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Deoxygenative Coupling of Ketones and Alkenes by Tungsten(II) Compounds

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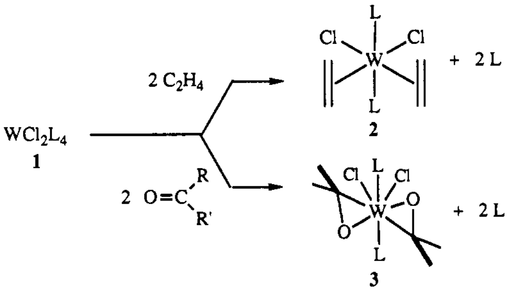
Tungsten(II) compounds such as $WCl_2(PMePh_2)_4$ (1) react with acetone and ethylene to give a good yield of the tungsten(IV)–oxo complexes $W(O)(CH_2{=}CH_2)Cl_2(PMePh_2)_2$ (4) and a moderate amount of 3-methyl-1-butene. Cyclopentanone and ethylene plus 1 yield 4 and vinylcyclopentane; methyl vinyl ketone and ethylene give 4 and 3-methyl-1,4-pentadiene. The reaction of cyclopentanone and propylene with 1 yields a small amount of 2-cyclopentylpropene. Intramolecular deoxygenative coupling occurs with 6- and 7-en-2-ones to form 1-methyl-2-methylene-substituted cyclopentyl and cyclohexyl ring systems, respectively. The net result of these reactions is transfer of the ketone oxygen atom to tungsten, accompanied with its replacement by a hydrogen and a vinyl group. The suggested mechanism for this deoxygenative coupling (Scheme I) is coordination of both the ketone and ethylene to tungsten, coupling to form a 2-oxametallacyclopentane, β-hydrogen elimination to an allyloxy hydride species, C–O bond cleavage to an oxo allyl hydride complex, and reductive elimination of alkene. Consistent with the suggestion of an oxametallacycle, hydrolysis of the reaction mixture of 1 and 6-hepten-2-one provides stereospecifically *trans*-1,2-dimethylcyclopentanol. The enones methyl vinyl ketone and 5-hexen-2-one react with 1 to form stable complexes in which the enone is bound in an η^4 fashion, similar to the proposed mixed alkene ketone intermediates in the coupling reactions. A related tungsten(II) butadiene complex, $WCl_2(CH_2{=}CHCH{=}CH_2)(PMePh_2)_2$, has also been isolated.

Introduction

Unsaturated organic molecules react with electron-rich transition-metal complexes in a variety of ways, including simple coordination to the metal as a ligand, typically with both donor and π-acceptor interactions, or coupling to form a metallacycle, which is a valuable way to form carbon–carbon bonds.[4,5] Two alkenes undergo coupling to form a metallacyclopentane; ketones can couple in either a symmetrical or unsymmetrical fashion. Oxophilic early transition metals typically form symmetrical glycolate-type products,[6] while head-to-tail isomers are often formed with the later transition metals.[7] A variety of substituted metallacycles can result when two different unsaturated ligands react with a metal complex.[5b,c,f,8]

The tungsten(II) complex $WCl_2(PMePh_2)_4$ (1)[9] reacts rapidly with unsaturated ligands such as ethylene[9a] and ketones or aldehydes[10] to form the bis adducts $WCl_2(CH_2{=}CH_2)_2(PMePh_2)_2$ (2) and $WCl_2(O{=}CR_2)_2(PMePh_2)_2$ (3) (eq 1; L = $PMePh_2$). The bis(ethylene) complexes are



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stable and do not form metallacyclopentane complexes.[9a] The bis(ketone) complexes rearrange with cleavage of a C–O double bond to give oxo alkylidene compounds, the reactions proceeding via ketone loss rather than an oxametallacycle.[10] In this report we describe reactions of tungsten(II) complexes in the presence of both alkenes and ketones. Novel cross-coupling reactions are described, in which the ketone oxygen is transferred to the metal and the assembled organic fragment is released into solution. The scope and mechanism of these deoxygenative coupling reactions are the subject of this report.

Experimental Section

General procedures and techniques were as previously described.[10] C_6D_6 was used as the solvent for NMR spectra unless otherwise noted. ^1H NMR spectra were recorded on Varian VXR-300 and Bruker WM-500 and AC-200 spectrometers and are reported in δ, referenced to TMS or residual solvent resonances. ^{13}C and $^{31}P\{^1H\}$ NMR spectra were obtained on a Varian VXR-300 spectrometer and were referenced to solvent or to $PMePh_2$ (δ −27.6, relative to H_3PO_4). Coupling constants are reported in Hz. IR spectra were obtained as Nujol mulls and are reported in units of cm^{-1}.

Generally the coupling reactions were done in sealed NMR tubes. In a typical procedure, an NMR tube sealed to a ground-glass joint was charged with 25 mg of 1 and 0.5 mL of C_6D_6 in the glovebox and capped with a Teflon or ground-glass valve. The whole assembly was removed to a vacuum line and the

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(4) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. Nakamura, A. *Coord. Chem. Rev.* **1991**, *109*, 207–222.

(5) (a) Pillai, S. M.; Ravindranathan, M.; Sivaram, S. *Chem. Rev.* **1986**, *86*, 353–399. (b) Erker, G.; Krüger, C.; Müller, G. *Adv. Organomet. Chem.* **1985**, *24*, 1–39. (c) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047–1058. (d) Brookhart, M.; Sabo-Etienne, S. *J. Am. Chem. Soc.* **1991**, *113*, 2777–2779. (e) Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1991**, *10*, 15–16 and references therein. (f) Mayer, J. M. Ph.D. Thesis, California Institute of Technology, 1982; Chapter 5.

(6) McMurry, J. E. *Chem. Rev.* **1989**, *89*, 1513–1524. Okuda, J.; Herberich, G. E. *Organometallics* **1987**, *6*, 2331–2336. Pasquali, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1981**, *20*, 349–355.

(7) Browning, J.; Empsall, H. D.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1973**, 381–387.

