Acknowledgment. We thank Paul R. Shafer and David J. Robinson for assistance with the NMR measurements; the NMR spectrometer was purchased in part with funds from the National Science Foundation. We thank Charles C. McCormick for helpful discussions and assistance with the amino acid sequence analysis. F.J.K. and M.F.R. thank the Richter Memorial Trust for Research Grant Awards that supported this research, which was also aided by Grant IN-157B from the American Cancer Society.

Registry No. MT-2 (α-domain), 124650-77-7; MT-2 (β-domain), 124620-43-5; NcMT, 73665-13-1; $CdCl_2$, 10108-64-2; Ag(I), 14701-21-4; $Cu(CH_3CN)_2Cl$, 124685-75-2; ^{113}Cd, 14336-66-4.

Oxidative Addition of Carbon–Oxygen and Carbon–Nitrogen Double Bonds to $WCl_2(PMePh_2)_4$. Synthesis of Tungsten Metallaoxirane and Tungsten Oxo- and Imido–Alkylidene Complexes

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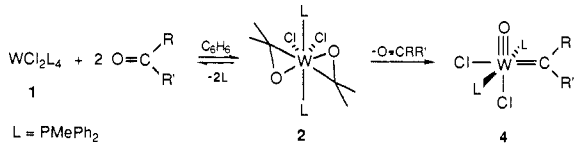
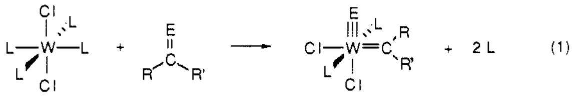
Abstract: WCl_2L_4 (**1**, L = $PMePh_2$) reacts rapidly with a variety of ketones and aldehydes to form bis(η^2-ketone) or bis(η^2-aldehyde) complexes $WCl_2(\eta^2\text{-}O{=}CRR')_2L_2$ (**2**, **3**). When the ketone is part of a five-membered ring (cyclopentanone, 2-indanone, etc.), **2** rearranges with loss of ketone to give tungsten(VI) oxo-alkylidene products, $W(O)(CRR')Cl_2L_2$ (**4**) in high yield. The net reaction is insertion of the tungsten center into the ketone carbon–oxygen double bond, a four-electron oxidative addition. Insertion into the carbon–nitrogen double bond of *N*-cyclopentyl-*p*-toluidine yields the analogous imido-alkylidene complex $W(N\text{-}Tol)[C(CH_2)_4]Cl_2L_2$. With other ketones, an oxo-alkylidene product is observed only in the reaction of **1** with 1 equiv of ketone and is not seen on decomposition of **2**. This is due to further reaction of the alkylidene complex with free ketone. Aromatic ketones such as benzophenone react with **1** apparently by a radical pathway to give $W(O)Cl_2L_3$ and the olefin derived from two ketones ($Ph_2C{=}CPh_2$), without formation of an observable bis(ketone) intermediate. The two-electron oxidative addition of heterocumulenes is also observed: for example CO_2 is cleaved to form the oxo-carbonyl complex $W(O)(CO)Cl_2L_2$. These are remarkable reactions because of the strength of the carbon–oxygen double bonds being cleaved under very mild conditions. A substantial driving force for the reactions is the formation of a tungsten–oxygen multiple bond, which is estimated to be >138 kcal/mol. The mechanism of double-bond cleavage is proposed to involve an η^2-ketone or cumulene adduct. Based on the spectroscopic data for compounds **2** and **3** and the X-ray crystal structure of the bis(acetone) adduct **2g**, the η^2-ketone intermediates are best described as three-membered rings (metallaoxiranes). The oxo-alkylidene products are apparently formed upon opening of this ring. The preference for these two- or four-electron double-bond oxidative addition reactions versus one-electron (radical) chemistry is discussed.

Oxidative addition reactions are traditionally defined in terms of the scission of a single bond into two monovalent fragments. The oxidative additions of H_2 and MeI to Vaska's complex, $IrCl(CO)(PPh_3)_2$, are typical examples of this fundamental and well-studied transition-metal reaction.[2] In these reactions there is a formal two-electron transfer from the metal to the substrate: two nonbonding electrons on the d^8 iridium center become involved in metal–ligand bonding in the d^6 product.

This paper describes a new type of oxidative addition reaction in which a double bond is cleaved to form two divalent ligands.[3] Ketones and imines oxidatively add to the tungsten(II) complex $WCl_2(PMePh_2)_4$ (**1**),[4] forming tungsten oxo- and imido-alkylidene complexes (eq 1[5]). These are *four*-electron oxidative addition reactions, as four nonbonding electrons in **1** are converted to tungsten–ligand bonding electrons in the tungsten(VI) products.

Scheme I

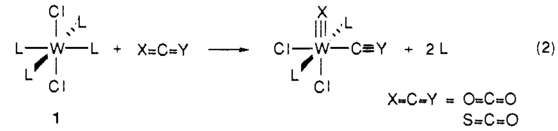




(1)

E = O, NTol; L = $PMePh_2$

The oxidative addition of heterocumulenes such as carbon dioxide and isocyanates (eq 2) also involves simple insertion of



(2)

X=C=Y = O=C=O
S=C=O
RN=C=O
RN=C=NR
S=C=NR

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(1) Presidential Young Investigator, 1988–1993; Sloan Foundation Fellow, 1989–1991.

(2) (a) 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; Chapter 5. (b) Lukehart, C. M. *Fundamental Transition Metal Organometallic Chemistry*; Brooks/Cole: Monterey, CA, 1985; Chapter 10.

(3) Portions of this work have been published: Bryan, J. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 7213–7214.

(4) (a) Sharp, P. R. *Organometallics* **1984**, *3*, 1217–1223. (b) Sharp, P. R.; Bryan, J. C.; Mayer, J. M. *Inorg. Synth.*, in press.

(5) Tungsten–oxygen and tungsten–nitrogen multiple bonds are written as triple bonds because that is the best description in typical coordination environments. See Chapter 2 of ref 5a. (a) Nugent, W. A.; Mayer, J. M. *Metal–Ligand Multiple Bonds*; Wiley-Interscience, New York, 1988.

0002-7863/90/1512-2298\$02.50/0

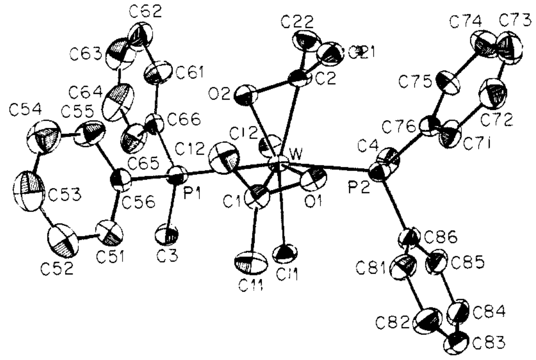


Figure 1. ORTEP drawing of $WCl_2(\eta^2\text{-}O{=}CMe_2)_2(PMePh_2)_2$ (**2g**).

the tungsten center into a double bond.[6,7] For instance, carbon dioxide reacts to form an oxo-carbonyl complex. These are formally two-electron oxidative addition reactions, but an unusual type of oxidative addition that forms a divalent group and a neutral ligand.

These reactions are remarkable because of the strength of the bond that is broken. Cleavage of a carbon-oxygen double bond in CO_2 requires 127 kcal/mol[8] and the C=O bond strength in acetone is estimated to be 160 kcal/mol.[9] In fact these are the strongest bonds that have been simply cleaved to two fragments that remain on a single metal center.[10] From a thermodynamic standpoint, it is perhaps surprising that the reactions are exoergic. Clearly, the tungsten-oxygen and tungsten-carbon multiple bonds must be quite strong (see below). It is also remarkable that there is a kinetic pathway for the cleavage of double bonds at room temperature in nonpolar solvents, without forcing conditions or additional reagents. The mechanism of double-bond cleavage is thus of particular importance.

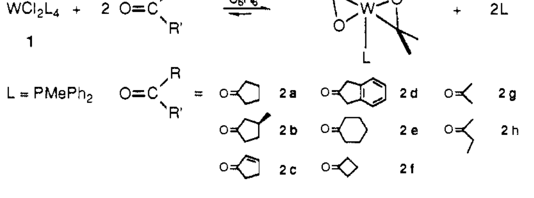
The key to the mechanism appears to be the bis(η^2-ketone) complexes **2** observed in the course of the oxidative addition (Scheme I). We begin with the synthesis and characterization of these bis(ketone) complexes (interesting species in their own right), followed by a description of the oxidative addition reactions and the characterization of the tungsten alkylidene products.

Table I. Selected Bond Distances (Å) and Angles (deg) for $W(OCMe_2)_2Cl_2(PMePh_2)_2$ (**2g**)

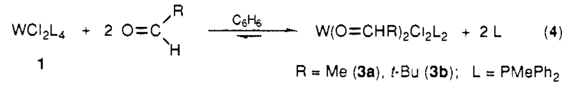
	Bond Distances		
W-O1	1.948 (4)	W-Cl1	2.432 (2)
W-O2	1.933 (4)	W-Cl2	2.437 (2)
W-C1	2.175 (7)	W-P1	2.626 (2)
W-C2	2.203 (7)	W-P2	2.606 (2)
O1-C1	1.379 (8)	C1-C12	1.527 (10)
O2-C2	1.390 (8)	C2-C21	1.534 (9)
C1-C11	1.520 (10)	C2-C22	1.509 (10)
	Bond Angles		
Cl1-W-Cl2	82.48 (6)	O1-W-O2	95.3 (2)
Cl1-W-P1	83.82 (6)	O1-W-C1	38.6 (2)
Cl1-W-P2	77.82 (6)	O1-W-C2	86.9 (2)
Cl1-W-O1	94.60 (14)	O2-W-C1	88.2 (2)
Cl1-W-O2	159.91 (14)	O2-W-C2	38.6 (2)
Cl1-W-C1	88.6 (2)	C1-W-C2	104.6 (3)
Cl1-W-C2	159.8 (2)	W-O1-C1	79.6 (4)
Cl2-W-P1	74.89 (6)	W-O2-C2	81.3 (3)
Cl2-W-P2	84.05 (6)	W-C1-O1	61.8 (3)
Cl2-W-O1	160.2 (2)	W-C1-C11	125.0 (5)
Cl2-W-O2	93.81 (14)	W-C1-C12	121.1 (5)
Cl2-W-C1	159.5 (2)	O1-C1-C11	113.8 (6)
Cl2-W-C2	89.3 (2)	O1-C1-C12	113.0 (6)
P1-W-P2	153.66 (6)	C11-C1-C12	110.9 (6)
P1-W-O1	124.4 (2)	W-C2-O2	60.2 (3)
P1-W-O2	76.16 (14)	W-C2-C21	121.6 (5)
P1-W-C1	85.9 (2)	W-C2-C22	123.5 (5)
P1-W-C2	111.9 (2)	O2-C2-C21	112.8 (6)
P2-W-O1	76.2 (2)	O2-C2-C22	114.8 (6)
P2-W-O2	121.6 (2)	C21-C2-C22	111.9 (6)
P2-W-C1	112.1 (2)	P2-W-C2	83.0 (2)

Results

Synthesis and Characterization of Bis(η^2-ketone) and Bis(η^2-aldehyde) Complexes 2 and 3. Benzene or toluene solutions of the tungsten(II) complex $WCl_2(PMePh_2)_4$ (**1**)[4] react rapidly with 2 equiv of a variety of ketones to form $W(\eta^2\text{-}O{=}CRR')_2Cl_2(PMePh_2)_2$, (**2a-h**), via substitution of two phosphine ligands (eq 3). Acetaldehyde and pivaldehyde react with **1**, forming related bis(aldehyde) adducts $W(\eta^2\text{-}O{=}CHR)_2Cl_2(PMePh_2)_2$, (**3a**,**b**, eq 4).



