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Stereochemical Studies on Thermal and Photochemical Reactions of η^5-$C_5H_5W(CO)_3$(phenethyl) Containing Deuterium-Labeled Phenethyl Ligands

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Reaction of *erythro*-$C_6H_5CHDCHDOS(O)_2C_6H_4CH_3$-*p* with $Na[\eta^5\text{-}C_5H_5W(CO)_3]$ proceeds with inversion of configuration at α-carbon to yield η^5-$C_5H_5W(CO)_3CHDCHDC_6H_5$-*threo* in ≥95% diastereomeric purity. This product reacts with liquid SO_2 at room temperature to give η^5-$C_5H_5W(CO)_3S(O)_2CHDCHDC_6H_5$-*erythro* and with 2 equiv of I_2 in $CHCl_3$ to afford *threo*-$C_6H_5CHDCHDI$ and η^5-$C_5H_5W(CO)_2I_3$. Iodine cleavage of η^5-$C_5H_5W(CO)_3CD_2CH_2C_6H_5$ yields isomerically pure $C_6H_5CH_2CD_2I$. These cleavage results are rationalized by electrophilic addition of I^+ to tungsten, reductive elimination of phenethyl iodide, and coordination of I^-, followed by oxidation of the resultant η^5-$C_5H_5W(CO)_3I$ to η^5-$C_5H_5W(CO)_2I_3$ with a second equivalent of I_2. Photolysis of η^5-$C_5H_5W(CO)_3CH_2CH_2C_6H_5$ in cyclohexane under argon or CO with 350-nm lamps affords η^5-$C_5H_5W(CO)_2(\eta^3\text{-}CH(CH_3)C_6H_5)$, which was isolated and characterized by ^1H and ^{13}C NMR and IR spectroscopy and mass spectrometry. It appears to be nonfluxional at temperatures up to 117 °C in toluene-d_8 by ^1H NMR spectroscopy. The same product obtains on irradiation of η^5-$C_5H_5W(CO)_3H$ and excess styrene and of η^5-$C_5H_5W(CO)_3CH(CH_3)C_6H_5$. Photolysis of η^5-$C_5H_5W(CO)_3CHDCHDC_6H_5$-*threo* in cyclohexane solution does not change its diastereomeric purity. This result is interpreted by the absence of any significant photochemically induced W–C σ bond homolysis. Irradiation of η^5-$C_5H_5W(CO)_3CD_2CH_2C_6H_5$ leads to no observable H–D scrambling in unreacted tungsten–phenethyl complex. The η^3-methylbenzyl complex η^5-$C_5H_5W(CO)_2(\eta^3\text{-}CH_{1-y}D_y(CH_{3-x}D_x)C_6H_5)$, isolated from photolysis of each of η^5-$C_5H_5W(CO)_3CHDCHDC_6H_5$ and η^5-$C_5H_5W(CO)_3CD_2CH_2C_6H_5$ in cyclohexane, shows essentially statistical distribution of ^1H between the $(CH_{3-x}D_x)(CH_{1-y}D_y)$ positions. These results are rationalized by rapid isomerization via hydrogen (or deuterium) shifts of photogenerated 16-electron η^5-$C_5H_5W(CO)_2CH_{2-x}D_xCH_{2-y}D_yC_6H_5$ to η^5-$C_5H_5W(CO)_2CH_{1-y}D_y(CH_{3-x}D_x)C_6H_5$, followed by collapse of the latter to η^5-$C_5H_5W(CO)_2(\eta^3\text{-}CH_{1-y}D_y(CH_{3-x}D_x)C_6H_5)$. β-Hydrogen (or -deuterium) transfer in η^5-$C_5H_5W(CO)_2$(phenethyl) to give η^5-$C_5H_5W(CO)_2$(H or D)(styrene) appears to be much faster than CO capture to yield η^5-$C_5H_5W(CO)_3$(phenethyl), even under 1 atm of CO.

Introduction

The α,β-dideuteriophenethyl group, $CHDCHDC_6H_5$, which exists in the threo and erythro diastereomeric forms, can be conveniently introduced onto a transition metal in its threo form.[1-3] When ligated, it has been successfully employed as a stereochemical probe for reactions that disrupt the M–C σ bond.[4] Investigated in this context have been the phosphine-induced CO insertion,[3] the SO_2,[3] $C_6H_5S(O)_2NSO$,[5] and $[p\text{-}XC_6H_4S(O)_2N]_2S$ (X = H, Cl)[5] insertions, the halogen-[2,6] and $HgCl_2$-induced[7] cleavage, and β-hydrogen elimination.[1] Useful mechanistic information was derived from each of the foregoing studies.

We now set out to determine whether the use of $CHDCHDC_6H_5$ can contribute to a better understanding of the mechanism of photochemical reactions of transition-metal–alkyl complexes. If homolysis of the M–$CHDCHDC_6H_5$ bond occurs, then the generated $\cdot CHDCHDC_6H_5$ radical is expected to undergo rapid epimerization, consistent with the behavior of organic alkyl radicals.[8] Recombination of $\cdot CHDCHDC_6H_5$ with the metal-centered radical would afford a mixture of diastereomeric $MCHDCHDC_6H_5$. In contrast, if no photochemically induced M–$CHDCHDC_6H_5$ bond homolysis takes place, then the diastereomeric composition of unreacted metal–alkyl complex will remain constant during the photolysis.

For the proposed study we chose to synthesize and examine the complex η^5-$C_5H_5W(CO)_3CHDCHDC_6H_5$. Our choice of the metal system was dictated by the relatively high thermal stability and the recent interest in the photochemistry of tungsten–alkyl complexes of the type η^5-$C_5H_5W(CO)_3R$.[9-11] Following our disclosure[12] of some preliminary results of this study, Wrighton and co-workers reported[13] on the photochemistry of η^5-$C_5H_5W(CO)_3CH_2CH_2C_6H_5$. Our approach, which is largely stereochemical and utilizes the deuterium-labeled η^5-$C_5H_5W(CO)_3CD_2CH_2C_6H_5$ in addition to η^5-$C_5H_5W(CO)_3CHDCHDC_6H_5$-*threo*, differs from that of Wrighton, and the results presented in this paper complement well his findings. We also report here on the stereochemistry

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of reactions of η^5-$C_5H_5W(CO)_3CHDCHDC_6H_5$-*threo* with SO_2 and I_2.

Experimental Section

General Procedures and Measurements. All thermal reactions were carried out under an atmosphere of purified nitrogen. Elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, TN. Melting points were measured in vacuo on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded on Perkin-Elmer Model 337 and 283 spectrophotometers and were calibrated with polystyrene. Mass spectra were obtained at 70 eV on an AEI Model MS-9 spectrometer by Mr. C. R. Weisenberger. ^1H NMR spectra were recorded on Varian Associates EM-360L and EM-390L and Bruker WM-300 spectrometers with use of Me_4Si as an internal reference. $^1H\{^2H\}$ NMR spectra were obtained on a Varian HA-100 spectrometer with a decoupling frequency of 7.6757 MHz. ^{13}C NMR spectra were recorded on the Bruker WM-300 at 75.478 MHz and on a home-built spectrometer equipped with a wide-band high-power probe and a Nicolet 1080 computer at 15.1 MHz by Dr. B.-M. Su. Chemical shifts are reported relative to Me_4Si at δ 0.