(8) Alt, H. G.; Herrmann, G. S.; Rausch, M. D.; Mallin, D. T. *J. Organomet. Chem.* **1988**, *356*, C53–C56. Buchwald, S. L.; Watson, B. T.; Wannamaker, M. W.; Dewan, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 4486–4494. Grossman, R. B.; Davis, W. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1991**, *113*, 2321–2322. Erker, G.; Dorf, U.; Czisch, P.; Peterson, J. L. *Organometallics* **1986**, *5*, 668–676. Kropp, K.; Skibbe, V.; Erker, G.; Krüger, C. *J. Am. Chem. Soc.* **1983**, *105*, 3353–3354. Christensen, N. J.; Legzdins, P.; Trotter, J.; Lee, V. C. *Organometallics* **1991**, *10*, 4021–4030. Hunt, M. M.; Kennitt, R. D. W.; Russell, D. R.; Tucker, P. A. *J. Chem. Soc., Dalton Trans.* **1979**, 287–294. Green, M. L. H.; Parkin, G. *J. Chem. Soc., Chem. Commun.* **1986**, 90–91.

(9) (a) Sharp, P. R. *Organometallics* **1984**, *3*, 1217–1223. (b) Sharp, P. R.; Bryan, J. C.; Mayer, J. M. *Inorg. Synth.* **1990**, *28*, 326–332.

(10) Bryan, J. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 2298–2308.

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reaction solution cooled to −196 °C and evacuated. Cyclopentanone (1 equiv) and ethylene (3 equiv) were condensed into the tube, which was then sealed with a torch. The reaction was monitored by NMR until complete; then the tube was cut open, and the volatiles were analyzed by GC/MS.

The syntheses of the unsaturated ketones 1-hepten-6-one, 1-octen-7-one, and methyl 1-(3-buten-1-yl)-2-oxocyclopentanecarboxylate were carried out using the described procedure.[11] Authentic samples of 1-methyl-2-methylenecyclopentane and 1-methyl-2-methylenecyclohexane were prepared by Takai olefination of 2-methylcyclopentanone and 2-methylcyclohexanone, respectively.[12] A diastereomeric mixture of *cis*- and *trans*-1,2-dimethylcyclopentanol was prepared by the addition of methylmagnesium bromide to 2-methylcyclopentanone. The ^1H NMR absorptions of the methyl groups are characteristic for the cis and trans isomers.[13] The peaks observed in C_6D_6 for the cis isomer are 0.79 (d, J = 7.1, 3 H) and 1.01 (s, 3 H); the trans isomer appears at 0.89 (d, J = 6.4, 3 H) and 1.08 (s, 3 H).

$WCl_2(O{=}CMe_2)_2(PMePh_2)_2$ (3) + 6-Hepten-2-one or 7-Octen-2-one. To a suspension of **3** (25 mg, 0.03 mmol) in C_6D_6 (0.5 mL) was added (6-hepten-2-one (4 mg, 0.03 mmol). The mixture formed an amber solution. The reaction mixture was stirred at ambient temperature for 0.5 h and then heated to 85 °C for 15 min. The volatiles were transferred in vacuo to afford 1-methyl-2-methylenecyclopentane (0.02 mmol, 70% yield). The product was identified by comparison of its ^1H NMR, GC elution time, and mass spectrum with those of an authentic sample. C_7H_{12} MS (40 eV): M^+ (96). ^1H NMR (C_6D_6): 4.95 (apparent s, 1 H), 4.88 (apparent s, 1 H), 1.04 (d, J = 7, 3 H), 1.2–2.3 (m, 7 H). The procedure described above with 7-octen-2-one (4 mg, 0.03 mmol) gave 1-methyl-2-methylenecyclohexane (0.01 mmol, 30% yield) after heating to 85 °C for 12 h. The product was identified by comparison of its ^1H NMR, GC elution time, and mass spectrum with those of an authentic sample. C_8H_{14} MS (40 eV): M^+ (110). ^1H NMR (C_6D_6): 4.74 (broad s, 1 H), 4.68 (apparent s, 1 H); the other peaks could not be identified because of other materials present.

$WCl_2(PMePh_2)_4$ (1) + Enones: Hydrolytic Workup. To a suspension of **1** (135 mg, 0.13 mmol) in benzene (5 mL) was added methyl-1-(3-buten-1-yl)-2-oxocyclopentanecarboxylate (25 mg, 0.13 mmol) via syringe. The reaction mixture was stirred at ambient temperature for 12 h. The mixture was worked up by washing with 2 mL of 5% (aqueous) NaOCl and 2 × 2 mL of H_2O and then dried over $MgSO_4$. The remainder was concentrated in vacuo and then chromatographed on a short column of silica (1 g) with CH_2Cl_2 as eluent. Removal of solvent in vacuo gave methyl 4-methyl-5-hydroxybicyclo[3.3.0]octane-1-carboxylate: 12 mg, 0.06 mmol, 48% yield. The product was identified by comparison of its ^1H NMR and ^{13}C NMR spectra with literature data.[25a] ^1H NMR ($CDCl_3$): 3.69 (s, 3 H), 2.58 (s, 1 H), 2.35 (m, 2 H), 1.4–1.9 (m, 8 H), 1.32 (m, 1 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 177.1, 92.8, 62.6, 52.0, 44.0, 39.8, 37.5, 36.1, 33.1, 23.3, 13.1.

