dark red)	32.5 (32.7) 3.3 (3.1)	^h
4, [W(η -EtC ₅ H ₄) ₂ Cl ₂] (green)	39.1 (39.1) 4.2 (4.1)	4.79 (8, c, br, 2 η -C ₅ H ₄), 7.50 (4, q, <i>J</i> = 7.2, 2 CH ₂), 8.75 (6, t, <i>J</i> = 7.2, 2 Me) ^f
5, [W(η -C ₅ H ₄ CH ₂ CH ₂)(η -C ₅ H ₄ Et)] (dark green)	33.5 (33.8) 3.5 ^c (3.4)	4.46, 4.85, 5.42, 5.60, 5.87, 5.92, 6.54, 6.87 ^d (2 η -C ₅ H ₄), 7.13 (1, ddd, <i>J</i> = 12.5, 11.0, 2.6), 7.43 (1, ddd, <i>J</i> = 12.5, 6.6, 7.5, ring-CH ₂), 7.91 (1, m (6 lines)), 8.03 (1, m (6 lines), CH ₂ or Et (as an AB group)), 9.09 (3, t, <i>J</i> = 7.5, Me), 9.70 (1, ddd, <i>J</i> = 11.0, 6.6, 7.5), 9.92 (1, ddd, <i>J</i> = 2.6, 11.0, 7.5, W-CH ₂) ^f
6, [W(η -C ₅ H ₄ CH ₂ CH ₂)(η -C ₅ H ₄ Et)(O ₂ CPh)] (dark red)	51.4 (51.4) 4.6 ^c (4.5)	1.65 (2, c), 2.91 (3, c, Ph), 3.88 (1, m (6 lines)), 5.12 (1, m (5 lines)), 5.59 (1, m, (6 lines)), 5.61 (1, m (6 lines)), 5.70 (1, m), 6.30 (1 (5 lines)), 6.34 (1, m), 6.82 (1, m, ^d 2 η -C ₅ H ₄), 7.03 (1, ddd, <i>J</i> = 12.9, 11.0, 3.6), 7.39 (1, ddd, <i>J</i> = 12.9, 6.2, 11.0, C(ring)CH ₂), 8.10, 8.16 (2, AB system, CH ₂ of Et), 9.15 (3, t, <i>J</i> (H-H) = 7.3, Me), 9.69 (1, ddd, <i>J</i> = 11.0, 6.2, 6.2), 10.34 (1, ddd, <i>J</i> = 3.6, 11.0, 6.2, W-CH ₂) ^f
7, [W(η -C ₅ H ₄ CH ₂ CH(PMe ₃))(η -C ₅ H ₄ Et)]HBF ₄ (pink)	38.4 (38.4) 5.1 (4.9)	4.68 (6 lines), 4.73 (3 lines), 5.01 (2 (6 lines)), 5.22 (3 lines), 5.25 (3 lines), 5.29, 5.69 ^d (2 η -C ₅ H ₄), 7.10 (1, dd, <i>J</i> = 13.7, 11.1), 7.43 (1, dd, <i>J</i> = 5.6, 13.7, ring-CH ₂), 7.57, 7.59 (m (9 lines), AB system of CH ₂ of Et), 8.30 (9, d, <i>J</i> (P-H) = 12.9, PMe ₃), 8.86 (3, t, <i>J</i> = 7.6, Me of Et), 9.37 (1, ddd, <i>J</i> = 5.6, 11.1, <i>J</i> (P-H) = 1.9, WCH), 22.02 (1, d, <i>J</i> = 12.0, <i>J</i> (W-H) = 7.5, WH) ^{i,j}
8, [W(η -C ₅ H ₄ CH ₂ CH ₂)(η -C ₅ H ₄ Et)PMe ₃]PF ₆ (red)	34.6 (34.6) 4.1 (4.4)	4.38 (1, m (7 lines), <i>J</i> (P-H) = 3.8), 4.57 (1, m (7 lines), <i>J</i> (P-H) = 1.2), 4.76 (1, m, <i>J</i> (P-H) = 1.4), 4.88 (1, m), 4.99 (1, m (9 lines), <i>J</i> (P-H) = 11.0), 5.18 (1, m), 5.24 (1, m (8 lines), <i>J</i> (P-H) = 3.4, ^d 2 η -C ₅ H ₄), 7.40 (1, ddd, <i>J</i> = 3.6, 12.3, 12.3), 7.49 (1, ddd, <i>J</i> = 6.6, 11.0, 12.3, C(ring)CH ₂), 7.75 (2, m (10 lines), CH ₂ of Et), 8.22 (9, d, <i>J</i> (P-H) = 9.3, PMe ₃), 8.8 (3, t, <i>J</i> = 7.5), 10.33 (1, dddd, <i>J</i> = 6.6, 7.5, 12.3, <i>J</i> (P-H) = 13.7), 10.74 (1, dddd, <i>J</i> = 23.6, 7.5, 11.0, <i>J</i> (P-H) = 14.2) ^f
9, [W(η -C ₅ H ₄ CH ₂ η -CH=CH- η -C ₅ H ₄)]PF ₆ (purple)	32.4 (32.8) 3.0 ^k (2.9)	2.85, 3.29 (6 lines), 3.94 (5 lines), 4.14 (5 lines), 4.45, 4.54, 5.14 (5 lines), 5.43 ^d (2 η -C ₅ H ₄), 5.68 (2, c, CH ^l and one hydrogen of CH ₂ ^l), 6.14 (1, dd, <i>J</i> = 3, 12.5), 6.28 (1, dd, <i>J</i> = 7.4, 12.5, CH ₂ ^m), 7.14 (1, dd, <i>J</i> = 6.2, 10.9, one hydrogen or CH ₂ ^l), 7.5 (1, ddd, <i>J</i> = 2.6, 6.6, 10.4, CH ₂), 19.0 (1, s, WH) ⁱ ¹³ C NMR 23.1 (t), 23.8 (t, 2CH ₂), 35.3 (d), 46.6 (d, CH=CH), 81.4 (d), 84.0 (d), 89.6 (d), 91.6 (d), 111.5 (d), 111.8 (d), 128.6 (d, 8 CH of 2 η -C ₅ H ₄) ⁱ
10, [W(η -C ₅ H ₄ CH ₂ η -CH=CH- η -C ₅ H ₄)] (pink)	45.6 (45.9) 3.9 (3.8)	4.89 (2, m (6 lines)), 5.55 (2, m), 5.90 (2, m), 6.49 (2, m (6 lines), 2 η -C ₅ H ₄), 6.31 (2, c), 6.42 (2, c, 2 ring-CH ₂), 6.61 (2, c, 2 CH) ^f