Irradiation Procedures. Solutions to be irradiated were degassed in four freeze–pump–thaw cycles and then hermetically sealed under argon (or CO, when so stated). All photoreactions were conducted at room temperature in Pyrex tubes equipped with a stirrer. Irradiations were performed with 350-nm lamps in a Rayonet Model RPR-100 photochemical reactor. Photolyzed solutions were analyzed by IR spectroscopy. Ferrioxalate actinometry[14] was used to determine lamp intensities that were on the order of 1×10^{-4} einstein/min.

Materials. THF was distilled from Na/K and benzophenone immediately before use. Reagent grade cyclohexane was further purified by distillation from a blue solution of sodium benzophenone ketyl. Chloroform and dichloromethane were distilled from P_4O_{10} and stored over 4-Å molecular sieves. Diethyl ether was passed through a column of alumina and distilled from sodium benzophenone ketyl under nitrogen. Other solvents were of reagent grade or equivalent quality and were dried over molecular sieves before use.

p-Toluenesulfonyl chloride (from MCB) was recrystallized from chloroform–petroleum ether (bp 35–60 °C). Ethyl phenylacetate and styrene (from Aldrich) were purified as described by Perrin.[15] Sulfur dioxide (from Matheson) was purified before use by passage through concentrated H_2SO_4 and a column packed with P_4O_{10}. Other commercially procured reagents were used as received. η^5-$C_5H_5W(CO)_3H$ was prepared as described in the literature.[16]

Preparation of η^5-$C_5H_5W(CO)_3CH_2CH_2C_6H_5$. To a solution of Na[$\eta^5$-$C_5H_5W(CO)_3$][16] (from 21.1 g, 60 mmol, of $W(CO)_6$ and NaC_5H_5) in 120 mL of THF was added 20.8 g (74 mmol) of $C_6H_5CH_2CH_2OS(O)_2C_6H_4CH_3$-*p*,[17] and the reaction mixture was stirred under reflux for 2 h. Solvent was removed on a rotary evaporator, and the solid residue was extracted with CH_2Cl_2. The extract was evaporated to dryness and most of the $W(CO)_6$ contaminant was sublimed off at 40 °C under vacuum. The residue was dissolved in minimum $CHCl_3$, and the solution was chromatographed on a column packed with grade III neutral alumina in cyclohexane. Elution with cyclohexane afforded a yellow band from which 10.5 g (40% yield based on $W(CO)_6$) of product was obtained on evaporation to dryness. Crystallization from $CHCl_3$–petroleum ether (bp 35–60 °C) afforded yellow needles: mp 116–117 °C; ^1H NMR ($CDCl_3$) δ 7.17 (s, 5 H, C_6H_5), 5.17 (s, 5 H, C_5H_5), 2.90–2.70, 1.84–1.63 (AA′XX′; 2 H, 2 H; CCH_2C, WCH_2, respectively); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ −8.6 (WCH_2), 42.8 ($C\mathit{C}H_2C$), 91.5 (C_5H_5), 125.5 (*p*-C of C_6H_5), 127.8, 128.3 (*o*,*m*-C of C_6H_5), 147.3 (ipso-C of C_6H_5), 217.8, 228.5 (CO); IR (C_6H_{12}) $\nu(C{\equiv}O)$ 2018 (5300), 2004 (w), 1926 (9500), 1892 (w) cm^{-1}; mass spectrum (probe 140 °C), *m/e* (relative intensity) 438 P^+ (9), 410 $(P - CO)^+$ (23), 382 $(P - 2CO)^+$ (1), 354 $(P - 3CO)^+$ (100), 105 $C_8H_9^+$ (57) ($P \equiv C_{16}H_{14}O_3{}^{184}W$).

Preparation of η^5-$C_5H_5W(CO)_3CD_2CH_2C_6H_5$. The procedure was the same as that for η^5-$C_5H_5W(CO)_3CH_2CH_2C_6H_5$, except that $C_6H_5CH_2CD_2OS(O)_2C_6H_4CH_3$-*p*, from $C_6H_5CH_2CD_2OH$[18] and *p*-$CH_3C_6H_4S(O)_2Cl$ in pyridine, was used in place of its perhydro analogue. The $C_6H_5CH_2CD_2OH$ contained 1.96 atoms of D/molecule by mass spectrometry. η^5-$C_5H_5W(CO)_3CD_2CH_2C_6H_5$: ^1H NMR ($CDCl_3$) δ 7.14 (s, 5 H, C_6H_5), 5.33 (s, 5 H, C_5H_5), 2.77 (br s, 2 H, CCH_2C).

Preparation of η^5-$C_5H_5W(CO)_3CHDCHDC_6H_5$-*threo*. The title complex was prepared by additon of *erythro*-$C_6H_5CHDCHDOS(O)_2C_6H_4CH_3$-*p*[2] to a THF solution of Na[η^5-$C_5H_5W(CO)_3$][16] and stirring the mixture at 35 °C for 17 h. Workup as above gave ca. 20% yield (based on $W(CO)_6$) of yellow crystals: $^1H\{^2H\}$ NMR ($CDCl_3$) δ (only <4) 2.77 (d, $^3J_{HH}$ = 4.6 Hz, 1 H, CCHDC), 1.71 (d, $^3J_{HH}$ = 4.6 Hz, 1 H, WCHD); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ (only <50) −8.5 (t, $^1J_{CD}$ = 20.3 Hz, WCHD), 42.7 (t, $^1J_{CD}$ = 19.6 Hz, C*C*HDC); mass spectrum (probe 120 °C) *m/e* (relative intensity) 440 P^+ (12), 412 $(P - CO)^+$ (28), 384 $(P - 2CO)^+$ (1), 356 $(P - 3CO)^+$ (100), 305 $(P - CO - C_8H_7D_2)^+$ (10), 277 $(P - 2CO - C_8H_7D_2)^+$ (12), 249 $C_5H_5W^+$ (12), 107 $C_8H_7D_2{}^+$ (3) ($P \equiv C_{16}H_{12}D_2O_3{}^{184}W$).