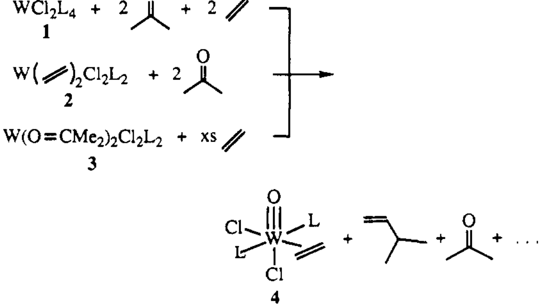
$W(O{=}CMeCH_2CH_2CH{=}CH_2)Cl_2(PMePh_2)_2$ (6a). 5-Hexen-2-one (0.051 mL, Aldrich) was added to a suspension of **1** (0.43 g) in 10 mL of toluene and stirred for 5 h. Volatiles were pumped away, and the residue was dissolved in 5 mL of diethyl ether. The mixture was concentrated to 1 mL, and 15 mL of heptane was added. The mixture was concentrated to 10 mL and filtered cold. The solids were dried in vacuo for 1 h, yielding 0.20 g (65%) of purple powder. Anal. Calcd for $C_{32}H_{36}Cl_2OP_2W$: C, 51.02; H, 4.82. Found: C, 50.09; H, 4.77. ^1H NMR: 7.83 (m, 4 H, Ph), 7.74 (t, J = 9, 2 H, Ph), 7.67 (t, J = 9, 2 H, Ph), 7.08 (m, 12 H, Ph), 4.60 (dd, J = 8, 14, 1 H), 3.35 (m, 2 H), 2.90 (m, 1 H), 2.54 (q, J = 11, 1 H), 2.37 (s, 3 H), 2.23 (d, $^2J_{PH}$ = 9, 3 H), 2.20 (d, $^2J_{PH}$ = 8, 3 H), 2.00 (t, J = 10, 1 H), 0.34 (m, 1 H). $^{13}C\{^1H\}$ NMR: 141.0 (d, Ph), 131.3 (d, Ph), 17 peaks between 132 and 136 (Ph), 6 peaks between 129 and 130.4 (Ph), 98.9 (~d, $^2J_{PC}$ = 16, MeC(O)CH_2–), 80.5 (broad d, $^2J_{PC}$ = 4, $CH{=}CH_2$), 75.2 (broad d, $^2J_{PC}$ = 6, $CH{=}CH_2$), 54.2 (s, CH_2), 36.8 (s, CH_2), 25.2 (s, C(O)CH_3), 16.0 (d, $^1J_{PC}$ = 29, PCH_3Ph_2), 12.3 (d, $^1J_{PC}$ = 28, $P(CH_3)Ph_2$). $^{31}P\{^1H\}$ NMR: −0.4 (d, $^2J_{PP}$ = 118, $^1J_{WP}$ = 170), −7.2 (d, $^2J_{PP}$ = 118, $^1J_{WP}$ = 182). IR: 1283, 1188 w, 1096 s, 1028 w, 892 vs, 742 vs, 728 sh, 694 vs, 650, 508 s, 485, 441.

$W[O{=}C(Me)CH{=}CH_2]Cl_2(PMePh_2)_2$ (6b). 3-Buten-2-one (0.062 mL, Aldrich) was added to a suspension of **1** (0.39 g) in 10 mL of toluene and stirred for 30 min. The reaction mixture was concentrated to 1 mL, and 15 mL of heptane was added. The resulting red solids were filtered and dried in vacuo for 16 h, yielding 0.204 g (60%) of a red powder. Anal. Calcd for $C_{30}H_{32}Cl_2OP_2W$: C, 49.68; H, 4.45. Found: C, 49.87; H, 4.52. ^1H NMR (−60 °C, toluene-d_8): 11.1 (m, 1 H), 7.84 (broad s, 2 H, Ph), 7.66 (broad s, 2 H, Ph), 7.40 (broad s, 2 H, Ph), 7.35 (broad s, 2 H, Ph), 7.18 (s, 2 H, Ph), 6.93 (broad s, 12 H, Ph), 6.88 (broad s, 2 H, Ph), 4.32 (s, 3 H, C(O)CH_3), 3.58 (m, 1 H), 3.11 (m, 1 H), 2.55 (d, $J_{PH} \approx 8$, 3 H, PCH_3Ph_2), 2.06 (d, $J_{PH} \approx 8$, 3 H, PCH_3Ph_2). $^{13}C\{^1H\}$ NMR (25 °C): 133.9 (broad multiplet), 130.0, 117.8, 82.0, 43.8, 15.9. $^{31}P\{^1H\}$ NMR (−60 °C, toluene-d_8): −49.6 (d, $^2J_{PP}$ = 150), −52.2 (d, $^2J_{PP}$ = 150). IR: 1282, 1267, 1186, 1098 vs, 1029, 1008, 898 vs, 808, 743 vs, 730, 719 s, 695 vs, 681 sh, 572 s, 501 s, 486 s, 447 s, 298.

$W(CH_2{=}CHCH{=}CH_2)Cl_2(PMePh_2)_2$ (7). A suspension of **1** (0.34 g) in 10 mL of toluene was stirred for 1 h under 1 atm of butadiene (Phillips 66). Volatiles were pumped away, and 6 mL of diethyl ether was added to the residue. The mixture was concentrated to 4 mL, and 8 mL of heptane was added. The red solids were filtered off and dried in vacuo for 1 h, yielding 0.12 g (65%) of red powder. A second crop (0.06 g) was obtained by suspending the filtrate residue in 1 mL of diethyl ether and adding 3 mL of heptane. The total yield was 0.18 g (81%). Anal. Calcd for $C_{30}H_{32}Cl_2P_2W$: C, 50.80; H, 4.55. Found: C, 50.38; H, 4.49. ^1H NMR: 11.67 (m, 2 H), 7.91 (m, 4 H), 7.55 (m, 4 H), 7.11–6.98 (m, 12 H), 6.10 (m, 2 H), 4.84 (m, 2 H), 2.02 (t, $^2J_{PH}$ = 8, 6 H). $^{13}C\{^1H\}$ NMR: 150.3 (d, J_{PC} = 39, ipso), 143.1 (d, J_{PC} = 38, ipso), 133.7 (d, $^2J_{PC}$ = 8, ortho), 133.2 (d, $^2J_{PC}$ = 8, ortho), 130.2 (s, Ph), 129.5 (s, Ph), 88.0 (s, $CH{=}CH_2$), 47.9 (s, $CH{=}CH_2$), 20.5 (d, J_{PC} = 8, $P(CH_3)Ph_2$), 20.1 (d, J_{PC} = 6, $P(CH_3)Ph_2$). $^{31}P\{^1H\}$ NMR: −107.6 (d, $^2J_{PP}$ = 139, $^1J_{WP}$ = 221), −111.9 (d, $^2J_{PP}$ = 139, $^1J_{WP}$ = 209). IR: 1094 s, 1070 w, 1028, 1000 w, 899 vs, 742 s, 694 vs, 508 s, 483, 449 s, 422, 290.