(3)



$$\underset{1}{WCl_2L_4} + 2\ O{=}C\begin{matrix}R\\H\end{matrix} \xrightleftharpoons{C_6H_6} W(O{=}CHR)_2Cl_2L_2 + 2\ L \qquad (4)$$

R = Me (**3a**), *t*-Bu (**3b**); L = $PMePh_2$

Reactions 3 and 4 are equilibria that strongly favor the products in all cases except for **2h**. In this case, NMR resonances for both **1** and **2h** are observed even in the presence of 3 equiv of 2-butanone, and addition of phosphine or ketone shifts the equilibrium as expected. 3-Pentanone does not react with **1**, presumably because the equilibrium is unfavorable for steric reasons. The $WCl_2(PMePh_2)_2$ fragment is thus quite crowded, as also suggested by the X-ray structure of **1**.[7] Solutions of **2g** do not contain significant amounts of **1** by NMR, but a facile equilibrium is indicated by the complete exchange of the acetone ligands with acetone-d_6 within 10 min of mixing. Significant exchange between **3a** and acetaldehyde-$^{13}C_2$, however, is observed only after a day at ambient temperatures.

Compounds **2** and **3** are the first examples of complexes with two η^2-bound ketone or aldehyde ligands on a single metal center.

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(6) Bryan, J. C.; Geib, S. J.; Rheingold, A. L.; Mayer, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 2826-2828.

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(8) The bond strength equals the difference in the heat of formation of the molecule and its fragments. For instance $\Delta H_f°(298)$ for CO_2, CO, and O atom in the gas phase are −94.1, −26.4, and 59.6 kcal/mol, so the O=CO bond strength is 127.3 (±0.1) kcal/mol. Heats of formation were obtained from: *JANAF Thermochemical Tables*, 3rd ed.; *J. Phys. Chem. Ref. Data* **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. $\Delta H_f°(298)$ for HNC [used in the calculation of D(O=CNH)] was calculated as the sum of $\Delta H_f°(298)$ for HCN (from JANAF) and the heat of isomerization of HCN to HNC (14.8 ± 2 kcal/mol) from: Pau, C.-F.; Hehre, W. *J. Phys. Chem.* **1982**, *86*, 321-322.

(9) Double-bond strengths in ketones and aldehydes cannot be accurately calculated because the heats of formation of the carbene formed on C=O cleavage are not known due to their rapid rearrangement. Formaldehyde is the only exception, with a bond strength of 180 ± 2 kcal/mol calculated by using the well-known heat of formation of CH_2.[8] G. J. Glockler (*J. Phys. Chem.* **1958**, *62*, 1049-1054) estimated the bond strength in ketones to be 160 kcal/mol based on a correlation with bond distance. This is consistent with the value of 156 kcal/mol for acetone derived by using a MNDO/3 calculation of $\Delta H_f°(298)$ for dimethylcarbene: Gey, E.; Kuhnel, W.; Ondruschka, B. *Z. Chem.* **1981**, *21*, 225. A "mean" C=O bond energy of 181 kcal/mol in ketones has been derived from heats of atomization (Levi, G. I.; Balandin, A. A. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1960**, 149-153), but this is different from a normal bond energy.[8]

(10) The cleavage of C≡O (257 kcal/mol)[8] apparently requires more than one metal center: LaPointe, R. E.; Wolczanski, P. T.; Mitchell, J. F. *J. Am. Chem. Soc.* **1986**, *108*, 6382-6384. Chisholm, M. H.; Heppert, J. A.; Huffman, J. C.; Streib, W. E. *J. Chem. Soc., Chem. Commun.* **1985**, 1771. The cleavage of N_2 (226 kcal/mol[8]) requires added acid: Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589-625. The scission of an quinolinyl phenyl ketone to give CO_2 and a bridging carbene has been reported: Suggs, J. W.; Wovkulich, M. J.; Lee, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 5546-5548. Cleavage of NO: Alt, H. G.; Hayen, H. I. *Angew. Chem.* **1985**, *97*, 506-507.

Table II. NMR Data for the Bis(ketone) Complexes $W(\eta^2\text{-}O{=}CRR')_2Cl_2(PMePh_2)_2$ (**2a–h**)[a]

ketone O=CRR′		$^{31}P\{^1H\}$			$^{13}C\{^1H\}$ NMR							^1H NMR							
					C_α			others				PCH_3Ph_2			others				
		δ	m	J_{WP}	δ	m	J_{PC}	δ	m	J_{PC}	assign.	δ	m	J_{PC}	δ	m	J	int	assign.
cyclopentanone	**2a**	−6.6	s	174	107.1[b]	t	8	12.5	t	14	PCH_3Ph_2	2.23	t	4.3	3.09	m		2 H	C*H*H
								39.0			CH_2				2.67	m		2 H	C*H*H
								36.9			CH_2				1.98	m		2 H	C*H*H
								29.0			CH_2				1.75	m		2 H	C*H*H
								28.1			CH_2				1.63	m		2 H	C*H*H
															1.31	m		4 H	C*H*H
															1.05	m		2 H	C*H*H
3-methylcyclopentanone	**2b**[c]	−6.4 to −7.6 (13 peaks obsd)										2.25[d]							
cyclopentenone	**2c**[c,e]	−2.1										2.2[d]							
		−2.2										2.1[d]							
		−2.5																	
		−2.9																	
2-indanone	**2d**	−2.2	s	176	104.3	t	8	13.0	t	15	PCH_3Ph_2	2.12	t	4.4	5.07	d	19	2 H	C*H*H
								45.8			CH_2				4.29	d	19	2 H	C*H*H
								43.8			CH_2				3.62	d	19	2 H	C*H*H
															2.80	d	19	2 H	C*H*H
cyclohexanone	**2e**	−5.2	s	173	103.5	t	9	12.2	t	15	PCH_3Ph_2	2.25	t	4.4	2.87	m		2 H	C*H*H
								36.5			CH_2				2.12	m		2 H	C*H*H
								34.1			CH_2				1.99	m		2 H	C*H*H
								33.7			CH_2				1.89	m		2 H	C*H*H
								31.6			CH_2				1.80	m		2 H	C*H*H
								27.6			CH_2				1.60	m		4 H	C*H*H
															1.46	m		2 H	C*H*H
															1.26	m		2 H	C*H*H
															1.12	m		2 H	C*H*H
cyclobutanone	**2f**	−5.5	s	179	100.8	t	8	12.5	t	15	PCH_3Ph_2	2.27	t	4.4	3.86	m		2 H	C*H*H
								39.3			CH_2				3.45	m		2 H	C*H*H
								38.8			CH_2				3.19	m		2 H	C*H*H
								20.1			CH_2				2.42	m		2 H	C*H*H
															2.24	m		2 H	C*H*H
															1.37	m		2 H	C*H*H
acetone	**2g**[f]	−5.5	s	171	96.7	t	9					2.21	t	4.5	2.63	s		6 H	CH_3
															1.76	s		6 H	CH_3
2-butanone	**2h**[c,g]	−3.4	s	174															
		−4.7	s	173															
		−3.9	d	175[h]															
		−4.2	d	172[h]															

[a] Procedures as described in the Experimental Section. [b] $^1J_{WC}$ = 24 Hz. [c] These complexes are formed as isomeric mixtures and give very complex ^1H and ^{13}C NMR spectra. In all cases ^1H NMR integrate for two ketones and two phosphines bound to tungsten, and 2 equiv of free phosphine are produced via eq 3. Second-order AB patterns ($J \sim \Delta$) are expected for "nonsymmetric" isomers in the $^{31}P\{^1H\}$ spectrum.[24] [d] Insufficient resolution to determine multiplicity, probably due to overlapping multiplets. [e] AB pattern for one of three isomers[c] in the $^{31}P\{^1H\}$ spectrum does not exhibit sufficient signal to noise to observe the "outside" (lower intensity peaks) halves of each doublet. The other two ("symmetric") isomers exhibit one singlet each. Therefore only four peaks (instead of six) are observed in the $^{31}P\{^1H\}$ spectrum, and multiplicity is not assigned. Poor signal to noise also prohibits observation of J_{WP}. [f] Insufficient signal to noise to observe additional ^{13}C resonances. [g] Partial ^1H and $^{13}C\{^1H\}$ NMR data for this compound are given in ref 14. [h] $^2J_{PP}$ = 132 Hz.

The η^2-bonding mode is not very common, particularly for ketones since they are larger than aldehydes. Of the reported η^2-ketone complexes,[11-13] most are stable only when the ketone contains electron-withdrawing substituents,[12] or when it bridges two metal centers.[13] Compounds **2** and **3** are analogous to the bis(ethylene) complexes that Sharp prepared by reaction of WCl_2L_4 (L = PMe_3, PMe_2Ph, $PMePh_2$) with ethylene.[4a] Compounds with both olefin and ketone ligands, such as 3-buten-2-one and 5-hexen-2-one adducts, can also be isolated.[14] Sharp also observed a paramagnetic monoethylene adduct, $WCl_2(C_2H_4)(PMe_3)_3$, but we have no evidence for significant concentrations of monoketone complexes.

The bis(acetone) complex $W(\eta^2\text{-}O{=}CMe_2)_2Cl_2(PMePh_2)_2$ has been characterized by an X-ray crystal structure determination.[3] It exhibits a cis ketone, trans phosphine, cis chloride configuration (Figure 1), analogous to the structure proposed for the bis-

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(11) Ketone complexes: (a) Harman, W. D.; Sekine, M.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 2439–2445. (b) Harman, W. D.; Fairlie, D. P.; Taube, H. *J. Am. Chem. Soc.* **1986**, *108*, 8223–8227. (c) $[(NH_3)_5Ru(O{=}CMe_2)]^{2+}$: Powell, D. W., The University of Sydney, personal communication, 1988. (d) Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5421–5422. (e) Mayer, J. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1982**, *104*, 2157–2165. (f) Tsou, T. T.; Huffman, J. C.; Kochi, J. K. *Inorg. Chem.* **1979**, *18*, 2311–2317. (g) Wiellstra; Y.; Gambrotta, S.; Roedelof, J. B.; Chiang, M. Y. *Organometallics* **1988**, *7*, 2177–2182. (h) Aldehyde complexes are more common: Huang, Y.-H.; Gladysz, J. A. *J. Chem. Educ.* **1988**, *65*, 298–303, and references therein and ref 7. (i) Imine complexes: Mayer, J. M.; Curtis, C. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2651–2660, and references therein. Brunner, H.; Wachter, J.; Bernal, I.; Creswick, M. *Ang. Chem., Int. Ed. Engl.* **1979**, *18*, 861–862. (j) η^2-CO_2 complexes; see: Sneeden, R. P. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, 1982; Vol. 8, pp 225–283.

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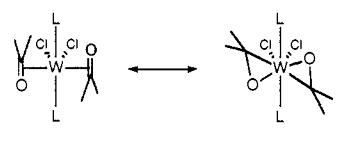
(14) Bryan, J. C. Ph.D. Thesis, University of Washington, 1988; pp 13–15.