Preparation of η^5-$C_5H_5W(CO)_3CHDCHDC_6H_5$-*threo*,*erythro* (50:50 Mixture). This 50:50 diastereomeric mixture was prepared by addition of 5.41 g (23.1 mmol) of *threo*,*erythro*-$C_6H_5CHDCHDI$ (50:50 mixture)[2] to a THF solution of Na[η^5-$C_5H_5W(CO)_3$][16] (from 7.03 g, 20 mmol, of $W(CO)_6$ and NaC_5H_5) and maintaining the resulting solution at reflux for 3 h. Usual workup followed: yield 2.0 g (23% based on $W(CO)_6$); $^1H\{^2H\}$ NMR ($CDCl_3$) δ (only <4) 2.77 (2d, $^3J_{HH}$ = 13.1 and 4.6 Hz, 1 H, CCHDC erythro and threo, respectively), 1.71 (2d, $^3J_{HH}$ = 13.1 and 4.6 Hz, 1 H, WCHD erythro and threo, respectively).

Preparation of η^5-$C_5H_5W(CO)_3CH(CH_3)C_6H_5$. To a solution of Na[$\eta^5$-$C_5H_5W(CO)_3$][16] (from 8.44 g, 24 mmol, of $W(CO)_6$ and NaC_5H_5) in 50 mL of THF was added 6.48 g (36 mmol) of $C_6H_5CH(CH_3)Cl$, and the reaction mixture was stirred at room temperature for 2.5 days. Solvent was removed, the residue was extracted with CH_2Cl_2, and the extract was chromatographed on a column packed with grade III neutral alumina in pentane. Elution with pentane afforded a yellow band which on removal of the solvent yielded an oil. Dissolution of the oil in cyclohexane and evaporation of the solvent afforded straw-colored crystals: 0.474 g (ca. 5% yield); ^1H NMR ($CDCl_3$) δ 7.27–6.83 (m, 5 H, C_6H_5), 5.11 (s, 5 H, C_5H_5), 3.75 (q, $^3J_{HH}$ = 7.5 Hz, 1 H, CH), 1.90 (d, $^3J_{HH}$ = 7.5 Hz, 3 H, CH_3); IR (C_6H_{12}) $\nu(C{\equiv}O)$ 2013 (vs), 1930 (vs), 1920 (vs) cm^{-1}.

Reaction of η^5-$C_5H_5W(CO)_3CHDCHDC_6H_5$-*threo* with SO_2. Reaction between the title tungsten complex (0.178 g, 0.404 mmol) and liquid SO_2 (12 mL) was conducted at room temperature for 16 days according to a general literature procedure.[19] Standard workup and crystallization from $CHCl_3$–petroleum ether (bp 35–60 °C) afforded 0.081 g (40% yield) of η^5-$C_5H_5W(CO)_3S(O)_2CHDCHDC_6H_5$-*erythro* as a yellow crystalline solid: mp 103–105 °C dec; $^1H\{^2H\}$ NMR ($CDCl_3$) δ 7.22 (s, 5 H, C_6H_5), 5.90 (s, 5 H, C_5H_5), 3.44, 3.10 (AB q, $^3J_{HH}$ = 12.0 Hz, 2 H, SCHD and CCHDC, respectively); IR ($CHCl_3$) $\nu(C{\equiv}O)$ 2049 (1900), 1962 (2400) cm^{-1}, (Nujol) $\nu(SO_2)$ 1190 (m), 1052 (s) cm^{-1}.

Reaction of η^5-$C_5H_5W(CO)_3CH_2CH_2C_6H_5$ with SO_2. Conducted as above, this reaction afforded a comparable yield of η^5-$C_5H_5W(CO)_3S(O)_2CH_2CH_2C_6H_5$: mass spectrum (probe 80 °C), *m/e* (relative intensity) 474 $(P - CO)^+$ (6), 438 $(P - SO_2)^+$ (12), 410 $(P - CO - SO_2)^+$ (28), 354 $(P - 3CO - SO_2)^+$ (80), 333 $(P - SO_2 - C_8H_9)^+$ (37), 249 $C_5H_5W^+$ (100), 105 $C_8H_9{}^+$ (>100) ($P \equiv C_{16}H_{14}O_5S^{184}W$). Anal. Calcd for $C_{16}H_{14}O_5SW$: C, 38.27; H, 2.81; S, 6.38. Found: C, 38.10; H, 2.90; S, 6.26.

Reaction of η^5-$C_5H_5W(CO)_3CHDCHDC_6H_5$-*threo* with I_2. This iodination reaction was carried out at room temperature by adding a $CHCl_3$ solution of 2 equiv of I_2 to a stirred $CHCl_3$ solution of the title tungsten complex. The reaction mixture was stirred for 1 h, the red precipitate was filtered off and identified as η^5-$C_5H_5W(CO)_2I_3$[20] by IR and ^1H NMR spectroscopy, and the

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Table I. Values of ${}^3J_{HH}$ for Some Alkyl and Sulfinato Compounds $C_6H_5CHDCHDY$ ($CDCl_3$ Solution)

Y	${}^3J_{HH}$(threo)	${}^3J_{HH}$(erythro)
η^5-$C_5H_5Fe(CO)_2$	4.8[a]	12.6[a]
cis-$Mn(CO)_4[P(C_2H_5)_3]$	4.6[b]	
trans-η^5-$C_5H_5W(CO)_2$-$[P(C_2H_5)_3]$	4.5[b]	
η^5-$C_5H_5W(CO)_3$	4.6[c]	13.1[c]
η^5-$C_5H_5Fe(CO)_2S(O)_2$		12.4[b]
cis-$Mn(CO)_4[P(C_2H_5)_3]S(O)_2$		12.6[b]
trans-η^5-$C_5H_5W(CO)_2$-$[P(C_2H_5)_3]S(O)_2$		12.5[b]
η^5-$C_5H_5W(CO)_3S(O)_2$		12.0[c]

[a] From ref 2. [b] From ref 3. [c] This work.

filtrate containing *threo*-$C_6H_5CHDCHDI$ was concentrated: ${}^1H\{{}^2H\}$ NMR ($CHCl_3$) of the filtrate δ (only <5) 3.30, 3.06 (AB q, ${}^3J_{HH}$ = 6.0 Hz, 2 H, CHDI and CCHDC, respectively).

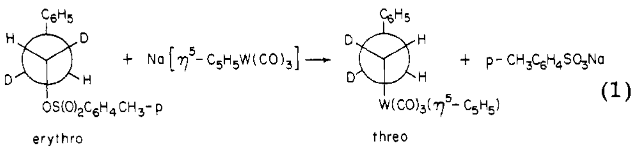
Reaction of η^5-$C_5H_5W(CO)_3CD_2CH_2C_6H_5$ with I_2. Conducted as above, the reaction yielded comparable results: ${}^1H$ NMR ($CHCl_3$) of the filtrate δ (only <5) 3.06 (s, 2 H, CCH_2C).