Results

Reactions with Alkenes and Ketones. Benzene solutions of $WCl_2(PMePh_2)_4$ (**1**) react with acetone and ethylene to give a 31% yield of 3-methyl-1-butene and an essentially stoichiometric amount (94%) of the oxo ethylene compex $W(O)(CH_2{=}CH_2)Cl_2(PMePh_2)_2$ (**4**), as well as other uncharacterized products (eq 2; L = $PMePh_2$). Similar distributions are obtained on reacting the bis(ethylene) complex **2** with 2 equiv of acetone or the bis(acetone) complex **3** with excess ethylene. The tungsten product **4** was identified by comparison of its ^1H and $^{31}P\{^1H\}$ NMR spectra with those of authentic samples.[14a] The



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[11] Sowinski, A. F.; Whitesides, G. M. *J. Org. Chem.* **1979**, *44*, 2369–2376. For other references to reductive couplings, see ref 25.

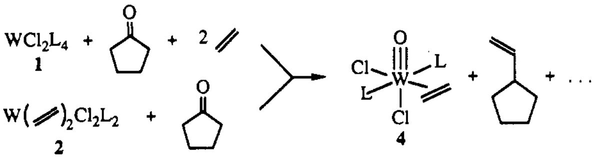
[12] Hibino, J.; Okazoe, T.; Takai, K.; Nozaki, H. *Tetrahedron Lett.* **1985**, *26*, 5579–5580.

[13] Kariv-Miller, E.; Mahachi, T. J. *J. Org. Chem.* **1986**, *51*, 1041–1045.

[14] (a) Su, F.-M.; Bryan, J. C.; Jang, S.; Mayer, J. M. *Polyhedron* **1989**, *8*, 1261–1277. (b) Jang, S.; Atagi, L. M.; Mayer, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 6413–6414. (c) Brock, S. L.; Mayer, J. M. *Inorg. Chem.* **1991**, *30*, 2138–2143. (d) Atagi, L. M.; Over, D. E.; McAlister, D. R.; Mayer, J. M. *J. Am. Chem. Soc.* **1991**, *113*, 870–874. (e) Atagi, L. M. Ph.D. Thesis, University of Washington, 1992.

methylbutene—and in general all the organic products reported here—were identified by NMR, GC, and mass spectra and, when possible, by comparison with samples commercially obtained or independently synthesized.

Cyclopentanone and ethylene react with **1** to give **4** and vinylcyclopentane, in a 3:1 ratio. Again, similar products are obtained on reacting **2** with cyclopentanone and ethylene (eq 3; L = PMePh$_2$). The reaction of ethylene-d_4 with **1** and cyclopentanone yields vinylcyclopentane-d_4, with the vinyl and allylic positions deuterated (by ^{1}H NMR and GC/MS; eq 4). 2-Cyclopentenone reacts to form **4** and a small amount of 3-vinylcyclopentene (eq 5; L = PMePh$_2$).



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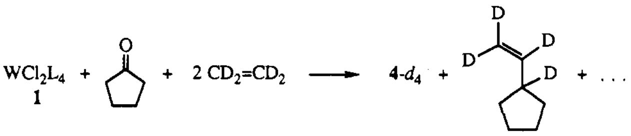

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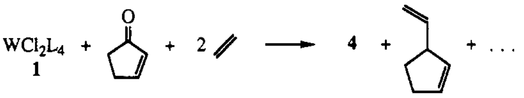

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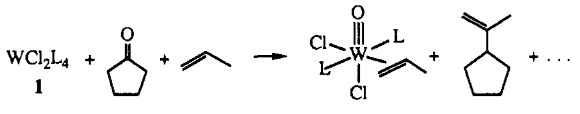
Acetaldehyde and ethylene react with **1** to initially form the three isomers of the bis(acetaldehyde) complex WCl$_2$(O=CHMe)$_2$(PMePh$_2$)$_2$.[10] Although this complex is stable in the absence of ethylene, it decomposes under these conditions over a period of days to give ca. 20% of **4** and a trace of the oxo aldehyde complex W(O)Cl$_2$(O=CHMe)(PMePh$_2$)$_2$.[14a]

The intermolecular coupling reaction is less efficient upon substitution of propene for ethylene. Reaction of **1** with propene and cyclopentanone gives a small amount of 2-cyclopentylpropene, along with an equilibrium mixture[14a] of W(O)Cl$_2$(CH$_2$=CHMe)(PMePh$_2$)$_2$ (68%) and W(O)Cl$_2$(PMePh$_2$)$_3$[15] (**5**; 10%; eq 6). With acetone and propene, **3** is formed initially, and following its decomposition in solution[10] we were unable to detect formation of C$_6$ products by GC/MS. Propene and cyclopentenone react with **1** to give the bis(cyclopentenone) complex, which decomposes cleanly to an oxo alkylidene complex, just as in the absence of propene.[10]



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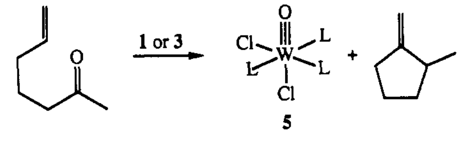
Reactions with Enones. Intramolecular deoxygenative coupling occurs on reacting WCl$_2$(PMePh$_2$)$_4$ (**1**) with unsaturated ketones when five- or six-membered rings can be formed. Reaction of **1** with 6-hepten-2-one afforded 1-methyl-2-methylenecyclopentane in 30% yield (eq 7). The reaction proceeds at 25 °C with rapid initial disappearance of **1** and the starting ketone, followed by slow appearance of W(O)Cl$_2$(PMePh$_2$)$_3$ (**5**) and the free alkene. The highest yield of alkene (70%) was obtained from reaction of the enone with the bis(acetone) complex **3** upon heating the sealed tube to 85 °C briefly after an initial time of 0.5 h at 25 °C. Similarly, reaction of **1** or **3** with 7-octen-2-one afforded 1-methyl-2-methylenecyclohexane in 30% yield (eq 8).