Table III. Comparative Spectral and Structural Data for Selected η^2-Ketone Complexes

complex	δC_α, ppm	$\Delta\delta$ C_α, ppm	ν_{CO}, cm^{-1}	C–O, Å	ΔC–O, Å	β, deg	ref
$(PMePh_2)_2Cl_2W(Me_2CO)_2$	96.7	118	1230	1.390 (8)	0.17	44	
				1.379 (8)	0.16	46	
$Me_2Cp^*Ta(Me_2CO)$	111	104	1200				11d
$(bpy)(CO)Cp^*Ta(Me_2CO)$	87.5	128					11e
$[(NH_3)_5Os(Me_2CO)]^{2+}$	83	132	1330	1.322 (13)	0.10	55	11a,b
$[(NH_3)_5Ru(Me_2CO)]^{2+}$			1277				11c
$(PEt_3)_2Ni(Ph_2CO)$				1.335 (4)	0.10	63	11f
$(PPh_3)_2Ni[(CF_3)_2CO]$				1.32 (2)	0.09	48	12d

(ethylene) complex $WCl_2(C_2H_4)_2(PMePh_2)_2$.[4a] Selected bond lengths and angles are given in Table I. The geometry about tungsten is best described as a distorted octahedron, considering the acetone ligands to each occupy one coordination site. There is an approximate (noncrystallographic) 2-fold axis of symmetry relating the pairs of acetone, phosphine, and chloride ligands. The phosphorus and chlorine atoms are bent away from the acetones [∠Cl1–W–Cl2 = 82.48 (6)° and ∠P1–W–P2 = 153.66 (6)°], due to the steric bulk of the η^2-acetone ligands and/or to the electronic influence of two π-acid ketones in a formally d^4 complex.[15] The W–Cl [av 2.435 (2) Å] and W–P [av 2.616 (2) Å] distances are typical of those observed for similar tungsten compounds.[7,16]

The tungsten–acetone interaction is best described as a three-membered ring, a metallaoxirane (B), rather than as an acetone π complex (A).[17] The C–O bond distances of 1.390 (8) and 1.379 (8) Å are considerably longer than in free acetone [1.210 (4) Å][18] and approach the C–O single-bond length of 1.41 Å.[19] The acetone ligands are distinctly nonplanar. The average angles about the carbonyl carbon are closer to tetrahedral than trigonal planar [∠O–C–C = 113.6 (6)° and ∠C–C–C = 111.4 (6)°] and the β angle, defined as the angle between the O–C bond and the normal to the plane of the three acetone carbons, is 45° compared to β = 90° in free acetone. The tungsten–oxygen bonds are shorter than tungsten–carbon distances [W–O = 1.948 (4), 1.933 (4) Å; W–C = 2.175 (7), 2.203 (7) Å], consistent with the high oxophilicity of tungsten.



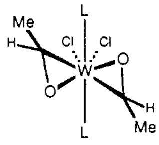
A B

Spectroscopic data for the bis(ketone) and bis(aldehyde) complexes (Table II) are consistent with the solid-state structure determined for **2g** and support their description as metallaoxiranes.[20] The C–O stretching frequency for **2g** of 1230 cm^{-1} ($\nu_{C^{18}O}$ = 1220 cm^{-1}) is much lower than free acetone (1715 cm^{-1}) and is almost within the range normally observed for C–O stretches of alcohols and ethers (1200–1050 cm^{-1}).[21] The ^{13}C chemical shifts of the carbonyl carbons are in the range δ 96.7–107.1, roughly 120 ppm upfield from the free ketones.[11] In olefin complexes, a relationship has been suggested between upfield shift for the olefinic carbon and the degree of metallacycle character.[22] In comparison to other reported η^2-ketone complexes (Table III), compounds **2** appear to have the most metallacycle character—in other words, π back-bonding from tungsten to the ketone ligands is very strong. The amount of back-bonding is surprising since there are two ketones removing electron density from the tungsten.

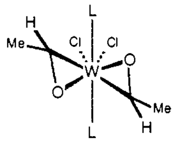
The lack of reaction of **1** with ethyl acetate, γ-butyrolactone, or diphenyl carbonate is probably due to these compounds being poorer π acceptors than ketones or aldehydes.[23] Butyrolactone is essentially the same size as cyclopentanone, so steric effects are not responsible for the lack of coordination. To our knowledge there are no examples of η^2-ester complexes.

The NMR spectra of **2a–h** are remarkably similar, for instance with ^{31}P chemical shifts in the range δ −2.1 to −7.6 ($^1J_{WP}$ = 171–179 Hz). Complexes of symmetric ketones (cyclopentanone **2a**, 2-indanone **2d**, cyclohexanone **2e**, cyclobutanone **2f**, and acetone **2g**) exist as a single isomer containing a 2-fold axis, which relates the pairs of ketone and phosphine ligands. A virtual triplet is observed for the phosphine methyl groups in the ^1H and $^{13}C\{^1H\}$ NMR spectra and a singlet is seen in the $^{31}P\{^1H\}$ NMR spectrum, indicating trans, equivalent phosphines.[24] The ^{13}C and ^1H NMR spectra are consistent with C_2 molecular symmetry. For instance, the cyclopentanone complex **2a** shows, in the ^{13}C NMR, a carbonyl resonance at δ 107.1, four methylene carbon signals at δ 28–39, and eight resonances in the ^1H NMR for the cyclopentanone hydrogens.

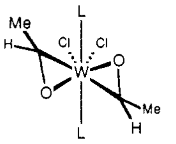
Complexes of the asymmetric ligands cyclopentenone (**2c**), 2-butanone (**2h**), and acetaldehyde (**3a**) are found as three geometric isomers in roughly equal proportions, the isomers differing only in the relative orientation of the ketone ligands. Isomers C and D (depicted here for **3a**) retain a 2-fold axis of symmetry and



C



D



E

therefore give rise to NMR spectra analogous to those described above for the symmetric ketones. The third isomer, E, does not have a symmetry axis and therefore gives rise to more complex NMR spectra, including two doublets for the inequivalent phosphine methyl groups in the ^1H NMR, and an AB pattern in the $^{31}P\{^1H\}$ NMR spectrum. The $^2J_{PP}$ value is large supporting the trans phosphine orientation.[24] The 3-methylcyclopentanone complex, **2b**, is a more complex mixture of isomers because the ketone is chiral.[25] The isolated pivaldehyde complex **3b** is apparently a mixture of isomers C and D.

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(15) Kubácek, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4320–4332.

(16) Chiu, K. W.; Lyons, D.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *Polyhedron* **1983**, *2*, 803. Bradley, D. C.; Hursthouse, M. B.; Malik, K. M. A.; Nielson, A. J.; Short, R. L. *J. Chem. Soc., Dalton Trans.* **1983**, 2651–2666.

(17) Ittel, S. D.; Ibers, J. A. *Adv. Organomet. Chem.* **1976**, *14*, 33–61, and references therein. See also: Reference 2.

(18) Iijima, T. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3526–3530.

(19) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; p 19.

(20) The metallaoxirane description is also supported by chemical evidence: **2g** reacts with water (and $PMePh_2$) to give 1 equiv each of 2-propanol, acetone, and **5**; presumably after hydrolysis of one acetone ligand to 2-propanol, the remaining acetone ligand does not back-bond strongly to the tungsten(IV)-oxo complex and dissociates (although $W(O)Cl_2(MeCHO)(PMePh_2)_2$ is stable[7]).

(21) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 3rd ed.; Wiley: New York, 1974; p 91 ff.

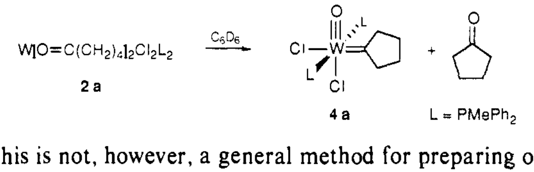
(22) Tolman, C. A.; English, A. D.; Manzer, L. E. *Inorg. Chem.* **1975**, *14*, 2353–2356.

(23) The presence of an oxygen lone pair to the carbonyl group in esters raises the energy of the carbonyl π^* orbital. See: Reference 11a,h. Evans, D. H. In *Encyclopedia of Electrochemistry of the Elements*, Bard, A. J., Lund, H., Eds.; M. Dekker: New York, 1987; Vol. XII, pp 1–260.

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

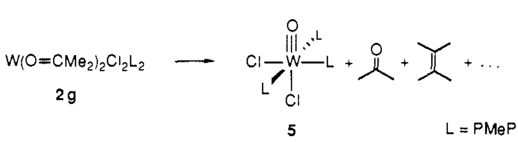
(25) The $^{31}P\{^1H\}$ NMR of **2b** shows 13 peaks. Up to 10 isomers are possible (4 with a 2-fold symmetry axis and 6 chiral isomers), so as many as 16 major peaks could be present in the $^{31}P\{^1H\}$ NMR: 4 singlets and 12 from the "inner" (high-intensity) peaks of AB patterns. Certain isomers may be formed in low concentration and there may be accidental degeneracies.

Oxidative Addition of Ketones To Form Tungsten Alkylidene Complexes. The bis(cyclopentanone) complex **2a** decomposes cleanly in benzene solution to the oxo–cyclopentylidene complex **4a** in a few days at ambient temperatures (eq 5). One equivalent of free cyclopentanone is formed in the reaction.



(5)

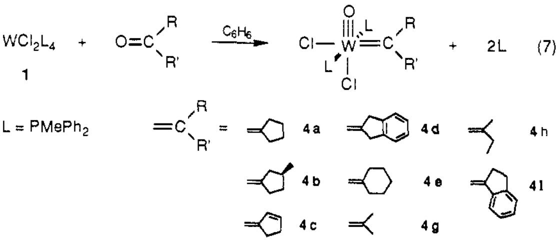
This is not, however, a general method for preparing oxo–alkylidene complexes. The bis(acetone) complex **2g**, for example, decomposes to nonstoichiometric mixtures of $W(O)Cl_2(PMePh_2)_3$ (**5**),[26] acetone, tetramethylethylene, and other uncharacterized products (eq 6). The oxo ligand of **5** is derived from acetone,



(6)

as shown by oxygen-18 labeling, so carbon–oxygen double-bond cleavage is occurring, but the oxo–isopropylidene complex **4g** is not observed.

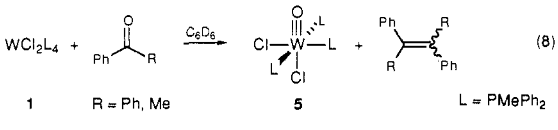
The key to a more general synthesis of alkylidene complexes is to minimize the concentration of free ketone, by adding only 1 equiv of ketone to **1**. A mixture of $^1/_2$ equiv each of **1** and **2** is formed within minutes, and this mixture converts to the oxo–alkylidene complexes $W(O)(=CRR')Cl_2(PMePh_2)_2$ over a period of hours or days (eq 7). Oxo–alkylidene products are also obtained on reacting the isolated bis(ketone) adducts with an equimolar amount of **1**. The amount of ketone must be limited because in most cases the alkylidene complex reacts with the free ketone. Thus, **4g** (formed by reaction 7) reacts rapidly with acetone to give roughly the same mixture of products as observed in the decomposition of **2g** (eq 6). The success of eq 5 is due to the low reactivity of **4a** toward cyclopentanone. No reaction is observed over a week at 25 °C and only a small amount of $(CH_2)_4C{=}C(CH_2)_4$ is formed after 16 h at 70 °C.



(7)

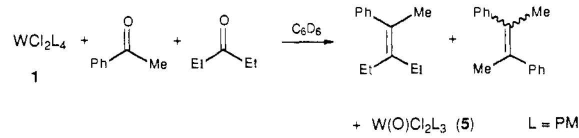
The nature of reaction 7 is very dependent on the ketone. High-yield, easily isolable products are obtained for the cyclopentylidene (**4a**), 3-methylcyclopentylidene (**4b**), 2-cyclopenten-1-ylidene (**4c**), and 2-indenylidene (**4d**) complexes. The reaction times for formation of **4a–d** under similar reaction conditions, varied from less than 3 h for **4c** to longer than 2 weeks for **4d**. Complexes **4e–h**, however, are formed in low yields (10–50% by NMR) along with other products and have therefore been identified only spectroscopically.

The reactions of **1** with the aromatic ketones benzophenone and acetophenone do not form ketone adducts or oxo–alkylidene complexes, rather they cleanly yield **5** and the olefin derived from coupling of two ketones, PhRC=CRPh (eq 8). When R = Me, the olefin produced is 10:1 trans to cis as determined by NMR.[27]



(8)

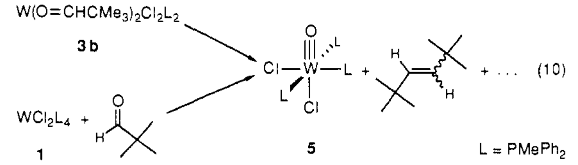
Addition of aromatic and α,β-unsaturated ketones to solutions of **1** rapidly gives deep blue or purple solutions, the dark color of which fades over several hours. This is suggestive of formation of ketyl radicals (see Discussion). Consistent with a mechanism that does not involve ketone complexes, **1** converts a 1:1 mixture of acetophenone and 3-pentanone to dimethylstilbenes and the olefin derived from both ketones (eq 9), despite the lack of reaction of **1** with pure 3-pentanone.