Photochemical Conversion of η^5-$C_5H_5W(CO)_3CH_2CH_2C_6H_5$ to η^5-$C_5H_5W(CO)_2(\eta^3$-$CH(CH_3)C_6H_5)$. A 0.01–0.02 M solution of the title complex in cyclohexane was irradiated for 30–60 min (until ca. 50% of the starting material disappeared). The red precipitate of $[\eta^5$-$C_5H_5W(CO)_3]_2$[10] was filtered off, and the filtrate was evaporated to dryness. The residue was dissolved in minimum CH_2Cl_2 and chromatographed on grade III neutral alumina. Cyclohexane first eluted unreacted η^5-$C_5H_5W(CO)_3CH_2CH_2C_6H_5$ and then η^5-$C_5H_5W(CO)_2(\eta^3$-$CH(CH_3)C_6H_5)$, which was obtained as a rust solid, mp 133–133.5 °C dec, in ca. 15% yield by removal of the solvent: ${}^1H$ NMR (C_6D_6, Bruker WM-300) δ 7.05 (d, 1 H, H(e)), 6.90 (t, 1 H, H(c)), 6.75 (t, 1 H, H(b)), 6.63 (t, 1 H, H(d)), 4.66 (s, 5 H, C_5H_5), 4.21 (d, 1 H, H(a)), 2.18 (d, ${}^3J_{HH}$ = 5.7 Hz, 3 H, CH_3), 1.62 (q, ${}^3J_{HH}$ = 5.7 Hz, 1 H, H(f)); ${}^{13}C$ NMR, gated (CD_2Cl_2, Bruker WM-300) δ 17.7 (q, J_{CH} = 127 Hz, C(8)), 30.6 (d, J_{CH} = 149 Hz, C(7)), 61.1 (d, J_{CH} = 164 Hz, C(2)), 90.7 (d, J_{CH} = 176 Hz, C_5H_5), 105.8 (s, C(1)), 122.5 126.8, 128.0 (3d, J_{CH} = 173, 161, 151 Hz, respectively, C(3), C(4), C(5)), 135.6 (d, J_{CH} = 161 Hz, C(6)), 231.0, 233.7 (2s, 2CO); IR (C_6H_{12}) $\nu(C\equiv O)$ 1950 (6300), 1875 (6300) cm^{-1}; mass spectrum (probe 100 °C), *m/e* (relative intensity) 410 P^+ (28), 382 $(P - CO)^+$ (v weak), 354 $(P - 2CO)^+$ (100), 276 $C_5H_5WC_2H_3^+$ (15), 104 $C_8H_8^+$ (≫100), P^+ observed at *m/e* 410.050898, calcd 410.050373 ($P \equiv C_{15}H_{14}O_2{}^{184}W$). Anal. Calcd for $C_{15}H_{14}O_2W$: C, 43.93; H, 3.44. Found: C, 43.72; H, 3.50.

Photochemical Reaction of η^5-$C_5H_5W(CO)_3H$ with Styrene. A cyclohexane solution of the hydrido complex (0.02 M) and ca. tenfold excess of styrene was irradiated for 30 min. Workup followed as in the preceding reaction to afford ca. 10% yield of η^5-$C_5H_5W(CO)_2(\eta^3$-$CH(CH_3)C_6H_5)$ based on η^5-$C_5H_5W(CO)_3H$.

Results and Discussion

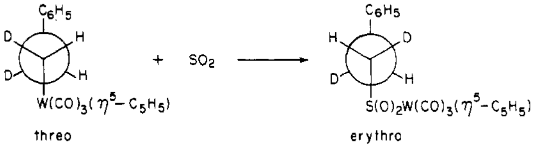
Preparation of η^5-$C_5H_5W(CO)_3CHDCHDC_6H_5$-*threo*. Reaction of *erythro*-$C_6H_5CHDCHDOS(O)_2C_6H_4CH_3$-*p* with $Na[\eta^5$-$C_5H_5W(CO)_3]$ requires higher temperatures or longer reaction times than that with $Na[\eta^5$-$C_5H_5Fe(CO)_2]$.[2] When conducted at 35 °C for 17 h, it affords η^5-$C_5H_5W(CO)_3CHDCHDC_6H_5$-*threo* (eq 1) in ≥95% diastereomeric purity. The stereochemistry of the α,β-dideuteriophenethyl group was elucidated by ${}^1H\{{}^2H\}$ NMR specroscopy and rests on the observations[2,3,7,21] that the vicinal coupling constants for various threo and erythro diastereomers containing $CHDCHDC_6H_5$ are not equal, ${}^3J_{HH}$(threo) < ${}^3J_{HH}$(erythro). The coupling constant of 4.6 Hz for the product compares well with that for other transition-metal $CHDCHDC_6H_5$-*threo* complexes listed in Table I. Reaction of an equilibrium mixture (50:50) of *threo,erythro*-$C_6H_5CHDCHDI$ with $Na[\eta^5$-$C_5H_5W(CO)_3]$ yielded a diastereomeric mixture (50:50) of η^5-$C_5H_5W(CO)_3CHDCHDC_6H_5$-*threo,erythro*, for which a ${}^3J_{HH}$(erythro) = 13.1 Hz (cf. Table I) was measured. η^5-$C_5H_5W(CO)_3CHDCHDC_6H_5$-*threo*, as well as the similarly prepared perhydro and $CD_2CH_2C_6H_5$ analogues, were characterized by a combination of ${}^1H$ and ${}^{13}C$ NMR and IR spectroscopy and mass spectrometry as detailed in Experimental Section.



(1)

The foregoing stereochemical result parallels that obtained for the reactions of each of $Na[\eta^5$-$C_5H_5Fe(CO)_2]$,[2] $Na[Mn(CO)_4P(C_2H_5)_3]$,[3] and $Na[\eta^5$-$C_5H_5W(CO)_2P(C_2H_5)_3]$[3] with *erythro*-$C_6H_5CHDCHDOS(O)_2C_6H_4CH_3$-*p*. The formation of the M–$CHDCHDC_6H_5$ bond proceeds with inversion of configuration at carbon, presumably through nucleophilic displacement of *p*-$CH_3C_6H_4SO_3^-$ by the metal carbonyl anion.

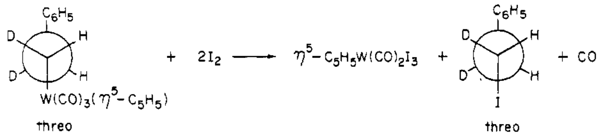
Sulfur Dioxide Insertion Reaction of η^5-$C_5H_5W(CO)_3CHDCHDC_6H_5$-*threo*. Sulfur dioxide insertion into the W–C σ bond of η^5-$C_5H_5W(CO)_3CHDCHDC_6H_5$-*threo* proceeds slowly (16 days) in neat SO_2 in a closed vessel at room temperature to afford η^5-$C_5H_5W(CO)_3S(O)_2CHDCHDC_6H_5$-*erythro* as depicted in eq 2. The diastereomeric nature of the product was determined from the value of its ${}^3J_{HH}$, 12.0 Hz (cf. Table I). The stereochemistry of this SO_2 insertion is thus the same as that observed for other 18-electron transition-metal carbonyl alkyls.[3,4b,22] A proposed mechanism, which is based on inversion at α-carbon, was elaborated elsewhere.[23,24]



(2)

Iodine Cleavage Reactions of η^5-$C_5H_5W(CO)_3CHDCHDC_6H_5$-*threo* and η^5-$C_5H_5W(CO)_3CD_2CH_2C_6H_5$. Iodine cleavage reactions of these two differently labeled tungsten–phenethyl complexes were carried out by using 2 equiv of I_2 in order completely to convert the metal–alkyl complex to phenethyl iodide and the sparingly soluble η^5-$C_5H_5W(CO)_2I_3$. This clean conversion permits an ${}^1H$ (or ${}^1H\{{}^2H\}$) NMR spectrum of the phenethyl iodide to be recorded on the filtrate from the reaction mixture, without need for further separation and purification. Use of 1 equiv of I_2, on the other hand, affords a mixture of η^5-$C_5H_5W(CO)_2I_3$, η^5-$C_5H_5W(CO)_3I$, phenethyl iodide, and unreacted tungsten–phenethyl complex; this complicates characterization by NMR spectroscopy without prior separation.