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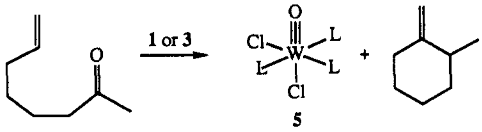

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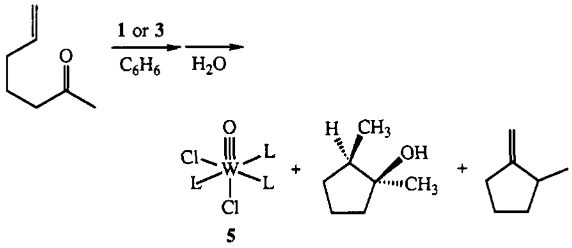
The rapid disappearance of starting materials coupled with the slow formation of alkene suggested the presence of intermediate(s) in significant quantity. While we have not been able to isolate or identify any intermediates by NMR, hydrolysis of some of the reaction mixtures yielded cyclized alcohols as well as alkenes. Reacting 6-hepten-2-one with **1** or **3** in benzene for 12 h, followed by workup with aqueous NaOCl, yielded *trans*-1,2-dimethylcyclopentanol in addition to 1-methyl-2-methylenecyclohexane (eq 9). None of the isomeric *cis*-1,2-dimethylcyclopentanol was detected by NMR or GC/MS when the spectrum was compared to those of authentic diastereomeric mixtures. Similarly, the reaction of methyl 1-(3-buten-1-yl)-2-oxocyclopentanecarboxylate with **1** followed by an aqueous workup provided the bicyclic cyclopentanol with an all-cis substitution pattern as the only diastereomer observed (eq 10). In this case, no alkene is formed. Hydrolysis of the reaction mixture of 7-octen-2-one resulted in formation of 1-methyl-2-methylenecyclohexane and unreacted ketone, but no corresponding cyclohexanols were detected. It should be noted that the alcohols are produced by intercepting an intermediate, not via subsequent hydrolysis of a product alkene, as evidenced by the diastereoselectivity and the lack of further reaction of the methylenecyclohexane.



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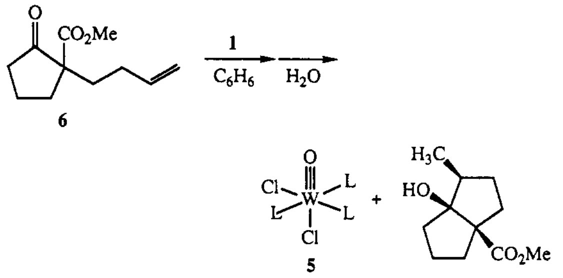

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In contrast, the reaction of WCl$_2$(PMePh$_2$)$_4$ (**1**) with 5-hexen-2-one, with only two methylenes between the vinyl and ketone functionalities, rapidly gives the enone complex W[η^4-O=CMe(CH$_2$)$_2$CH=CH$_2$]Cl$_2$(PMePh$_2$)$_2$ (**6a**), with displacement of two phosphine ligands (eq 11; L = PMePh$_2$). While this compound could potentially participate in either an inter- or intramolecular coupling reaction, it is found to be stable in solution for at least 1 week at ambient temperatures. The other observed inter- and

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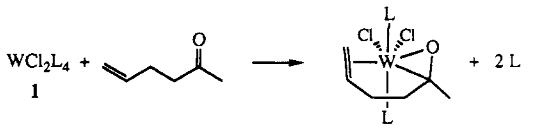
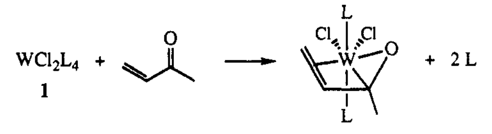
[15] Carmona, E.; Sanchez, L.; Poveda, M. L.; Jones, R. A.; Hefner, J. G. *Polyhedron* **1983**, *2*, 797.



7a (11)

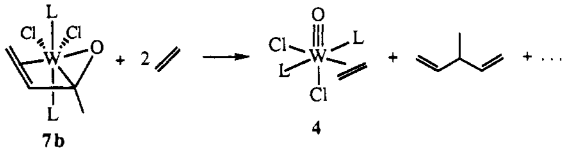
intramolecular coupling reactions were normally complete within a 24-h period at ambient temperatures. Heating a benzene solution of **6a** at 70 °C for 16 h resulted in fragmentation to nonstoichiometric amounts of W(O)-$Cl_2(PMePh_2)_3$ (**5**) and other unidentified products.

An enone complex is also formed with the α,β-unsaturated methyl vinyl ketone: W[η^4-O=CMeCH=CH$_2$]Cl$_2$-(PMePh$_2$)$_2$ (**6b**; eq 12). Ethyl vinyl ketone reacts similarly.



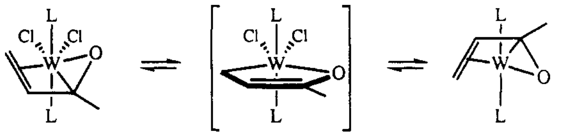
7b (12)

While **6b** is stable in benzene solution, treatment with ethylene results in *inter*molecular deoxygenative coupling to give 3-methyl-1,4-pentadiene and the oxo ethylene complex **4** in a 1:3 ratio, accompanied by other uncharacterized material (eq 13; L = PMePh$_2$).