(9)

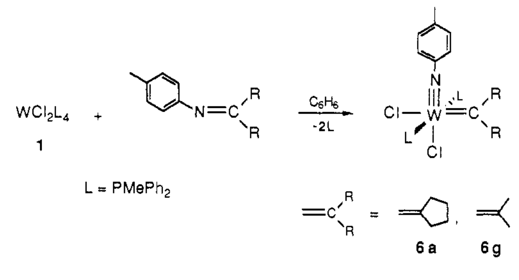
Oxo–alkylidene products are also not observed in reactions of **1** with cyclobutanone, acetaldehyde, or pivaldehyde, although these ligands do form tungsten adducts (eqs 3 and 4). The cyclobutanone reaction yields, after a week at 25 °C, one major and a number of minor tungsten products, and a nonstoichiometric amount of propene (by NMR).[28] A W≡O stretch is not observed in the IR spectrum of the solution, but there is a strong band at 1890 cm^{-1}. This and the formation of propene suggest that decarbonylation of cyclobutanone to a tungsten carbonyl species has occurred.

The bis(pivaldehyde) complex **3b** decomposes over several days to give nonstoichiometric amounts of **5**, $^tBuHC{=}CH^tBu$ (identified by ^1H NMR and mass spectra), and a number of uncharacterized products. A similar product distribution is observed when **1** reacts with 1 equiv of pivaldehyde (eq 10), in contrast to the reactions of acetone (eq 7). The bis(acetaldehyde) complex **3a** is stable in solution, unlike the bis(ketone) complexes and **3b**. Some interconversion of the A and B isomers is observed within a few days at 25 °C in benzene solution, together with formation of small amounts of **5**, but no further changes occur over 3 weeks.



(10)

Complex **1** also reacts with the imines *N*-cyclopentylidene-*p*-toluidine and *N*-isopropylidene-*p*-toluidine to form the tungsten(VI) imido–alkylidene complexes $W(N\text{-}Tol)(=CRR')Cl_2(PMePh_2)_2$ (**6**) by cleavage of the carbon–nitrogen double bond (eq 11).[29] As is the case for the analogous oxo complexes **4a** and **4g**, the imido–cyclopentylidene complex **6a** is easily and cleanly prepared in high yield, while the imido–isopropylidene **6g** complex is isolated only as an impure material in low yield.



(11)

Formation of the imido–alkylidene compounds is significantly slower than formation of the analogous oxo species under similar reaction conditions. Complex **4a** is formed in less than 24 h at room temperature, while **6a** requires roughly 3 days at 40 °C for complete reaction. Tungsten–imine intermediates similar to **2** are not observed by NMR.

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(26) Carmona, E.; Sānchez, L.; Poveda, M. L.; Jones, R. A.; Hefner, J. G. *Polyhedron* **1983**, *2*, 797–801.

(27) McMurray, J. E.; Fleming, M. P.; Lees, K. L.; Kranski, L. R. *J. Org. Chem.* **1978**, *43*, 3255–3266.

(28) The NMR spectra of the major product (^1H: δ 2.37 t, J_{PH} = 4.6 Hz, PCH_3Ph_2; $^{31}P\{^1H\}$: δ 8.3, $^1J_{WP}$ = 298 Hz) are close to but outside the range of values for the oxo–alkylidene complexes **4a–i**.

(29) Similar imido–neopentylidene complexes are reported in: Pedersen, S. F.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 7483–7491.

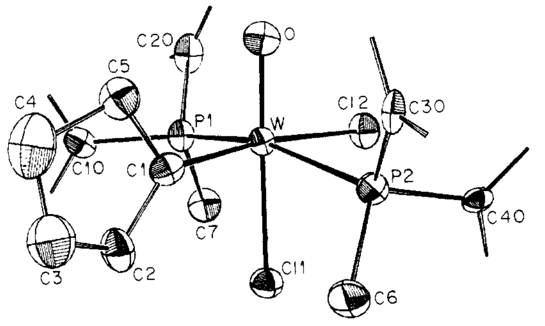


Figure 2. ORTEP drawing of $W(O)[=C(CH_2)_4]Cl_2(PMePh_2)_2$ (**4a**). Only the ipso carbons of the phenyl rings are shown.

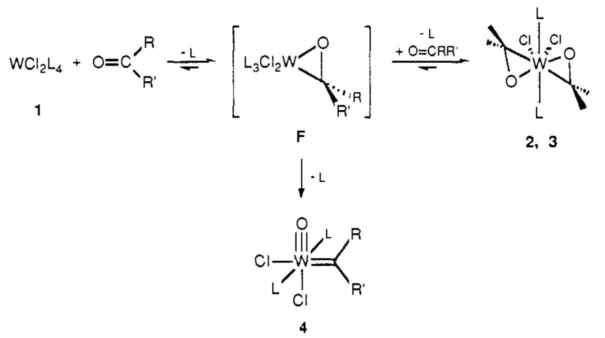
Table IV. Selected Bond Distances (Å) and Angles (deg) for $W(O)[C(CH_2)_4]Cl_2(PMePh_2)_2$ (**4a**)

	Bond Distances		
W-O	1.708 (8)	C1-C2	1.48 (2)
W-C1	1.980 (12)	C2-C3	1.52 (2)
W-Cl1	2.502 (3)	C3-C4	1.44 (3)
W-Cl2	2.511 (3)	C4-C5	1.55 (2)
W-P1	2.567 (3)	C1-C5	1.52 (2)
W-P2	2.563 (3)		
	Bond Angles		
O-W-C1	94.9 (4)	C1-W-Cl1	87.0 (4)
O-W-Cl1	178.0 (3)	C1-W-Cl2	170.8 (4)
O-W-Cl2	94.2 (3)	C1-W-P1	95.0 (3)
O-W-P1	97.4 (3)	C1-W-P2	89.8 (3)
O-W-P2	98.0 (3)	P1-W-P2	163.49 (10)
Cl1-W-Cl2	84.01 (11)	W-C1-C2	132.2 (10)
Cl1-W-P1	83.05 (11)	W-C1-C5	120.5 (9)
Cl1-W-P2	81.42 (11)	C2-C1-C5	107.2 (11)
Cl2-W-P1	81.94 (11)	C1-C2-C3	107.3 (13)
Cl2-W-P2	90.86 (10)	C1-C5-C4	103.3 (13)
C2-C3-C4	103 (2)	C3-C4-C5	108 (2)

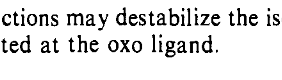
Characterization of the Alkylidene Complexes. The molecular structure of **4a**, determined by X-ray crystallography (Figure 2, Table IV),[3] is similar to the structures of the closely related oxo–neopentylidene complexes $W(O)(=CHCMe_3)Cl_2(PR_3)_2$ (R = Me, Et),[30] and of the oxo–carbonyl, oxo–ethylene, and imido-carbonyl complexes $W(O)(CO)Cl_2(PMePh_2)_2$, $W(O)(CH_2CH_2)Cl_2(PMePh_2)_2$, and $W(N\text{-}Tol)(CO)Cl_2(PMePh_2)_2$.[7] These six structures adopt similar distorted octahedral configurations with a noncrystallographic mirror plane relating to two phosphines. The cis relationship between the π-bonding oxo and alkylidene or π-acid ligands is required by their electronic structure.[5a,7,31] The structures also show similar bond distances and angles. The W≡O [1.708 (8) Å] and W=C1 [1.980 (12) Å] bond distances in **4a** are typical of these linkages.[32] The oxo–tungsten–alkylidene angle is larger than octahedral [∠O–W–C1 = 94.9 (4)°], as is typical of molecules with two multiple bonds.[33] In addition, the cyclopentylidene ligand is bent away from the oxo group [∠W–C1–C2 = 132.2 (10)°, ∠W–C1–C5 = 120.5 (9)°], perhaps due to steric crowding with the oxo ligand. Distances and angles within the five-membered ring are indistinguishable from those reported for gas-phase cyclopentanone.[34]

Spectroscopic data for the oxo- and imido-alkylidene complexes **4a–i**, **6a**, and **6g**—^1H, $^{31}P\{^1H\}$, ^{13}C NMR, and IR spectra (Table V)—are consistent with the structure determined for **4a**. Data for the related oxo–alkylidene complex $W(O)(=CHCMe_3)Cl_2(PMe_2Ph)_2$[35] are also given in Table V. The ^1H NMR spectra integrate for one alkylidene and two phosphines per tungsten. The spectra of **4a** and **4c–i** show singlets in the $^{31}P\{^1H\}$ NMR (in the narrow range δ 11.9–16.1, $^1J_{WP}$ = 326–333 Hz) and virtual triplets in the ^1H (δ 2.36–2.43) and $^{13}C\{^1H\}$ NMR ($\delta \approx 13$) for the phosphine methyl groups, indicating equivalent trans phosphine ligands.[24] The $^{13}C\{^1H\}$ NMR spectra also exhibit a triplet assigned to the α-carbon of the alkylidene (δ 311–333, $^2J_{PC}$ = 9–10 Hz). For complexes **4a** and **4c–e**, the carbons of the alkylidene ring are all inequivalent but the two hydrogens of each methylene group are equivalent, consistent with the C_s symmetry of **4a** in the solid state. The presence of the oxo group is indicated by a strong IR absorbance ($\nu_{W\equiv O}$) at 980–950 cm^{-1}.[36] The IR spectrum of the imido complex **6a** is similar, except for the absence of a tungsten–oxo stretch and the addition of the tolyl group; the absorbances of the imido group (ν_{WNC}) could not be confidently assigned.

Scheme II



Complexes **4b**[37] and **4c** are formed as a 1:1 mixture of two geometric isomers because the alkylidene ligand can adopt two different orientations (as illustrated for **4c**). The initial 1:1



4c

mixture of **4c** isomers changes over several days to a roughly 3:1 ratio. The slow rate of equilibration indicates that the barrier to rotation of the alkylidene group is significant,[38] consistent with NMR studies of **4a** showing no fluxionality of the cyclopentylidene ligand at 60 °C in C_6D_6. Two isomers are also possible for the 2-butylidene and 1-indenylidene complexes **4h** and **4i**, but only one is observed. Based on the distortions observed in the structure of **4a**, steric interactions may destabilize the isomer that has the bulky group directed at the oxo ligand.

Discussion

The oxidative addition of carbon–oxygen and carbon–nitrogen double bonds to a single tungsten center is a remarkable and unprecedented reaction. That these reactions are thermodynamically favorable indicates that the tungsten–oxygen, –nitrogen, and –carbon multiple bonds must be very strong. This conclusion can be made more quantitative for the oxo–trisphosphine complex **5**, using the reaction with CO_2 (eq 12). The overall conversion

$$\begin{gathered}WCl_2L_4 + CO_2 \xrightarrow[C_6H_6]{} \\ W(O)Cl_2(CO)L_2 + 2\,L \overset{K}{\rightleftharpoons} W(O)Cl_2L_3 + CO + L\end{gathered} \tag{12}$$

of WCl_2L_4 (**1**) to $W(O)Cl_2L_3$ (**5**) involves the loss of one phosphine

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(30) Churchill, M. R.; Rheingold, A. L. *Inorg. Chem.* **1982**, *21*, 1357–1359. Churchill, M. R.; Rheingold, A. L.; Youngs, W. J.; Schrock, R. R.; Wengrovius, J. H. *J. Organomet. Chem.* **1981**, *204*, C17–C20.