^a Data given as chemical shift (τ) (relative intensity, multiplicity, *J* in Hz (refers to *J*(H-H) unless otherwise stated), assignment). ¹³C NMR data given in ppm. ^b For % C and % H respectively; calculated values given in parentheses. ^c Parent ion peak observed in the mass spectrum. ^d Eight separate multiplets, each of four main lines of relative intensity 1, unless otherwise indicated. ^e Also shows bands due to coupling with the ¹⁸³W nucleus. ^f In C₂D₆. ^g In CD₂Cl₂. ^h No spectrum observed, presumably due to the expected paramagnetism. ⁱ In (CD₃)₂CO. ^j ν (W-H) = 1900 cm⁻¹. ^k ν (W-H) = 1780 cm⁻¹. ^l On adjacent carbons of one CH₂-CH system. ^m On adjacent carbons of the other CH₂-CH system.



(i) benzoic acid in tetrahydrofuran, 90%; (ii) PhICl_2 in tetrahydrofuran, 70%; (iii) Na/Hg in tetrahydrofuran at room temperature for 5 h, 70%; (iv) Me_3SiI in tetrahydrofuran at room temperature for 2 h, 90%; (v) AgPF_6 in tetrahydrofuran at room temperature 95%; (vi) Na/Hg in tetrahydrofuran, >90%; (vii) hydrogen chloride at room temperature for 5 min, >90%; (viii) $[\text{Ph}_3\text{C}]^+\text{PF}_6^-$ in dichloromethane with 1 at room temperature for 1 week or Ph_3C in tetrahydrofuran on 3 at 50 °C for 4 h, 70%; (ix) sodium hydroxide at room temperature, >90%

Cooper has shown that treatment of $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{Me}_2]^+$ with the Ph_3C radical gives the hydridoethylene cation $[\text{W}(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_2\text{H}_4)\text{H}]^+$.¹¹ By analogy with this work we propose the mechanism for the conversion of 1 to 9 shown in Scheme I.



(i) PMe_3 and thallium tetrafluoroborate in acetone at room temperature for 2 h, $\text{A} = \text{BF}_4^-$; (ii) proposed reversible 1,2-hydrogen shift giving hydridocarbene intermediate; (iii) heat at 70 °C for 10 h, >95%; (iv) PMe_3 in acetone at 70 °C for 3 days, 50%

The reaction between 5 and Me_3P giving first 7 and then 8 presumably proceeds via a reversible tungsten methyl \rightleftharpoons tungsten methylene hydride equilibrium (Scheme II), as is proposed elsewhere for related systems.¹² This reaction provides further support for our proposal that reversible 1,2-hydrogen shift processes are likely to be a general feature of transition-metal alkyl chemistry.¹²

The rapid and high-yield formation of 1 by successive ring closure reactions during the reduction of 2 is an interesting reaction. In a separate experiment we have shown that reduction of $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{I}_2]$ in the presence of excess of iodomethane with sodium amalgam does not give any of the dimethyl derivative $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{Me}_2]$.¹³ The tungsten-carbon bond forming step in these ring closure reactions is presumably favored by a "proximity" effect which entails advantageous entropy contributions. A detailed study of the mechanism of this and related reactions is in progress.

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