7b 4 (13)

Complexes **6a** and **6b** have been characterized by spectroscopy and by analogy with **2** and **3**. Their ^{1}H NMR spectra are integrated for one enone and two phosphines per tungsten. Separate resonances with complex coupling patterns are observed for all methylene and methyne protons. The $^{31}P\{^1H\}$ NMR spectra exhibit AB patterns with a large P–P coupling ($^2J_{PP} \approx 118$–150 Hz), consistent with inequivalent, trans phosphine ligands.[16] The $^{13}C\{^1H\}$ NMR of **6a** shows three doublets assigned to three carbons bound to tungsten (evidently one of the two $^2J_{PC}$ values is ~0 in each case). This and the lack of a substantial band in the IR between 2800 and 1500 cm^{-1} ($\nu_{C=O}$) indicate that the enone ligand is held to tungsten in an η^4 fashion.

^{1}H NMR spectra of the α,β-unsaturated ketone complex **6b** at room temperature exhibit considerable broadness of the resonances due to the phosphine methyl and phenyl groups (the ethyl vinyl ketone analog is similar). The enone resonances are sharp, but one is shifted unusually far downfield (δ 13.7 ppm). At lower temperatures the phosphine resonances separate and sharpen, and the downfield enone peak shifts upfield, to δ 11.1 ppm at −60 °C. Added PMePh$_2$ does not seem to affect the resonances of the bound phosphines, nor is the chemical shift or width of the free PMePh$_2$ peaks affected by whatever process is causing the apparent coalescence of the phosphine resonances. This indicates that phosphine dissociation is not part of the observed phenomenon. A possible explanation might be that the enone ligand "spins" on tungsten in a manner similar to that for cyclopentadienyl ligands. The enone would remain rigidly planar so that all three olefinic protons remain inequivalent, while the phosphines become equivalent. Another explanation is that the enone ligand flips back and forth as depicted below, creating an effective mirror of symmetry relating the two phosphine ligands:



Both rotation and flipping mechanisms have been proposed for transition-metal butadiene complexes.[5b,17] Flipping should equilibrate the terminal olefinic protons (=CH$_2$), while rotation would not. None of the enone resonances are observed to coalesce, even at +60 °C. However, if the difference in chemical shifts between coalescing protons is sufficiently large (i.e., if the peak far downfield is due to one of the two terminal olefinic protons), a higher coalescence temperature may be required.[18] The 5-hexen-2-one complex **6a** does not exhibit this behavior, probably due to the lack of conjugation between the unsaturated groups.

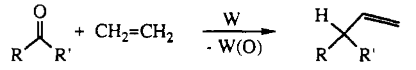
Butadiene reacts similarly with **1** to give a related diene complex, W(η^4-CH$_2$=CHCH=CH$_2$)Cl$_2$(PMePh$_2$)$_2$ (**7**; eq 14). Isoprene reacts similarly. Like the enone complexes,

$$\mathrm{WCl_2L_4 + CH_2{=}CHCH{=}CH_2 \rightarrow \underset{\textbf{7}}{W(\eta^4\text{-}CH_2{=}CHCH{=}CH_2)Cl_2(PMePh_2)_2}} \quad (14)$$

7 exhibits ^{1}H NMR spectra that are integrated for one diene and two phosphines per tungsten, with complex coupling for the diene protons. The $^{31}P\{^1H\}$ spectrum of **7** exhibits an AB pattern with a large $^2J_{PP}$ value (139 Hz), again indicating inequivalent, trans phosphine ligands.[16] The presence of inequivalent trans phosphines indicates that the butadiene is bound in an *s-cis*, rather than *s-trans* fashion. No major spectral changes are observed in the NMR spectra of **7** over the temperature range −60 to +60 °C. Thus, **7**, unlike the methyl vinyl ketone complex **6b**, does not appear to be fluxional.

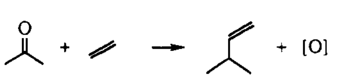
Discussion

Reaction of ethylene and a ketone with **1** results in replacement of the carbonyl oxygen with a hydrogen and a vinyl group; the oxygen remains on the tungsten (eq 15).



(15)

While low yields of the α-olefin are generally observed, this is mechanistically a very interesting transformation, involving carbon–carbon bond formation, hydrogen migration, and deoxygenation. The driving force for the reactions is the formation of a very strong W≡O bond (estimated to be ≥138 kcal/mol[10]); ketone/alkene coupling to give an oxygen atom is, of course, thermodynamically quite unfavorable (eq 16; ΔH calculated from gas-phase heats



$\Delta H^\circ = +92$ kcal/mol (16)

of formation[19]). Complex **1** is a very potent oxygen atom acceptor and will even deoxygenate CO$_2$, for which $\Delta H^\circ(CO_2 \rightarrow CO + [O]) = 127$ kcal/mol.[10,14] These values

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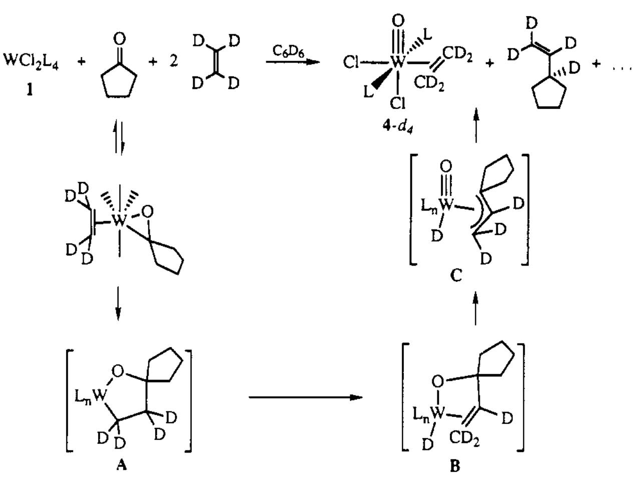
[16] Drago, R. S. *Physical Methods in Chemistry*; Saunders: Philadelphia, 1977; pp 222–223. Redfield, D. A.; Nelson, J. H.; Cory, L. W. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 727.

[17] Fryzuk, M. D.; Haddad, T. S.; Rettig, S. J. *Organometallics* **1989**, *8*, 1723–1732.