(31) Wengrovius, J. H.; Schrock, R. R. *Organometallics* **1982**, *1*, 148–155. Tatsumi, K.; Hoffmann, R. *Inorg. Chem.* **1980**, *19*, 2656–2658 and references therein.

(32) Mayer, J. M. *Inorg. Chem.* **1988**, *27*, 3899–3903. Reference 5a, pp 151–152, 188.

(33) Reference 5a, pp 157–158.

(34) Tamagawa, K.; Hilderbrandt, R. L.; Shen, Q. *J. Am. Chem. Soc.* **1987**, *109*, 1380–1383.

(35) Wengrovius, J. H., ref 31. Schrock, R. R.; Rocklage, S.; Wengrovius, J. H.; Rupprecht, G.; Fellmann, J. *J. Mol. Catal.* **1980**, *8*, 73–83.

(36) Reference 5a, pp 112–118.

(37) Complex **4b** is also different from the other oxo–alkylidene complexes in that none of its isomers contain a plane of symmetry. The NMR data for **4b** (Table V) are consistent with two geometric isomers: one exhibits an AB pattern in the $^{31}P\{^1H\}$ NMR, the other a single resonance, presumably an unresolved AB pattern.

(38) Schrock, R. R. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum: New York, 1986; pp 221–283.

Table V. NMR and IR Data[a] for the Oxo– and Imido–Alkylidene Complexes **4** and **6**

complex =CRR′		^{31}P{^{1}H}		^{13}C{^{1}H} NMR							^{1}H NMR					IR $\nu_{W\equiv O}$
				C_α			others									
		δ	J_{WP}	δ	m	J_{PC}	δ	m	J_{PC}	assign.	δ	m	J	int	assign.	
cyclopentylidene	**4a**	13.7	332	331.8	t	10[b]	13.2	t	18	$\mathrm{P}\mathit{C}\mathrm{H_3Ph_2}$	2.40	t	4.6	6 H	$\mathrm{PC}\mathit{H}_3\mathrm{Ph_2}$	952
							54.8	s		$\mathit{C}\mathrm{H_2}$	5.23	m		2 H	$\mathrm{CC}\mathit{H}_2\mathrm{CH_2}$	
							49.5	s		$\mathit{C}\mathrm{H_2}$	3.91	m		2 H	$\mathrm{CC}\mathit{H}_2\mathrm{CH_2}$	
							28.5	s		$\mathit{C}\mathrm{H_2}$	0.88	quint	7	2 H	$\mathrm{CH_2C}\mathit{H}_2\mathrm{CH_2}$	
							27.1	s		$\mathit{C}\mathrm{H_2}$	0.52	quint	7	2 H	$\mathrm{CH_2C}\mathit{H}_2\mathrm{CH_2}$	
3-methylcyclopentylidene	**4b**[c]	13.8	332	332.7	t	9					2.41	m			$\mathrm{PC}\mathit{H}_3\mathrm{Ph_2}$	962
		13.7	333	332.5	t	10										
		13.8	332													
cyclopentenylidene	**4c**[d]	16.1	329	314.0	t	10	12.4	t	17	$\mathrm{P}\mathit{C}\mathrm{H_3Ph_2}$	2.41	t	4.7	6 H	$\mathrm{PC}\mathit{H}_3\mathrm{Ph_2}$	953
							148.1	s		$\mathit{C}\mathrm{H}$	7.92	m		1 H	$\mathrm{C}\mathit{H}$	
							146.0	s		$\mathit{C}\mathrm{H}$	4.71	m		1 H	$\mathrm{C}\mathit{H}$	
							44.2	s		$\mathit{C}\mathrm{H_2}$	3.35	m		2 H	$\mathrm{C}\mathit{H}_2$	
							37.0	s		$\mathit{C}\mathrm{H_2}$	2.56	m		2 H	$\mathrm{C}\mathit{H}_2$	
		13.8	327	311.4	t	9	13.4	t	17	$\mathrm{P}\mathit{C}\mathrm{H_3Ph_2}$	2.36	t	4.6	6 H	$\mathrm{PC}\mathit{H}_3\mathrm{Ph_2}$	953
							144.8	s		$\mathit{C}\mathrm{H}$	7.63	m		1 H	$\mathrm{C}\mathit{H}$	
							144.2	s		$\mathit{C}\mathrm{H}$	4.51	m		1 H	$\mathrm{C}\mathit{H}$	
							47.8	s		$\mathit{C}\mathrm{H_2}$	5.06	m		2 H	$\mathrm{C}\mathit{H}_2$	
							37.7	s		$\mathit{C}\mathrm{H_2}$	2.88	m		2 H	$\mathrm{C}\mathit{H}_2$	
2-indylidene	**4d**	15.2	330								2.37	t	4.7	6 H	$\mathrm{PC}\mathit{H}_3\mathrm{Ph_2}$	964[e]
											5.22	m		2 H	$\mathrm{C}\mathit{H}_2$	
cyclohexylidene	**4e**	11.9	328													
2-propylidene	**4g**[f]	14.1	330	322.4	t	10					2.39	t	4.6	6 H	$\mathrm{PC}\mathit{H}_3\mathrm{Ph_2}$	962[e]
											4.08	t	3.1	3 H	$\mathrm{CC}\mathit{H}_3$	
											2.66	t	3.3	3 H	$\mathrm{CC}\mathit{H}_3$	
2-butylidene	**4h**	14.5	330								2.43	m				
1-indylidene	**4i**	15.4	326								2.43	t	5	6 H	$\mathrm{PC}\mathit{H}_3\mathrm{Ph_2}$	972
											4.14	m		2 H	$\mathrm{C}\mathit{H}_2$	
											2.35	m		2 H	$\mathrm{C}\mathit{H}_2$	
$W(O)(=CH^tBu)Cl_2(PMe_2Ph)_2$[g]		1.4	334	320	dt	11										970
W(N-*p*-tolyl)[$=C(CH_2)_4$]Cl_2-($PMePh_2$)$_2$	**6a**	9.2	286	319.7	t	11	12.2	t	16	$\mathrm{P}\mathit{C}\mathrm{H_3Ph_2}$	2.41	t	4.4	6 H	$\mathrm{PC}\mathit{H}_3\mathrm{Ph_2}$	
							55.1	s		$\mathit{C}\mathrm{H_2}$	4.81	m		2 H	$\mathrm{CC}\mathit{H}_2\mathrm{CH_2}$	
							49.0	s		$\mathit{C}\mathrm{H_2}$	4.16	m		2 H	$\mathrm{CC}\mathit{H}_2\mathrm{CH_2}$	
							27.9	s		$\mathit{C}\mathrm{H_2}$	1.10	quint	7	2 H	$\mathrm{CH_2C}\mathit{H}_2\mathrm{CH_2}$	
							26.6	s		$\mathit{C}\mathrm{H_2}$	0.84	quint	7	2 H	$\mathrm{CH_2C}\mathit{H}_2\mathrm{CH_2}$	
							20.7	s		$\mathit{C}\mathrm{H_3}$	2.02	s		3 H	$\mathrm{PhC}\mathit{H}_3$	
W(N-*p*-tolyl)($=CMe_2$)Cl_2-($PMePh_2$)$_2$	**6g**	8.5	285								2.42	t	4	6 H	$\mathrm{PC}\mathit{H}_3\mathrm{Ph_2}$	
											3.91	t	4	3 H	$\mathrm{CC}\mathit{H}_3$	
											3.00	t	4	3 H	$\mathrm{CC}\mathit{H}_3$	
											2.00	s		3 H	$\mathrm{PhC}\mathit{H}_3$	

[a] Procedures as described in the Experimental Section. Complete IR spectra for **4a–c** and **6a** are reported in the Experimental Section. [b] $^1J_{WC}$ = 150 Hz. [c] Formed as a mixture of two geometric isomers, neither of which contains a mirror of symmetry relating the phosphine ligands. ^{1}H NMR data are given in the Experimental Section. [d] Formed as a mixture of two isomers; the first data reported are for the thermodynamic isomer. [e] IR spectrum taken in C_6D_6 solvent. [f] ^{13}C{^{1}H} spectrum obtained in C_6D_6 using acetone-*2*-^{13}*C*. [g] See ref 35.

from **1** and the addition of an oxygen atom. Phosphine loss is estimated to require at least 15 kcal/mol[39] and the oxygen atom is obtained from cleavage of CO_2, with $\Delta H(CO_2 \rightarrow CO + O)$ = 127 kcal/mol.[8] After correction for the equilibrium constant between $W(O)Cl_2(CO)L_2$ and **5** ($K \cong 10^{-3}$, $\Delta G_{eq} \cong 4$ kcal/mol[40]), the fact that reaction 12 occurs implies that the tungsten–oxygen bond strength in **5** is at least 138 kcal/mol.[41] This value is consistent with the 150 kcal/mol average tungsten–oxygen bond strength in WO_3 in the gas phase.[42] The formation of such a strong W$\equiv$O bond clearly provides much of the driving force for the oxidative addition reactions.

Even with favorable thermodynamics, it is surprising that there is a facile kinetic pathway for cleavage of the 127 kcal/mol bond in CO_2 and the ~160 kcal/mol double bond in ketones. Our studies, described below, support the mechanism shown in Scheme II. The initial step is the formation of an η^2-ketone, imine, or cumulene complex, F, by substitution of a phosphine ligand. A related paramagnetic monoethylene adduct $W(C_2H_4)Cl_2(PMe_3)_3$ has been reported,[4a] but F has not been directly observed. F can substitute a second phosphine, as for ketones (**2**) and aldehydes (**3**), or it can decompose by phosphine loss and cleavage of the carbon–oxygen or carbon–nitrogen bond.

The formation of F most likely proceeds by dissociation of a phosphine ligand followed by coordination of the C–O or C–N double bond. Phosphine loss is suggested by the steric crowding in the structure of **1**[7] and is indicated by inhibition of its reactions by added phosphine, for instance with CO_2.[43] CO_2 reacts much more slowly with $WCl_2(PMe_3)_4$, from which phosphine loss is less favorable. Similarly, decomposition of the bis(ketone) complexes **2** is strongly inhibited by excess ketone. A solution of **2a** with 5 equiv of cyclopentanone is essentially unchanged after 2 weeks at 25 °C, while conversion of **2a** to **4a** in the presence of **1**—added to keep the concentration of free cyclopentanone small—is complete within a day. Thus, conversion of **2a** to **4a** involves preequilibrium formation of F. Equilibrium loss of ketone from **2** is

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(39) The rate of phosphine loss from **1** is slow on the NMR time scale: no exchange or broadening of free phosphine resonances is observed in the presence of **1**.

(40) Su, F.-M.; Cooper, C.; Geib, S. J.; Rheingold, A. L.; Mayer, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 3545–3547. See also: Reference 7.

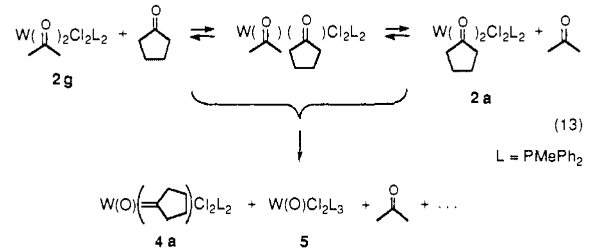
(41) This rough calculation assumes that the enthalpy of the reactions is roughly the same as the free energy and that the gas-phase bond dissociation energy of CO_2 can be used in solution.

(42) Bond energies: O_2W–O = 147 kcal/mol, OW–O = 143 kcal/mol, and W–O = 161 kcal/mol. Glidewell, C. *Inorg. Chim. Acta* **1977**, *24*, 149–157. Reference 5a, p 32, has a more general discussion. See also: Sanderson, R. T. *Inorg. Chem.* **1986**, *25*, 3518–3522.