Cleavage of the W–C σ bond proceeds with the stereochemistry shown in eq 3 and 4. Retention of configuration



(3)

$$\eta^5\text{-}C_5H_5W(CO)_3CD_2CH_2C_6H_5 + 2I_2 \rightarrow \eta^5\text{-}C_5H_5W(CO)_2I_3 + C_6H_5CH_2CD_2I + CO \quad (4)$$

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(20) Green, M. L. H.; Lindsell, W. E. *J. Chem. Soc. A* **1967**, 686.

(21) Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1977**, *99*, 1808.

(22) Review: Flood, T. C. *Top. Stereochem.* **1981**, *12*, 37.

(23) Wojcicki, A. *Adv. Organomet. Chem.* **1974**, *12*, 31.

(24) Miles, S. L.; Miles, D. L.; Bau, R.; Flood, T. C. *J. Am. Chem. Soc.* **1978**, *100*, 7278.

at carbon in the cleavage of η^5-$C_5H_5W(CO)_3CHDCHDC_6H_5$-*threo* follows from the value of $^3J_{HH}$, 6.0 Hz, of the filtrate from the reaction mixture, which is identical with the value reported for *threo*-$C_6H_5CHDCHDI$. The iodination of η^5-$C_5H_5W(CO)_3CD_2CH_2C_6H_5$ affords $C_6H_5CH_2CD_2I$ as the only isomer of phenethyl iodide; this was inferred from the ^1H NMR spectrum of soluble product (see Experimental Section). The former result is qualitatively the same as that for the iodination of η^5-$C_5H_5Fe(CO)_2CHDCHDC_6H_5$-*threo*[2] and *cis*-$Mn(CO)_4[P(C_2H_5)_3]CHDCHDC_6H_5$-*threo*[6] under similar conditions. However, the observed degree of retention (≥90%) is greater than that for the iron (~80%) and manganese (63–72%) complexes. The latter result of our study contrasts with that reported[25] for the iodination of η^5-$C_5H_5Fe(CO)_2CD_2CH_2C_6H_5$ which yields a 50:50 mixture of $C_6H_5CH_2CD_2I$ and $C_6H_5CD_2CH_2I$. However, it accords with the stereochemistry of I_2 cleavage of $Co(py)(Hdgy)_2CD_2CH_2C_6H_5$ (py = pyridine, Hdgy = dimethylglyoximato) to give isomerically pure $C_6H_5CH_2CD_2I$.[25]

The foregoing stereochemical findings may be rationalized on the basis of initial electrophilic attack of I_2 on the metal in η^5-$C_5H_5W(CO)_3$(phenethyl) to afford $[\eta^5\text{-}C_5H_5W(CO)_3(\text{phenethyl})I]^+I^-$. Reductive elimination of phenethyl iodide and coordination of I^- to tungsten would then yield η^5-$C_5H_5W(CO)_3I$. Oxidation of η^5-$C_5H_5W(CO)_3I$ to η^5-$C_5H_5W(CO)_2I_3$ with a second equivalent of I_2[20] completes the reactions in eq 3 and 4. Such a mechanism, analogous to that proposed earlier[26,27] for electrophilic cleavage reactions of the Fe–C σ bond in η^5-$C_5H_5Fe(CO)(L)R$ (L = CO, PR'_3, etc.), would account for the retention of configuration at α-carbon and the absence of scrambling of the phenethyl methylene groups during cleavage. The difference in the stereochemistry of the iodination of η^5-$C_5H_5W(CO)_3CD_2CH_2C_6H_5$ and η^5-$C_5H_5Fe(CO)_2CD_2CH_2C_6H_5$ may be explained if η^5-$C_5H_5Fe(CO)_2I$ is a better leaving group than η^5-$C_5H_5W(CO)_3I$. This would result in the formation of the phenonium ion in the reaction of the iron complex[22]—but not of the tungsten complex—thus leading to CH_2–CD_2 scrambling. Evidence for a facile dissociation of η^5-$C_5H_5Fe(CO)_2E$ (E = electrophile such as HgCl) from several $[\eta^5\text{-}C_5H_5Fe(CO)_2(E)R]^+$ species has been presented.[28]

Irradiation of η^5-$C_5H_5W(CO)_3CH_2CH_2C_6H_5$ and Its Dideuterio Analogues. (a) Photochemistry. Photolysis of ca. 1 × 10^{-2} M solutions of η^5-$C_5H_5W(CO)_3CH_2CH_2C_6H_5$ in cyclohexane under argon leads to the appearance of two new IR $\nu(C{\equiv}O)$ absorptions at 1950 and 1875 cm^{-1} after about 2 min. These bands have been assigned to η^5-$C_5H_5W(CO)_2(\eta^3\text{-}CH(CH_3)C_6H_5)$ (vide infra), formed according to eq 5. Continued irradiation leads to an increase

$$\eta^5\text{-}C_5H_5W(CO)_3CH_2CH_2C_6H_5 \xrightarrow{h\nu} \eta^5\text{-}C_5H_5W(CO)_2(\eta^3\text{-}CH(CH_3)C_6H_5) + CO \quad (5)$$

in intensity of the aforementioned absorptions and, after ca. 45 min, to the appearance of $\nu(C{\equiv}O)$ absorptions characteristic of η^5-$C_5H_5W(CO)_3H$[16] (2028 and 1938 cm^{-1}) and $[\eta^5\text{-}C_5H_5W(CO)_3]_2$ (1963 and 1914 cm^{-1}). The tungsten dimer was later isolated and identified by comparison of its ^1H NMR and mass spectra with the corresponding

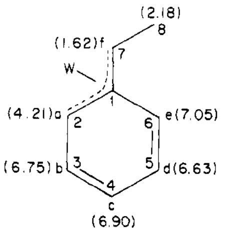


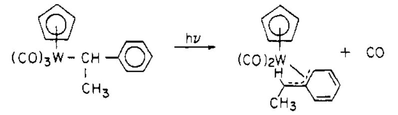
Figure 1. The lettering scheme for the protons a–f and the numbering scheme for the carbons 1–8 of the η^3-methylbenzyl ligand of η^5-$C_5H_5W(CO)_2(\eta^3\text{-}CH(CH_3)C_6H_5)$. The chemical shifts of the protons are given in parentheses.

spectra of an authentic sample. Longer irradiation times generate somewhat higher concentrations of the products. However, the concentration of $[\eta^5\text{-}C_5H_5W(CO)_3]_2$ builds up with time, and conversions of only 50–70% were realized after 1–2 h.