[18] Sandström, J. *Dynamic NMR Spectroscopy*; Academic: London, 1982; p 79 ff.

[19] JANAF Thermochemical Tables, 3rd ed. *J. Phys. Chem. Ref. Data Ser.* **1985**, *14*, Supplement 1. *Thermodynamic Tables*; Thermodynamic Research Center, Texas A&M University: College Station, TX, 1986. Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969.

Scheme I. Suggested Mechanism for Ketone–Alkene Deoxygenative Coupling (L = PMePh$_2$)

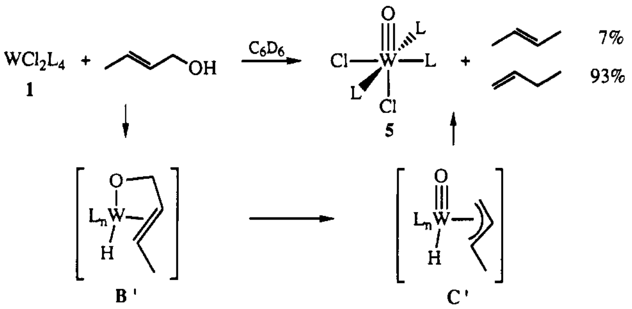


suggest that the deoxygenative coupling of ketones and ethylene by 1 is exothermic by ≥35 kcal/mol.[20] The substantially larger yields of 4 than of organic products suggests that there are routes to 4 other than the pathway that yields coupled organics, consistent with the large thermodynamic driving force.

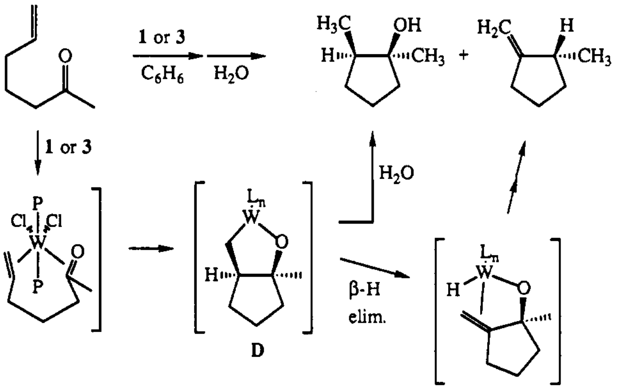
A likely mechanism for the deoxygenative coupling is illustrated in Scheme I for the reaction of cyclopentanone and ethylene-d_4. Coordination of both substrates gives a species similar to the isolated enone complexes **6a,b** and analogous to **2** and **3**. Coupling gives the 2-oxametallacyclopentane intermediate A,[21] which can β-eliminate to the allyloxy hydride complex B. Carbon–oxygen bond cleavage in B gives the oxo allyl intermediate C, and reductive elimination leads to vinylcyclopentane and the ethylene complex **4**. As shown in Scheme I, this mechanism is consistent with the results of the labeling experiment. It is less likely, though possible, that B is directly converted to products by concerted hydrogen addition and C–O cleavage, without the intermediate oxo allyl species C (see below).[22]

The combination of metallacycle formation and β-hydrogen elimination is well precedented, for instance in the catalytic dimerization of olefins.[5a] Molybdenum(IV) oxametallacyclopentane complexes related to A have been prepared by olefin insertion of allylic alcohols into $Cp_2MoH_3^+$ and deprotonation.[23] There are, however, few precedents for carbon–oxygen bond cleavage reactions such as the conversion of B to C. We have recently proposed the same step in the deoxygenation of allylic alcohols by **1** (B′ to C′, Scheme II),[14b] and we have recently isolated a tungsten oxo allyl complex from reaction of **1** with (allyloxy)trimethylsilane.[24] In the allylic alcohol reactions, double-bond migration was observed on deoxygenation, with 2-buten-1-ol yielding mostly 1-butene (Scheme II).

Scheme II. Proposed Mechanism for Allyl Alcohol Deoxygenation by 1 (L = PMePh$_2$)[14b]



Scheme III



This indicates the presence of an allyl intermediate and rules out the direct conversion of B′ to products by concerted hydrogen addition and C–O bond cleavage.[14b,e] The mechanisms in Schemes I and II are similar not only in how the C–O bond is broken but also in that reductive elimination occurs preferentially to the more substituted carbon. The preference for formation of α-olefin also applies to the intramolecular cyclizations, as only exocyclic alkene products are formed.

Propene is much less efficient in these coupling reactions because of its poorer ligating ability: ethylene rapidly displaces two phosphines from **1** to give **2**, but propene and other monoalkenes do not. In order to form a mixed ketone alkene metal complex, the substituted alkene must compete with free phosphine displaced from **1** for an available coordination site. The coupling reactions with substituted alkenes are most effective when the isolated bis(ketone) complexes $W(O{=}CR_2)_2Cl_2L_2$ are used, because the concentration of free phosphine (L) during the reaction is kept to a minimum.

It should be noted that the coupling reactions do not occur by initial ketone cleavage to an oxo alkylidene species, even though **1** is known to react with ketones such as cyclopentanone and acetone to form oxo alkylidene complexes.[10] Treating the isolated oxo cyclopentylidene complex $W(O)[{=}C(CH_2)_4]Cl_2(PMePh_2)_2$ with ethylene under the same experimental conditions gave no reaction. Additionally, the methyl vinyl ketone complex **6b** is stable to C–O cleavage and does not form oxo alkylidene complexes, but it does undergo reaction with ethylene to form the coupled product (eq 13). The bis(acetaldehyde) complex $WCl_2(O{=}CHMe)_2(PMePh_2)_2$ also does not cleave to an alkylidene,[10] but it reacts with ethylene to yield oxo products.

In the reactions of **1** or **3** with 6-hepten-2-one, coordination and coupling lead to the bicyclic intermediate D in Scheme III. β-Hydrogen elimination from D is apparently inhibited by the rigidity of the bicyclic system, so that the metallacycle can be intercepted on hydrolysis.