(43) Inhibition by added phosphine has also been observed in reactions of **1** with epoxides[44] and alcohols:[43a,b] (a) Jang, S. Masters Thesis, University of Washington, 1988. (b) Jang, S.; Atagi, L. M.; Mayer, J. M., manuscript in preparation.

(44) Atagi, L. M.; Over, D. E.; McAlister, D. R.; Mayer, J. M., manuscript in preparation.

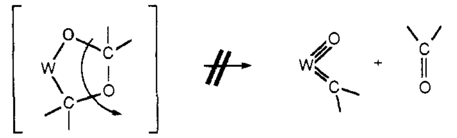
also supported by the equilibrium between 2-butanone and **2h**, and the rapid exchange of ketone ligands (c.f. above and eq 13).



(13)

N-tolylimines have not been observed to form complexes analogous to **2**, probably because of the steric bulk of the substituent (note that ketones larger than acetone do not bind strongly to **1**).[11i] CO_2, OCS, isocyanates, and thioisocyanates also do not bind well to tungsten. In both cases, equilibrium between **1** and a small amount of an η^2 adduct is probably established since dissociation of a phosphine from **1** is much more rapid than double-bond cleavage. At the other extreme, the bis(acetaldehyde) complex **3a** is stable in solution at ambient temperatures at least in part because acetaldehyde dissociation is not facile.

To test the possibility of alternative mechanisms involving two tungsten centers and/or two substrate molecules, crossover experiments have been performed: **1** was reacted with a roughly equimolar mixture of cyclopentanone-^{18}O and cyclopentanone-*1*-^{13}C, and with $C^{18}O_2$ and $^{13}CO_2$. In both cases, the isotopic composition of the cyclopentanone or CO_2 remaining at the end of the experiment was the same as that of the starting materials. This result eliminates the pathway shown in eq 14, since loss of ketone or CO_2 from the metallacycle as shown would result in isotope scrambling in the cyclopentanone or CO_2. (Metallacycles of this kind have been formed from ketones, imines, or CO_2 on group VIII metal centers,[45] and the reactions of **1** with mixtures of a ketone and ethylene appear to proceed via related oxatungstacyclopentane intermediates.[46]) The metallacycle mechanism is also inconsistent with the inhibition of decomposition of the bis(ketone) complexes **2** by excess ketone, which indicates that less than two molecules of ketone are involved in the rate-determining step. The isotopic composition of the tungsten products of the crossover experiments, **4a** and $W(O)Cl_2(CO)(PMePh_2)_2$, could, unfortunately, not be determined by either NMR or mass spectroscopy. Thus, intermediates with two tungsten centers, such as a W–O–CR_2–W–O–CR_2–metallacycle, cannot be ruled out.[47]



(14)

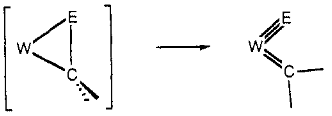
The isotopic labeling experiments are consistent with simple intramolecular decomposition of the intermediate F. The ketone, imine, or cumulene ligand in F is undoubtedly bound in an η^2 fashion, by analogy with compounds **2** and **3**. The tungsten(II) center has a high affinity for π-acid ligands and does not strongly bind saturated ligands: for instance, phosphine is rapidly displaced by small amounts of acetone or ethylene but phosphine loss is not observed in THF solution.

The regiochemistry and relative rates of the cumulene oxidative addition reactions are also consistent with the formation of an η^2 intermediate. OCS and ^tBuNCS are expected to bind η^2 through the carbon–sulfur bond and isocyanates through the C=N bond,[48] and these are the bonds that are cleaved. An isolated niobium isocyanate complex, bound through the C=N bond, has been observed to decompose to an imido compound and free CO.[49] The recently reported cleavage of a C–C double bond in carbon suboxide (O=C=C=C=O) by **1**[50] seems to require initial η^2 coordination. The regiochemistry of cumulene cleavage is also undoubtedly influenced by the very large disparity of the C–O versus C–N or C–S bond strengths: for OCS there is a 87 kcal/mol difference in the two double-bond strengths, for OCNH a 42 kcal/mol difference (bond strengths, in kcal/mol: O=CS, 160; OC=S, 73; O=CNH, 130; OC=NH 88).[8]

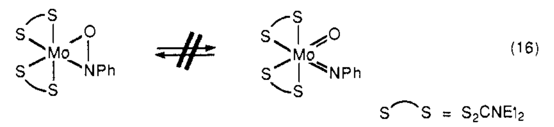
The apparent rate of cleavage is fairly insensitive to steric factors, since ^tBuNCO, *p*-TolNCO, and ^tBuNCS all react at roughly the same rate, even though cleavage occurs next to the substituent for the first two and away from it for the last. In contrast, the reactions of **1** with aziridines, $\overline{CH_2CH_2N}R$, thought to proceed through an N-coordinated η^1 adduct, are strongly affected by the nature of the R group.[44] The absence of a large steric effect for isocyanates is therefore more consistent with an η^2, π-bound intermediate than an η^1 adduct.

Compounds **2** and **3** and the intermediate F are best described as tungsten(VI) and tungsten(IV), not as ketone or aldehyde adducts of tungsten(II) (e.g., A). They are therefore examples of the "traditional" oxidative addition of double bonds to transition metals,[2] in which coordination removes the π component of the double bond but the two atoms remain attached to each other through a σ bond.

In the ketone, imine, and cumulene reactions described here, the cleavage of C–O or C–N double bond appears to proceed in two steps. The formation of the adduct F effectively removes the π bond, as described above. Then we suggest opening of the metallacycle occurs by cleavage of the σ bond (eq 15). σ-Bond cleavage is a feature of classical oxidative addition reactions, such as the addition of H_2,[2] but the H_2 molecule binds to a metal through the σ-bonding orbital while in F the C–O σ orbital is not involved in metal–ligand bonding. This opening of a three-atom metallacycle is not a well-precedented reaction. It may be occurring in the photochemical conversion of a bis(peroxo) molybdenum porphyrin complex to a dioxo compound,[51] although the mechanism of this reaction has not been established. In contrast, an isolated nitrosobenzene complex does not interconvert with a known oxo–imido compound (eq 16).[52] This transformation would be quite similar to the facile F → **4** conversion observed here, involving the same d^0–d^2 electronic configurations and apparently the same coordination geometries. The reasons



(15)



(16)

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(45) Reference 2a, pp 496–499. (a) Herskovitz, T.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1976**, *98*, 1615–1616. (b) Hou, Z.; Takamine, K.; Aoki, O.; Shiraraishi, H.; Fujiwara, Y.; Taniguchi, H. *J. Chem. Soc., Chem. Commun.* **1988**, 668–670. (c) Pizzotti, M.; Porta, F.; Cenini, S.; Demartin, F.; Masciocchi, N. *J. Organomet. Chem.* **1987**, *330*, 265–278. References 12a,e and 13a. (d) Note that $Mo(CO_2)_2(PMe_3)_4$ (Alvarez, R.; Carmona, E.; Marin, J. M.; Poveda, M. L.; Butierrez-Puebla, E.; Monge, A. *J. Am. Chem. Soc.* **1986**, *108*, 2286–2294) does not readily rearrange to a metallacycle. It also does not open to a molybdenum(II) oxo–carbonyl complex, presumably because this would be an unfavorable d^4 oxo species.

(46) Reference 14, pp 16–18.

(47) Compounds with bridging ketones and aldehydes are known,[13] but they have not been observed to decompose in this fashion. A closely related intermediate has been suggested to explain the cleavage of O_2 by chromium(II): Brynildson, M. E.; Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 4579–4583.

(48) (a) Ibers, J. A. *Chem. Soc. Rev.* **1982**, *11*, 57. (b) Rosi, M.; Sgamellotti, A.; Tarantelli, F.; Floriani, C. *Inorg. Chem.* **1987**, *26*, 3805–3811, and references therein.

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(50) List, A. K.; Hillhouse, G. L.; Rheingold, A. L. *Organometallics* **1989**, *8*, 2010–2016.

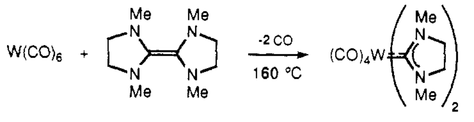
(51) Ledon, H.; Bonnet, M.; Lallemand, J.-Y. *J. Chem. Soc., Chem. Commun.* **1979**, 702–704.

(52) Maatta, E. A.; Wentworth, R. A. D. *Inorg. Chem.* **1979**, *18*, 2409–2413; **1980**, *19*, 2597–2599.

for this difference in reactivity are not known. Complex **1** reacts rapidly with nitrosobenzene to give a mixture of products including **5**, $W(NPh)Cl_2(PMePh_2)_3$,[53] and $OPMePh_2$.

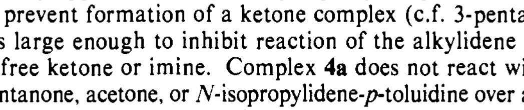
The isomerization in eq 15 probably also involves simultaneous rotation of the alkylidene fragment, as cleavage without rotation would place the alkylidene ligand in an unfavorable orientation. According to the spectroscopic data for **4** and **6** and the structure of **4a**, the alkylidene substituents lie in the mirror plane of the molecule, not bisecting it as in the metallacycle. The lack of alkylidene rotation on the NMR time scale and the slow isomerization of **4c** on the chemical time scale show that the unfavorable alkylidene rotamer is a high-energy species. A recent theoretical study[54] of the suggested mode of decomposition of a platinum(II) ketone complex[55] emphasizes the importance of methylene rotation concurrent with C–C bond cleavage.[56] A reviewer noted the analogy between this rearrangement and the disrotatory ring opening of the cyclopropyl carbanion to form the allyl anion.

This insertion of a metal center into a C–O double bond is an unprecedented four-electron oxidative addition reaction. The most similar reported reactions are the oxidative addition of ketones to a dinuclear tungsten center to form a μ-oxo, μ-alkylidene complex,[57] and the formation of carbene compounds from highly electron rich olefins (e.g., eq 17).[58] The latter case involves quite unusual olefins with very weak carbon–carbon bonds. An interesting theoretical discussion of ethylene and acetylene cleavage reactions such as eq 17 emphasizes the importance of electron-donating substituents in lowering the activation energy.[59] In contrast, the double-bond cleavages reported here are prevented by the presence of electron-donating substituents (esters vs ketones).



(17)

Even small changes in the ketone have a substantial effect on the ketone cleavage reactions. Clean formation of alkylidene products are observed only when the C–O or C–N double bond is exocyclic to a five-membered ring (**4a**–**d**, **6a**), and not in conjugation with an aromatic ring (see below). The origin of this selectivity appears to be that a cyclopentyl ring is not so bulky as to prevent formation of a ketone complex (c.f. 3-pentanone) but is large enough to inhibit reaction of the alkylidene ligand with free ketone or imine. Complex **4a** does not react with cyclopentanone, acetone, or *N*-isopropylidene-*p*-toluidine over a week at ambient temperatures, while **4g** reacts quickly with acetone. Steric effects appear to be the dominant factor in these rates since **4a** does react with acetaldehyde within 2 days at 25 °C, yielding a mixture of products including ethylidenecyclopentane (eq 18).



(18)

4a L = $PMePh_2$

A large steric effect has been observed in other Wittig-type reactions of tungsten alkylidenes.[60] The Wittig-type reactions of compounds **4** occur with substantial decomposition, which probably accounts for the nonstoichiometric nature of the reactions of **1** with small ketones, with pivaldehyde, and with *N*-isopropyl-*p*-toluidine. The reactivity of the alkylidene product with the ketone, aldehyde, or imine reactant limits the utility of the double-bond cleavage reaction as a synthetic route to alkylidene complexes.