Similar results were obtained when the photolysis was conducted under CO. The starting material was observed to disappear essentially at a comparable rate.

Irradiation of η^5-$C_5H_5W(CO)_3H$ and excess styrene in cyclohexane under argon also affords η^5-$C_5H_5W(CO)_2(\eta^3\text{-}CH(CH_3)C_6H_5)$ as the only detectable product during short reaction times (eq 6). Photolysis of η^5-$C_5H_5W(CO)_3CH(CH_3)C_6H_5$ in cyclohexane gives η^5-$C_5H_5W(CO)_2(\eta^3\text{-}CH(CH_3)C_6H_5)$ as well, according to eq 7, along with $[\eta^5\text{-}C_5H_5W(CO)_3]_2$.

$$\eta^5\text{-}C_5H_5W(CO)_3H + C_6H_5CH{=}CH_2 \xrightarrow{h\nu} \eta^5\text{-}C_5H_5W(CO)_2(\eta^3\text{-}CH(CH_3)C_6H_5) + CO \quad (6)$$



(7)

Wrighton and co-workers reported[11,13] that low-temperature (77K) irradiation of η^5-$C_5H_5W(CO)_3CH_2CH_2C_6H_5$ followed by warming affords *trans*-η^5-$C_5H_5W(CO)_2(H)(CH_2{=}CHC_6H_5)$, which can still be observed at room temperature before rearrangement to η^5-$C_5H_5W(CO)_2(\eta^3\text{-}CH(CH_3)C_6H_5)$. Furthermore, they were able to detect *trans*-η^5-$C_5H_5W(CO)_2(H)(CH_2{=}CHC_6H_5)$ on irradiation of η^5-$C_5H_5W(CO)_3H$ in the presence of styrene. Under the conditions employed in our study, the photoreactions in eq 5–7 all generate η^5-$C_5H_5W(CO)_2(\eta^3\text{-}CH(CH_3)C_6H_5)$ as the first product present in sufficient concentration for detection by IR spectroscopy. Apparently under these conditions *trans*-η^5-$C_5H_5W(CO)_2(H)(CH_2{=}CHC_6H_5)$ undergoes a more rapid conversion to η^5-$C_5H_5W(CO)_2(\eta^3\text{-}CH(CH_3)C_6H_5)$ than under the conditions of Wrighton's study. Prolonged irradiation yields η^5-$C_5H_5W(CO)_3H$ and/or $[\eta^5\text{-}C_5H_5W(CO)_3]_2$ as secondary product(s).

(b) Characterization of η^5-$C_5H_5W(CO)_2(\eta^3\text{-}CH(CH_3)C_6H_5)$. Workup of the irradiated solution after ca. 50% of the starting material had disappeared led to the isolation of η^5-$C_5H_5W(CO)_2(\eta^3\text{-}CH(CH_3)C_6H_5)$ as described in Experimental Section. This compound was characterized by elemental analysis, exact molecular weight determination by mass spectrometry, and IR and NMR spectroscopy. The IR spectrum shows two $\nu(C{\equiv}O)$ absorptions which are within 10 cm^{-1} of the values reported[29] for the related complex η^5-$C_5H_5W(CO)_2(\eta^3\text{-}CH_2C_6H_4CH_3\text{-}p)$. The 300-MHz ^1H NMR spectrum exhibits separate resonances for the various kinds of protons. The lettering scheme and the chemical shifts of these protons are presented in Figure

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(25) Flood, T. C.; DiSanti, F. J. *J. Chem. Soc., Chem. Commun.* **1975**, 18.

(26) Attig, T. G.; Teller, R. G.; Wu, S.-M.; Bau, R.; Wojcicki, A. *J. Am. Chem. Soc.* **1979**, *101*, 619.

(27) Flood, T. C.; Miles, D. L. *J. Organomet. Chem.* **1977**, *127*, 33.

(28) Dizikes, L. J.; Wojcicki, A. *J. Am. Chem. Soc.* **1977**, *99*, 5295.

(29) Cotton, F. A.; Marks, T. J. *J. Am. Chem. Soc.* **1969**, *91*, 1339.

1. The assignments were made with the aid of homonuclear decoupling experiments. Thus, irradiation at the frequency of the δ 2.18 signal collapses the δ 1.62 quartet to a singlet. Similarly, irradiation at the δ 4.21 and 7.05 signals resulted in a collapse of the apparent triplets at δ 6.75 and 6.63, respectively, to doublets. All resonances in the gated ^{13}C NMR spectrum were assigned as well and are given in Experimental Section.

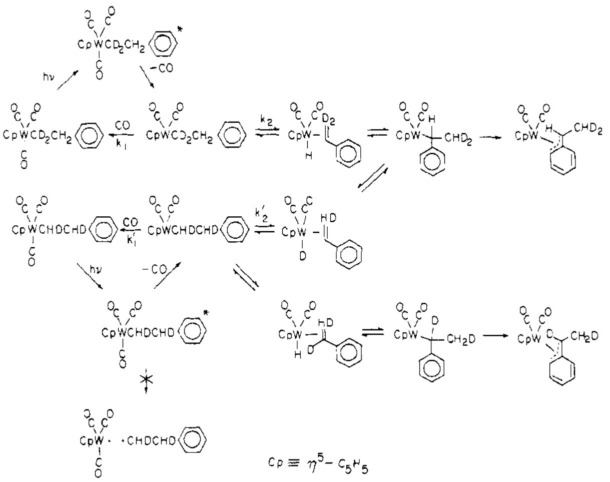
Since η^5-$C_5H_5W(CO)_2(\eta^3$-$CH_2C_6H_4CH_3$-*p*) is fluxional in the temperature range from −30 to +60 °C,[29] we examined ^{1}H NMR spectra of η^5-$C_5H_5W(CO)_2(\eta^3$-$CH(CH_3)C_6H_5)$ at higher termperatures to ascertain possible fluxional behavior of this molecule. These measurements were made in C_6H_6 and toluene-d_8 solutions at temperatures up to 117 °C. No broadening of the signals was noticeable; in particular, the resonances of protons a and e remain essentially as sharp as they are at room temperature. Lack of exchange between protons a and e militates against a fluxional process that would involve rearrangement of η^3-$CH(CH_3)C_6H_5$ to η^1-$CH(CH_3)C_6H_5$ followed by a 180° rotation about the C(7)–C(1) bond and return to η^3-$CH(CH_3)C_6H_5$. Suprafacial shifts[29] of η^5-$C_5H_5W(CO)_3$, i.e., movements from η^3-C(7)C(1)C(2) to the more sterically hindered η^3-C(7)C(1)C(6), are also precluded by the ^{1}H NMR data. However, antarafacial shifts[29] of tungsten between the two faces of the benzyl group in the η^3-C(7)C(1)C(2) coordination environment may be occurring, but if so, without rotation about the C(7)–C(1) bond. A modification in the structure of our η^3-benzyl ligand such as substitution of $CH(CH_3)_2$ at C(4) would be necessary to resolve this last point.