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(20) Reaction of 1 with CO_2 yields $W(O)(CO)Cl_2(PMePh_2)_2$, which is roughly as stable as the oxo ethylene complex 4 that is the typical product of these reactions. The carbonyl and ethylene complexes are slightly more stable than $W(O)Cl_2(PMePh_2)_3$ ($K_{eq} \approx 10^3$).[14a]

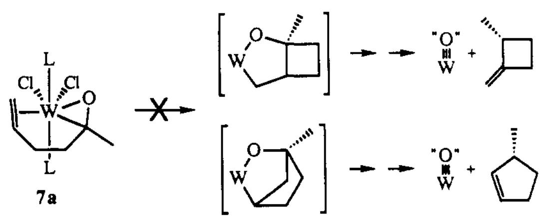
(21) An alternative metallacycle could be drawn with the carbonyl carbon attached to tungsten rather than the oxygen, but the W–O bond strength is probably much greater than the W–C bond strength and this would also bring the bulky cyclopentyl group closer to the metal.

(22) (a) Direct elimination of arene from a d^0 arenethiolate hydride complex to give a terminal sulfido complex has been suggested;[22b] because of the electron count, migration of the arene to the metal (analogous to B → C) cannot occur. (b) Listemann, M. L.; Schrock, R. R.; Dewan, J. C.; Kolodziej, R. M. *Inorg. Chem.* **1988**, *27*, 264–271.

(23) Ito, T.; Igarashi, T. *Organometallics* **1987**, *6*, 199–201.

(24) Atagi, L. M.; Critchlow, S. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 1483–1484.

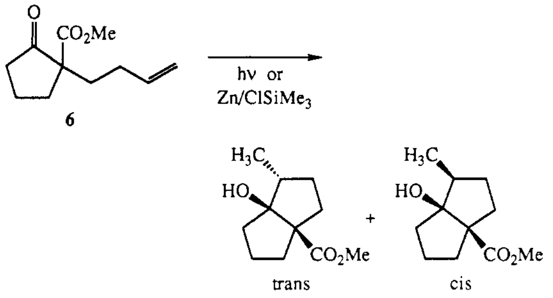
Scheme IV



6-Hepten-2-one, however, gives a more flexible intermediate with a cyclohexane ring, in which β-hydrogen elimination is too facile for the metallacycle to build up in concentration. Thus, no alcohol is observed on hydrolysis.

The stereochemistry of the observed hydrolysis product from the cyclization of 6-hepten-2-one is a consequence of the oxametallacycle intermediate, which contains cis-oriented alkoxy and alkyl substituents (Scheme III). Nonselective intramolecular reductive coupling of 6-hepten-2-one has been observed with sodium/*tert*-butyl alcohol mixtures in *N*-ethylpyrrolidone and yields a diastereomeric mixture of *cis*- and *trans*-1,2-dimethylcyclopentanols along with a small amount of 1-methylcyclohexanol and 5-hepten-1-ol.[11] This reaction proceeds by direct electron transfer, resulting in intermediate ketyl radical anions or α-hydroxy radicals and nonselective cyclization. In contrast, cathodic reduction results in exclusive formation of *cis*-1,2-dimethylcyclopentanol.[13]

Reductive cyclization of methyl 1-(3-buten-1-yl)-2-oxocyclopentanecarboxylate to the bicyclic alcohol (eq 10) has been accomplished by photochemical means and by zinc trimethylchlorosilane (eq 17).[25] These reactions form both cis- and trans-substituted bicyclic alcohols, with the trans isomer predominating by 29:1 and 5:1, respectively. The cis relationship between the methyl and hydroxyl groups in the cyclopentanol products obtained here using the tungsten-mediated cyclization is thus unusual and may be advantageous for applications in synthetic organic chemistry.



(17)

The 5-hexen-2-one complex **6a** does not undergo any intramolecular coupling at ambient temperatures. In this case, the mechanism proposed in Scheme I would require formation of the metallacycle containing a cyclobutane ring or, if coupling can occur to the terminal carbon, a cyclopentane ring (Scheme IV). This would predict methylene-2-methylcyclobutane or 3-methyl-1-cyclopentene as the product, neither of which is observed. The reluctance of this system to react may be due either to an unfavorable orientation of the π systems or to energetically prohibitive metallacycle formation. The reductive coupling of 5-hexen-2-one with dissolving-metal mixtures also gives very low yields of 1,2-dimethylcyclobutanol and 1-methylcyclopentanol products,[11] consistent with these observations.

A remaining puzzle is the reason the bis(ethylene) and bis(ketone) complexes **2** and **3** do not react further to form metallacycles: **2** is stable at 25 °C, and **3** decomposes by loss of ketone to give oxo alkylidene compounds.[10] Simple orbital correlation analysis suggests that ethylene coupling to a metallacyclopentane is forbidden in C_{2v} symmetry but would be allowed in the likely C_s symmetry of the transition state; coupling of two ketones in C_2 symmetry also appears to be allowed. Apparently there are a number of reaction pathways available to the tungsten(II) compounds, particularly if a strong tungsten–oxygen multiple bond can be formed. Note that the yields of tungsten–oxo species in the coupling reactions described here are usually larger than the yields of organic products. Deoxygenative coupling is a major path when both the ketone and vinyl groups bind strongly to the metal, either by using ethylene in intermolecular coupling or by cyclizing a potentially chelating enone, if a favorable ring size is formed.

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[25] (a) Photochemical: Belotti, D.; Cossy, J.; Pete, J. P.; Portella, C. *J. Org. Chem.* **1986**, *51*, 4196–4200. (b) Zn/Me$_3$SiCl: Corey, E. J.; Pyne, S. G. *Tetrahedron Lett.* **1983**, *24*, 2821–2824. (c) For other reductive cyclizations, see: Swartz, J. E.; Mahachi, T. J.; Kariv-Miller, E. *J. Am. Chem. Soc.* **1988**, *110*, 3622–3628. Molander, G. A.; Kenny, C. *J. Am. Chem. Soc.* **1989**, *111*, 8236–8246 and references therein.