It is interesting to contrast the double-bond oxidative addition reactions with the reactions of **1** with benzophenone and acetophenone. With these aromatic ketones, η^2 complexes are not observed, and the final products are not alkylidene complexes but rather **5** and the olefin formed by coupling of two ketones, tetraphenylethylene or dimethylstilbene (eq 8). It is unlikely that the reactions involve formation of an alkylidene and subsequent Wittig-like reaction with a second ketone, given the steric bulk of the ketones, the dark color, and the rapidity and stoichiometric nature of the reactions (the Wittig reactions such as eq 18 form **5** only in low yields). These reactions appear to proceed by a single-electron transfer to form ketyl radicals, as indicated by the immediate formation of the dark blue-purple color.[61] Electron transfer is a common pathway for unsaturated and aromatic ketones because they are easily reduced.[23]

The reductive coupling of ketones to pinacols or olefins by electron transfer to form ketyl radicals is a classic organic reaction.[62] The ketyl radicals are converted to pinacolate ions, which can be subsequently deoxygenated to olefins. Low-valent titanium,[63] tungsten,[64] and other reagents[65] have been used. Complex **1** reacts by this one-electron pathway only with easily reducible ketones; it does not appear to be a potent one-electron reductant in nonpolar media. The mechanism of reaction of **1** with most substrates involves *two-electron* steps (Scheme II). The partitioning between one- and two-electron pathways can be a subtle one: 1-indanone reacts with **1** to give roughly 50% of **5** and the olefin and 50% of the alkylidene complex **4i**.

The driving force for reactions of **1** is the formation of π bonds to the tungsten center, either metal–ligand multiple bonds or back-bonding to a π-acid ligand. In order for the tungsten to form a strong multiple bond to an oxo or imido ligand, it must be at a +4 or higher in oxidation state: only in high oxidation states are the d orbitals empty to permit π donation from the ligand to the metal.[66] There are no examples of tungsten(II) or tungsten(III) terminal oxo or imido compounds.[45d,66] This electronic requirement that **1** be oxidized by two electrons in order to form the multiple bond, coupled with the strength of the $W{\equiv}O$, $W{\equiv}N$, and $W{=}C$ bonds formed, are the primary reasons for the preference for two-electron chemistry. They are the critical factors leading to the remarkable double-bond cleavage reactions.

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(61) (a) See, for example: Maryama, K.; Hayami, J.-I.; Katagiri, T. *Chem. Lett.* **1986**, 601–604. Hirota, N.; Weissman, S. I. *J. Am. Chem. Soc.* **1964**, *86*, 2538–2545. Walling, C. *J. Am. Chem. Soc.* **1988**, *110*, 6846–6850, and references therein. (b) Presumably the ketyls are coordinated or exist as tight ion pairs in benzene solution. (c) Similar dark colors are observed in the reactions of α,β-unsaturated ketones with **1** during the synthesis of the ketone complexes (e.g., **2c**). Benzophenone and acetophenone are apparently too big to form η^2 adducts and another reaction channel is observed.

(62) Reference 19, p 1111–1113. Ho, T. L. *Synthesis* **1979**, 1–20. Dams, R.; Malinowski, M.; Westdorp, I.; Geise, H. Y. *J. Org. Chem.* **1982**, *47*, 248–259.

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Experimental Section

General Considerations. All reactions and preparations were performed under nitrogen or argon using standard vacuum line techniques[67] except as indicated. Compounds were stored and handled in a glovebox equipped with a freezer (−20 °C). Benzene, pentane, heptane, triethylamine, and toluene were vacuum transferred from CaH_2, diethyl ether, and THF from sodium/benzophenone, and methylene chloride from activated 4-Å sieves. Ketones and aldehydes (Aldrich) were vacuum transferred before use. ^1H NMR spectra were recorded on Varian VXR-300 and Bruker WM-500 spectrometers. Data for complexes **2a–h**, **4a–i**, and **6a,g** are presented in Tables II and V; resonances in the aromatic region are not reported. The VXR-300 was used for ^{13}C (75.4-MHz) and $^{31}P\{^1H\}$ (121.4-MHz) NMR spectra; the latter were internally referenced to $PMePh_2$ (δ −27.6, relative to H_3PO_4). ^1H and ^{31}P NMR spectra were obtained in C_6D_6 and ^{13}C spectra in CD_2Cl_2 solvent unless otherwise indicated. Coupling constants are reported in hertz. IR spectra were obtained as Nujol mulls (except as indicated) with Perkin-Elmer 283, 1602FT, and 225 spectrometers and are reported in reciprocal centimeters. Mass spectra were recorded on a Hewlett-Packard 5985 GC/MS instrument. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Vancouver.

Compounds **1**,[4] $WCl_2(PMe_3)_4$,[4] and **5**[26] were prepared following published procedures. Acetone-^{18}O and cyclopentanone-^{18}O were formed from $H_2{}^{18}O$ (Cambridge Isotope) and the 1,3-propanediol ketal;[68] carbon-13 labeled materials were used as received (Cambridge Isotope, MSD Isotope). *N*-Cyclopentylidene-*p*-toluidine and *N*-isopropylidene-*p*-toluidine were prepared by stirring the ketone and the amine in toluene over 4-Å sieves.[69]

Some complexes, particularly those of limited stability or those formed as part of a mixture of products, were only observed by NMR. In a typical procedure an NMR tube sealed to a ground-glass joint was charged with reagents and solvent in the glovebox and capped with a Teflon or ground-glass valve. The whole assembly was removed to a vacuum line, and the reaction solution was cooled to −196 °C and evacuated. Any other (volatile) reagents were vacuum transferred into the tube and the tube sealed with a torch.[67] This procedure was also used for the reaction of **1** with a mixture of cyclopentanone-^{18}O and cyclopentanone-^{13}C and for the reaction of **1** with $C^{18}O_2$ and $^{13}CO_2$. The isotopic composition of the cyclopentanone or CO_2 was examined by $^{13}C\{^1H\}$ NMR[70] and by mass spectroscopy.

$W[O{=}C(CH_2)_4]_2Cl_2(PMePh_2)_2$ (2a). Cyclopentanone (0.40 mL) was added to a suspension of **1** (0.49 g) in 5 mL of toluene and stirred for 10 min. The mixture was concentrated to 1 mL, and 2 mL of Et_2O and 20 mL of pentane were added. The solids were filtered and dried in vacuo for 1 h, yielding 0.29 g (76%) of red-orange powder. Anal. Calcd for $C_{36}H_{42}Cl_2O_2P_2W$: C, 52.51; H, 5.14. Found: C, 52.30; H, 5.07. IR: 1094, 890 (vs), 742 (s), 732 (s), 690 (vs), 511 (vs), 469, 428, 298.

$W[O{=}C(CH_2CH(CH_3)CH_2CH_2)]_2Cl_2(PMePh_2)_2$ (2b). 3-Methyl-cyclopentanone (0.21 mL) was added to a suspension of **1** (0.22 g) in 5 mL of toluene and stirred for 15 min. Volatiles were pumped away and the residue was dissolved in 1 mL of Et_2O. Pentane (10 mL) was added and the mixture was filtered at −78 °C, yielding 0.078 g (44%) of tan powder after drying in vacuo. Anal. Calcd for $C_{38}H_{46}Cl_2O_2P_2W$: C, 53.60; H, 5.45. Found: C, 54.33; H, 5.27.

$W[O{=}C(CH{=}CHCH_2CH_2)]_2Cl_2(PMePh_2)_2$ (2c). Complex **2c** was detected by NMR when 2-cyclopenten-1-one (2 μL) was exposed to **1** (24 mg) in C_6D_6 in a sealed NMR tube.

$W(O{=}C_9H_8)_2Cl_2(PMePh_2)_2{\cdot}Et_2O$ (2d). 2-Indanone (0.60 g) and **1** (0.40 g) were suspended in 12 mL of toluene and stirred for 16 h. The reaction mixture was concentrated to 4 mL, and 10 mL of heptane was added. The mixture was filtered and all volatiles were pumped away from the filtrate. Et_2O (5 mL) and then 13 mL of heptane were added; filtration yielded 0.19 g (52%) of orange **2d**. Anal. Calcd for $C_{48}H_{52}Cl_2O_3P_2W$: C, 58.02; H, 5.27. Found: C, 58.32, 58.23, 58.45; H, 5.34, 5.58, 5.38. IR: 1271, 1117 (s), 1027 (w), 977, 894 (vs), 743 (vs), 698 (vs), 626 (w), 611, 506 (vs), 487.

$W[O{=}C(CH_2)_5]_2Cl_2(PMePh_2)_2$ (2e). Following the procedure for **2b**, cyclohexanone (0.52 mL) and **1** (0.20 g) in 15 mL of benzene were reacted for 14 h, yielding 0.04 g (25%) of yellow-brown powder. Anal. Calcd for $C_{38}H_{46}Cl_2O_2P_2W$: C, 53.60; H, 5.45. Found: C, 53.04; H, 4.92.

$W[O{=}C(CH_2)_3]_2Cl_2(PMePh_2)_2$ (2f). Following the procedure for **2e**, cyclobutanone (0.50 mL) and **1** (0.20 g) gave 0.02 g (13%) of **2f** as a yellow-brown powder.

$W(O{=}CMe_2)_2Cl_2(PMePh_2)_2$ (2g). Acetone (0.12 mL) was added to a suspension of **1** (0.40 g) in 10 mL of benzene and stirred for 15 min. The reaction mixture was concentrated to 4 mL, and 12 mL of pentane was added. The solids were filtered and dried in vacuo for 1 h, yielding 0.22 g (77%) of red-orange powder. Anal. Calcd for $C_{32}H_{38}Cl_2O_2P_2W$: C, 49.83; H, 4.97. Found: C, 50.03; H, 5.03. IR: 1230 (ν_{CO}) [1220 ($\nu_{C^{18}O}$)], 1087, 898, 887, 741, 733, 689, 619 (ν_{WO}) [598 ($\nu_{W^{18}O}$)], 516, 429, 306, 251.

$W(O{=}CHMe)_2Cl_2(PMePh_2)_2$ (3a). Acetaldehyde (0.5 mL) was added to a suspension of **1** (0.31 g) in 5 mL of benzene and stirred for 15 min. Volatiles were pumped away and the residue was dissolved in 1 mL of Et_2O and 0.25 mL of MeCHO; then 18 mL of pentane was added. The mixture was filtered at −78 °C and the solids were dried in vacuo for 1 h, yielding 0.18 g (82%) of peach colored powder. ^1H NMR: 4.77 (m), 4.72 (m), 3.88 (m), 3.76 (m), 2.71 (d, J = 5), 2.42 (m), 2.25 (m), 2.19 (m), 2.03 (m). $^{13}C\{^1H\}$: 94.1 (t, $^2J_{PC}$ = 8, O*C*HMe, isomer A), 92.7, 92.6, 92.4, 92.0 (observed peaks probably due to two overlapping AXY patterns for isomer C), 91.2 (t, $^2J_{PC}$ = 8, OCHMe, isomer B), 18.0 (s, C*C*H$_3$, A), 17.8 (s, C*C*H$_3$, C), 16.8 (s, C*C*H$_3$, C), 16.6 (s, C*C*H$_3$, B), 12.3 (t, J_{PC} = 16, P*C*H$_3$), 12.1 (d, J_{PC} = 30, P*C*H$_3$, C), 11.7 (d, J_{PC} = 29, P*C*H$_3$, C), 11.3 (t, J_{PC} = 16, P*C*H$_3$). $^{31}P\{^1H\}$ NMR: 0.6, (d, $^2J_{PP}$ = 129, $^1J_{WP}$ = 178, C), −0.8 (s, $^1J_{WP}$ = 180, A), −0.9 (s, $^1J_{WP}$ = 176, B), −2.2, (d, $^2J_{PP}$ = 129, $^1J_{WP}$ = 179, C). IR: 1287 (w), 1171, 1097, 1069, 896 (vs), 752 (s), 735, 697 (vs), 642, 616 (w).