(c) Stereochemistry of η^5-$C_5H_5W(CO)_3CHDCHDC_6H_5$-*threo*. Stereochemical fate of η^5-$C_5H_5W(CO)_3CHDCHDC_6H_5$-*threo* (≥95% diastereomeric purity) during irradiation was investigated by photolyzing its solutions (2×10^{-2} M) in cyclohexane under argon until ca. 30% of the complex was consumed (~45 min). Unreacted η^5-$C_5H_5W(CO)_3CHDCHDC_6H_5$ was then isolated as described in Experimental Section and analyzed by ^{1}H{^{2}H} NMR spectroscopy for diastereomeric purity. In general, three to four samples were examined in each run. All measurements showed η^5-$C_5H_5W(CO)_3CHDCHDC_6H_5$ to be ≥ 95% threo. Irradiation of a 1.2×10^{-2} M cyclohexane solution of η^5-$C_5H_5W(CO)_3CHDCHDC_6H_5$-*threo* of 67% diastereomeric purity gave similar results.

The foregoing findings suggest that very little, if any, W–$CHDCHDC_6H_5$ bond homolysis occurs during photolysis. Since the disappearance on irradiation at 366 nm of tungsten–alkyl complexes of the type η^5-$C_5H_5W(CO)_3R$ proceeds with a quantum yield, Φ, of less than 0.4,[13] a good number of photons absorbed by η^5-$C_5H_5W(CO)_3R$ cause no net chemical reaction. If such a "no reaction" process were cleavage of the W–$CHDCHDC_6H_5$ bond and recombination of the radicals, then some epimerization of η^5-$C_5H_5W(CO)_3CHDCHDC_6H_5$-*threo* would have been expected as stated in Introduction. Our inference that W–$CHDCHDC_6H_5$ bond cleavage is not an important primary photochemical process accords with the conclusions of other studies on irradiation of metal carbonyl alkyl complexes.[10,11,13,30]

(d) Scrambling of Hydrogen and Deuterium from η^5-$C_5H_5W(CO)_3CHDCHDC_6H_5$-*threo,erythro* and η^5-$C_5H_5W(CO)_3CD_2CH_2C_6H_5$. Possible hydrogen–deuterium scrambling in the phenethyl group of η^5-$C_5H_5W(CO)_3CD_2CH_2C_6H_5$ was examined during irradiation of a 1.8×10^{-2} M solution of this complex in cyclohexane under argon for 2 h. Aliquots of the photolyzed solution were withdrawn periodically (in general, three to four times) and the unreacted alkyl complex was separated and analyzed by ^{1}H NMR spectroscopy. Only the $CH_2C_6H_5$ methylene proton signal was observed at δ 2.77. The absence of a resonance at δ 1.71, due to WCH_2 or WCHD, indicates that no hydrogen–deuterium scrambling took place. A similar experiment was conducted under CO for 1 h, and again all deuterium remained in the WCD_2 methylene group. Furthermore, when the foregoing reactions under argon and CO were followed by IR spectroscopy, η^5-$C_5H_5W(CO)_3CD_2CH_2C_6H_5$ was found to disappear at about the same rate (±4% error in experimental data).

Scheme I



After 1–2 h of photolysis, η^5-$C_5H_5W(CO)_2(\eta^3$-methylbenzyl) was isolated from each reaction mixture and the isotopic distribution of hydrogen between the $C(8)H_{3-x}D_x$ and $C(7)H_{1-y}D_y$(f) (cf. Figure 1) groups was determined by ^{1}H NMR spectroscopy. Essentially three times as much ^{1}H was found in $C(8)H_{3-x}D_x$ as in $C(7)H_{1-y}D_y$(f), i.e. $x = {}^3/_2$ and $y = {}^1/_2$. Thus, isotopic distribution between the two positions is statistical.

The same statistical distribution of ^{1}H was observed for a sample of η^5-$C_5H_5W(CO)_2(\eta^3$-methylbenzyl) prepared by photolysis of η^5-$C_5H_5W(CO)_3CHDCHDC_6H_5$-*threo,erythro* under argon.

These photochemical results on hydrogen–deuterium distribution in the reactant and the product may be rationalized by the reactions set out in Scheme I. The primary photoreaction is loss of CO from electronically excited η^5-$C_5H_5W(CO)_3$(phenethyl) to give η^5-$C_5H_5W(CO)_2$(phenethyl), rather than W–C σ bond homolysis. The 16-electron η^5-$C_5H_5W(CO)_2$(phenethyl) undergoes β-hydrogen (or -deuterium) transfer to yield η^5-$C_5H_5W(CO)_2$(H or D)(styrene), which converts to another 16-electron species, η^5-$C_5H_5W(CO)_2$(methylbenzyl). The observed formation of η^5-$C_5H_5W(CO)_2(\eta^3$-$CH(CH_3)C_6H_5)$ from the reaction of η^5-$C_5H_5W(CO)_3H$ and styrene under irradiation (vide supra) arises via initial CO substitution by styrene to give η^5-$C_5H_5W(CO)_2(H)(CH_2{=}CHC_6H_5)$. Although η^5-$C_5H_5W(CO)_2$(H)(styrene) can exist in the cis and trans isomeric forms, we do not include this isomerism in Scheme I, since it has no bearing on the isotopic distribution and, besides, was already discussed by Wrighton and co-workers.[13]

Since photolysis of η^5-$C_5H_5W(CO)_3CD_2CH_2C_6H_5$ or η^5-$C_5H_5W(CO)_3CHDCHDC_6H_5$ does not lead to observable hydrogen–deuterium scrambling in the phenethyl group of the alkyl complex, even when conducted under CO, the

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[30] Kazlauskas, R. J.; Wrighton, M. S. *Organometallics* **1982**, *1*, 602.

value of k_1[CO] (or k_1'[CO]) must be very small compared to k_2 (or k_2') (cf. Scheme I). In other words, 16-electron η^5-$C_5H_5W(CO)_2$(phenethyl) species essentially always transfer β-hydrogen (or -deuterium) to give η^5-$C_5H_5W(CO)_2$(H or D)(styrene) rather than capture CO to yield η^5-$C_5H_5W(CO)_3$(phenethyl). Unfortunately no rate data are available for β-hydrogen transfer[31] and CO capture of η^5-$C_5H_5W(CO)_2R$ to scrutinize this conclusion. However, it was recently shown[32] that α-hydrogen transfer in the complex $(\eta^5\text{-}C_5H_5)_2NbCH_2OZr(H)[\eta^5\text{-}C_5(CH_3)_5]_2$ is roughly 4100 times faster than CO trapping at 1 atm. Thus, our observations seem to be entirely reasonable. Perhaps at higher pressures of CO some hydrogen–deuterium scrambling in the phenethyl group of η^5-$C_5H_5W(CO)_3CD_2CH_2C_6H_5$ or η^5-$C_5H_5W(CO)_3CHDCHDC_6H_5$ would be observable; however, we did not conduct irradiation experiments at pressures above 1 atm.