$W[O{=}CHCMe_3]_2Cl_2(PMePh_2)_2$ (3b). Pivaldehyde (0.041 mL) was added to a suspension of **1** (0.20 g) in 0.5 mL of benzene and the resultant mixture stood for 30 min. Volatiles were pumped away, the residue was dissolved in 2 mL of Et_2O, and 4 mL of heptane was added. The mixture was concentrated to 4 mL, filtered, and dried in vacuo for 3 h, yielding 0.07 g (45%) solids. ^1H NMR: 5.35 (t, J = 3, 2 H, OC*H*), 4.61 (dd, J_{PH} = 2, 4, 2 H, OC*H*), 2.29 (dd, $^2J_{PH}$ = 6, $^4J_{PH}$ = 3, 6 H, PC*H*$_3$), 2.17 (dd, $^2J_{PH}$ = 5, $^4J_{PH}$ = 4, 6 H, PC*H*$_3$), 1.01 (s, 18 H, C(C*H*$_3$)$_3$), 0.92 (s, 18 H, C(C*H*$_3$)$_3$). $^{13}C\{^1H\}$ NMR: 104.9 (dd, J_{PC} = 9, J_{PC} = 6, ^{t}Bu*C*HO), 104.1 (dd, J_{PC} = 9, J_{PC} = 7, ^{t}Bu*C*HO), 37.2 (s, Me$_3$*C*C), 36.1 (s, Me$_3$*C*C), 32.2 (s, (*C*H$_3$)$_3$C), 31.1 (s, (*C*H$_3$)$_3$C), 12.9 (dd, P*C*H$_3$), 10.4 (dd, $^1J_{PC}$ = 18, $^3J_{PC}$ = 9.5 P*C*H$_3$). $^{31}P\{^1H\}$ NMR: −8.6 ($^1J_{WP}$ = 179), −8.7 ($^1J_{WP}$ = 174). IR: 1175 (m br), 1097, 1074, 1028 (w), 1000 (w), 979 (w), 892 (s), 743 (s), 696 (vs).

$W(O)[{=}C(CH_2)_4]Cl_2(PMePh_2)_2$ (4a). Cyclopentanone (0.017 mL) was added to a suspension of **1** (0.20 g) in 25 mL of toluene and the resultant mixture stirred for 24 h. The mixture was concentrated to 5 mL, and 17 mL of pentane was added. Filtration and washing with 5 mL of pentane gave 0.10 g (74%) of yellow powder. Anal. Calcd for $C_{31}H_{34}Cl_2OP_2W$: C, 50.36; H, 4.64. Found: C, 50.84; H, 4.63. IR: 1098 (s), 952 (vs) (ν_{WO}), 889 (vs), 690 (vs), 510 (vs), 479, 439 (w), 429 (w), 257 (vw).

$W(O)[{=}C(CH_2CH(CH_3)CH_2CH_2)]Cl_2(PMePh_2)_2$ (4b). 3-Methylcyclopentanone (0.030 mL) was added to a suspension of **1** (0.30 g) in 12 mL of benzene and the resultant mixture stirred for 5 days. Volatiles were pumped away, the residue was dissolved in 1 mL of toluene, and 15 mL of heptane was added. The mixture was filtered and dried in vacuo over 16 h. Anal. Calcd for $C_{32}H_{36}Cl_2OP_2W$: C, 51.02; H, 4.82. Found: C, 51.07; H, 4.82. ^1H NMR (of a roughly 1:1 mixture of isomers): 5.45 (m, 1 H), 5.20–4.95 (m, 3 H), 4.20 (m, 2 H), 3.88 (m, 1 H), 3.40 (m, 1 H), 2.41 (m, 12 H, PC*H*$_3$Ph$_2$), 1.11 (m, 2 H), 0.88 (m, 2 H), 0.68 (d, $^3J_{HH}$ = 6.5, 3 H, HCC*H*$_3$), 0.49 (d, $^3J_{HH}$ = 6.5, 3 H, HCC*H*$_3$), 0.34 (m, 1 H), −0.12 (m, 1 H). IR: 962 (s) (ν_{WO}), 893 (vs), 742 (s), 692 (s), 692 (s), 506 (s), 482.

Compounds **4d**, **4e**, **4h**, and **4i** were detected by NMR on reaction of the ketone with **1** in C_6D_6. Reaction times were 2 days for **4i**, 1 week for **4d**, and 2 weeks for **4e** and **4h**. Complex **5** was formed in roughly equal amounts in the reaction that forms **4i**.

$W(O)[{=}C(CH{=}CHCH_2CH_2)]Cl_2(PMePh_2)_2$ (4c). 2-Cyclopenten-1-one (0.026 mL) was added to a suspension of **1** (0.30 g) in 12 mL of benzene and stirred for 3 h. The mixture was concentrated to ~2 mL, and 2 mL of Et_2O and 12 mL of pentane were added. The mixture was filtered and dried in vacuo over 16 h, yielding 0.185 g (88%) of yellow powder. Anal. Calcd for $C_{31}H_{32}Cl_2OP_2W$: C, 50.50; H, 4.37. Found: C, 50.70; H, 4.42. IR: 1286, 1097 (s), 953 (vs) (ν_{WO}), 890 (vs), 740 (vs), 694 (vs), 509 (vs), 479.

$W(O)({=}CMe_2)Cl_2(PMePh_2)_2$ (4g). Acetone (0.023 mL) was added to a suspension of **1** (0.33 g) in 10 mL of benzene and the resultant mixture heated to reflux for 5 h. Volatiles were removed by vacuum, and the residue was dissolved in 3 mL of Et_2O. Pentane (12 mL) was added and the mixture filtered, yielding 0.165 g of yellow-brown solids. ^1H

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NMR shows substantial amounts of $W(O)Cl_2(PMePh_2)_3$, and other uncharacterized impurities.

$W(N$-*p*-tolyl$)[{=}C(CH_2)_4]Cl_2(PMePh_2)_2$ (6a). *N*-Cyclopentylidene-*p*-toluidine (0.080 mL) was added to a suspension of **1** (0.51 g) in 12 mL of benzene and the resultant mixture stirred for 2 days. More imine (0.060 mL) was added and stirring was continued with heating to 40 °C for 20 h. Volatiles were pumped away and the resulting solids dissolved in 10 mL of Et_2O. The mixture was concentrated to 1 mL, and 10 mL of pentane was added. The solids were filtered and dried in vacuo for 3 h, yielding 0.18 g (45%) of yellow powder. Anal. Calcd for $C_{38}H_{41}Cl_2NP_2W$: C, 55.09; H, 4.99; N, 1.69. Found: C, 54.92; H, 4.98; N, 1.47. IR: 1349, 1309 (w), 1281 (w), 1191 (w), 1098, 1028 (w), 1016 (w), 1000 (w), 891 (vs), 816, 742 (s), 694 (vs), 517, 505 (s), 485, 441.

$W(N$-*p*-tolyl$)({=}CMe_2)Cl_2(PMePh_2)_2$ (6g). *N*-Isopropylidene-*p*-toluidine (0.075 mL) was added to a suspension of **1** (0.30 g) in 10 mL of benzene and the resultant mixture heated to reflux for 3 h. The mixture was concentrated to 1 mL, and 10 mL of heptane was added. The solids were filtered, yielding 0.135 g of green-grey solids, mostly **6g** by ^1H NMR.

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Synthesis and Structure of the Cationic *tert*-Butoxide Complexes $Y_3(OR)_7Cl(THF)_3^+$, $Y_2(OR)_4Cl(THF)_4^+$, and $Y(OR)Cl(THF)_5^+$: Representatives of a New Class of Yttrium Alkoxides[1]

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Abstract: $Y_3(OR)_7Cl_2(THF)_2$ (**1**) ($R = CMe_3$) reacts with $AgBPh_4$ to form a mixture of $[Y_3(\mu_3\text{-}OR)(\mu_3\text{-}Cl)(\mu\text{-}OR)_3(OR)_3(THF)_3][BPh_4]$ (**2**) and $[Y_2(\mu\text{-}Cl)(\mu\text{-}OR)_2(OR)_2(THF)_4][BPh_4]$ (**3**). At 0 °C the reaction favors **2**, which can be isolated by crystallization from toluene at −37 °C. **2** forms crystals in space group $P\bar{1}$ (C_i^1; No. 2) with $a = 14.131$ (3) Å, $b = 15.035$ (3) Å, $c = 18.712$ (5) Å, $\alpha = 85.01$ (2)°, $\beta = 85.02$ (2)°, $\gamma = 81.75$ (2)°, $V = 3908$ (2) Å^3, and $D_{calcd} = 1.23$ g cm^{-3} for $Z = 2$. Least-squares refinement of the model based on 4692 reflections converged to a final $R_F = 9.1\%$. The three yttrium atoms in **2** form an equilateral triangle with doubly bridging alkoxide groups along the edges and triply bridging alkoxide and chloride ligands above and below the plane of metals. The three terminal alkoxide groups are all on the μ_3-alkoxide side of the plane. At room temperature, the reaction of **1** with $AgBPh_4$ favors **3**, which can be isolated in 74% yield by reaction of the product mixture with $NaBPh_4$. **3** crystallizes from THF/toluene/hexane at −37 °C in space group $P4_2/n$ with $a = 18.424$ (5) Å, $c = 17.738$ (9) Å, $V = 6021$ (4) Å^3, and $D_{calcd} = 1.23$ g cm^{-3} for $Z = 4$. Least-squares refinement of the model based on 1099 reflections converged to a final $R_F = 9.9\%$. In **3**, two $Y(OR)(THF)_2$ units are connected by two alkoxide bridges and one chloride bridge to form a distorted face-shared bioctahedron. The six ligands around each yttrium atom are arranged such that the terminal alkoxide ligand is trans to the bridging chloride ion. **1** reacts with $NaBPh_4$ to form $[Y(OR)(Cl)(THF)_5][BPh_4]$ (**4**), which can be prepared in higher yield (85%) from the reaction of YCl_3 with NaOR and $NaBPh_4$. **4** crystallizes from THF/hexane at −37 °C in space group $P2_1/n$ with $a = 13.675$ (3) Å, $b = 12.418$ (3) Å, $c = 32.803$ (8) Å, $\beta = 90.43$ (2)°, $V = 5570$ (2) Å^3, and $D_{calcd} = 1.22$ g cm^{-3} for $Z = 4$. Least-squares refinement of the model based on 6073 reflections converged to a final $R_F = 8.1\%$. The OR and Cl ligands in **4** are located at the axial positions of a pentagonal bipyramid. The five THF ligands occupy the equatorial sites. **1** can be regenerated from **2** and **3** by reaction with NaCl.

Recent studies of the utility of simple alkoxide ligands as replacements for the $C_5H_5^-$ ion in organometallic complexes of yttrium and the lanthanides have shown that the *tert*-butoxide ligand can provide alkoxide analogues of cyclopentadienylyttrium complexes.[2-4] In addition, a very rich polymetallic chemistry has been revealed, which suggests that these complexes may be interesting vis-à-vis metal oxides. For example, the facile conversion of $Y_3(OR)_7Cl_2(THF)_2$ (**1**) ($R = CMe_3$) to the extended alkoxide oxide $Y_{14}(OR)_{28}Cl_{10}O_2(THF)_4$[4] provides an interesting contrast to traditional ideas of how metal alkoxides transform into metal oxides via sol-gel processes.[5] The chemistry of **1** is of interest not only because of this reaction but also because its terminal chloride ligand is a site of potential reactivity.

We report here the utility of **1** to generate a new class of yttrium alkoxide complexes: cationic yttrium alkoxides. Given the recent interest in the chemistry of yttrium, barium, and copper alkoxides as precursors to mixed-metal oxides such as the superconducting $YBa_2Cu_3O_{7-x}$,[6,7] the existence of this class of cationic complexes provides a new set of alternatives for the synthesis of heteropolymetallic alkoxide compounds. We also describe our observations on the structure and reactivity of these cations, which suggest that this class of alkoxides follows a broader set of generalizations than those developed so far for neutral yttrium alkoxides.[3,4,7b]

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