Acknowledgment. We are grateful to the National Science Foundation for support of this research through Grant CHE-7911882. We also thank Dr. C. E. Cottrell for his help in recording a number of NMR spectra. The Bruker WM-300 spectrometer used in this study was funded in part by the National Science Foundation, Grant CHE-7910019.

Registry No. η^5-$C_5H_5W(CO)_3CHDCHDC_6H_5$-*threo*, 86823-62-3; η^5-$C_5H_5W(CO)_3CHDCHDC_6H_5$-*erythro*, 86852-05-3; η^5-$C_5H_5W(CO)_3S(O)_2CHDCHDC_6H_5$-*erythro*, 86834-42-6; η^5-$C_6H_5W(CO_3S(O)_2CH_2CH_2C_6H_5$, 86834-43-7; η^5-$C_5H_5W(CO)_2(\eta^3\text{-}CH(CH_3)C_6H_5)$, 82615-33-6; η^5-$C_5H_5W(CO)_3CH(CH_3C_6H_5$, 82615-31-4; η^5-$C_5H_5W(CO)_3CD_2CH_2C_6H_5$, 86823-61-2; η^5-$C_5H_5W(CO)_3CH_2CH_2C_6H_5$, 82615-27-8; η^5-$C_5H_5W(CO)_3H$, 12128-26-6; Na[η^5-$C_5H_5W(CO)_3$], 12107-36-7; $C_6H_5CH_2CH_2OS(O)_2C_6H_4CH_3$-*p*, 4455-09-8; $C_6H_5CH_2CD_2OS(O)_2C_6H_4CH_3$-*p*, 36809-05-9; $C_6H_5CH_2CD_2OH$, 40638-92-4; *p*-$CH_3C_6H_4S(O)_2Cl$, 98-59-9; *erythro*-$C_6H_5CHDCHDOS(O)_2C_6H_4CH_3$-*p*, 26631-76-5; *threo*-$C_6H_5CHDCHDI$, 61012-86-0; *erythro*-$C_6H_5CHDCHDI$, 61012-88-2; $C_6H_5CH(CH_3)Cl$, 672-65-1; SO_2, 7446-09-5; I_2, 7553-56-2; styrene, 100-42-5.

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(31) A recent study[11] showed that, for η^5-$C_5H_5W(CO)_2C_2H_5$, β-hydrogen transfer to form *cis*-η^5-$C_5H_5W(CO)_2(H)(C_2H_4)$ occurs very rapidly compared to cis-to-trans isomerization of the ethylene hydride complex, thus precluding rate constant measurement for the former step.

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Metal-Induced Cleavage of Carbon–Sulfur Bonds in Thiolato Ligands. Thermolysis of $HOs_3(CO)_{10}(\mu\text{-}SC_6H_5)$ under CO Pressure. The Synthesis and Crystal and Molecular Structures of $Os_4(CO)_{13}(\mu_3\text{-}S)$ and $Os_5(CO)_{15}(\mu_4\text{-}S)$

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The thermolysis of $HOs_3(CO)_{10}(\mu\text{-}SC_6H_5)$, I, has been studied under carbon monoxide pressures of 200 and 1800 psi at 150 °C. At 200 psi, I eliminates C_6H_6 and forms the new compounds $Os_4(CO)_{13}(\mu_3\text{-}S)$, II, and $Os_5(CO)_{15}(\mu_4\text{-}S)$, III, and the known compounds $Os_3(CO)_9(\mu_3\text{-}S)_2$, IV, and $Os_3(CO)_{12}$. Compounds II and III have been characterized by X-ray crystallographic methods. For II: space group $P\bar{1}$, No. 2, a = 9.608 (2) Å, b = 15.402 (2) Å, c = 15.703 (3) Å, α = 113.29 (2)°, β = 99.04 (2)°, γ = 95.52 (2)°, V = 2077 (2) Å^3, Z = 4, ρ_{calcd} = 3.70 g/cm^3. The structure was solved by the heavy-atom method. For 3998 reflections ($F^2 \geq 3.0\sigma(F^2)$) R_F = 0.040 and R_{wF} = 0.046. The structure consists of a butterfly cluster of four osmium atoms with a triply bridging sulfido ligand on one triangular group of three. There are 13 linear terminal carbonyl ligands. When heated in the absence of CO, II loses 1 mol of CO and forms the $Os_4(CO)_{12}(\mu_3\text{-}S)$ which contains a closed tetrahedron of four metal atoms. For III: space group $Pna2_1$, No. 33, a = 19.119 (4) Å, b = 7.724 (6) Å, c = 16.417 (4) Å, V = 2424 (3) Å^3, Z = 4, ρ_{calcd} = 3.84 g/cm^3. The structure was solved by direct methods. For 1520 reflections ($F^2 \geq 3.0\sigma(F^2)$) R_F = 0.037 and R_{wF} = 0.042. The structure consists of a square-pyramidal cluster of five osmium atoms with a quadruply bridging sulfido ligand spanning the square base. Each metal atom contains three linear terminal carbonyl ligands. At 1800 psi of CO pressure thermolysis of I yields C_6H_6, $Os_3(CO)_9(\mu_3\text{-}S)_2$, and $Os(CO)_5$ only. A reaction mechanism involving $Os_3(CO)_9(\mu_3\text{-}S)$ and $Os(CO)_4$ intermediates is proposed and discussed.

Introduction

We have recently shown how the effects of polynuclear coordination promote the cleavage of carbon–sulfur bonds in organosulfur ligands in osmium carbonyl cluster compounds.[1-5] Cleavage of the carbon–sulfur bond of the thiolato ligand in the compound $HOs_3(CO)_{10}(\mu\text{-}SC_6H_5)$, I, is followed by the elimination of benzene and formation of a variety of new sulfido osmium carbonyl cluster compounds.[2] Cleavage of the carbon–sulfur bond in the related compound $HOs_3(CO)_{10}(\mu\text{-}SCH_2C_6H_5)$ occurs in two ways. One process leads to the elimination of toluene and the formation of sulfido osmium carbonyl clusters analogous to those obtained from compound I. However, by a second process, apparently an homolysis of the carbon–sulfur bond, dibenzyl, and several hydride-containing sulfido

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