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Coordination Chemistry Reviews 250 (2006) 976–990

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Review

Photochemical reactions of Group 6 metal carbonyls with alkenes

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Received 8 July 2005; accepted 2 December 2005
Available online 18 January 2006

Contents

Abstract

The aim of this survey article is to bring into focus intriguing areas of Group 6 metal alkene coordination chemistry that have not been extensively surveyed to date. Photochemical reactions of Group 6 transition metal carbonyls with alkenes and the formation of alkene carbonyl complexes of the type: $[M(CO)_5(\eta^2\text{-alkene})]$, $[M(CO)_4(\eta^2\text{-alkene})_2]$, and $[M(CO)_3(\eta^2\text{-alkene})_3]$ are the point of departure. The crystal structures of these compounds together with their spectroscopic characteristics in solution are discussed. An overview of the reactivity and catalytic activity of these compounds is also given. Special attention is given to catalytic reactions that lead to the formation of new carbon–carbon bonds, such as metathesis, ring-opening metathesis polymerization of cyclic olefins (ROMP), and the addition of haloalkanes to the double bond of olefin.

Keywords: Group 6 metals; η^2-Alkene complexes; Photochemistry; Homogeneous catalyst; Organometallic compounds

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doi:10.1016/j.ccr.2005.12.002

1. Introduction

Over the past few decades, considerable attention has been focused on the chemistry of Group 6 metal alkene–carbonyl complexes due to their applications in organometallic and catalytic chemistry [1–64]. η^2-Coordination of alkene to transition metal is the essence of many catalytic processes, such as isomerization [35–38], hydrogenation [15,16,38–44], hydrosilylation [45,46], dimerization [38,47–49], metathesis of acyclic, and metathesis polymerization of cyclic olefins [50–52], and other reactions of alkenes catalyzed by Group 6 metal carbonyls [33,38,51,53,54]. All transition-metal-catalyzed reactions of alkenes involve the formation and rupture of a metal–alkene bond at some stage of the catalytic cycle. The binding of an alkene to a transition metal has the effect of removing electron density from the carbon–carbon double bond. Stronger M–olefin binding yields a more significant increase in hybridization of olefin carbon towards sp^3, and hence a more reactive olefin ligand. As a result, the alkene ligand becomes susceptible to attack by electrophilic and nucleophilic reagents, including carboanion nucleophiles. All Group 6 metal carbonyls have been shown to undergo reactions with alkenes either by thermal substitution of ligands, such as NCMe [55–58], acetone [59,60], THF [61], or CO [62] or, more frequently, by photochemical substitution of carbonyl ligands in hexacarbonyls $M(CO)_6$ [1,4–7,10–12,15–19,22–28,32,33,35–46,51,63]. Group 6 metal carbonyls are the most useful sources for carbonyl–alkene complexes and have been applied in the synthesis of many different alkene complexes and used as catalyst precursors.

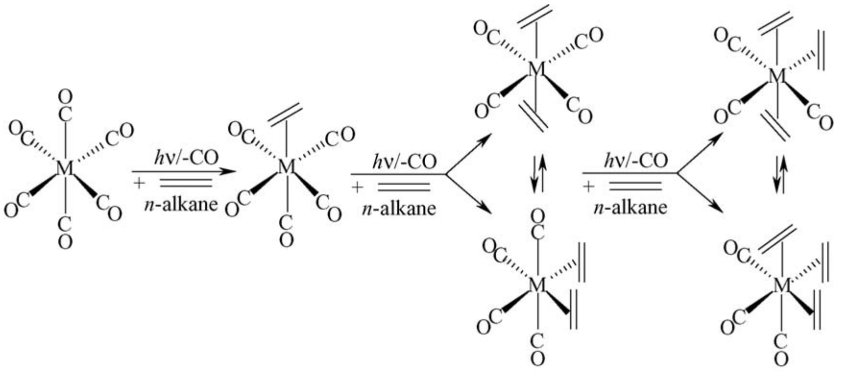
Alkene–carbonyl complexes of the type $[M(CO)_5(\eta^2\text{-alkene})]$ and *trans*-$[M(CO)_4(\eta^2\text{-alkene})_2]$ have been known since 1963, when Stolz et al. observed the substitution of CO ligands by alkene ligands by IR spectroscopy during UV photolysis of *n*-hexane solution of hexacarbonyls $M(CO)_6$ (M = Mo, W) and alkene, such as ethene, propene, butene, and butadiene [1]. Over the years, a number of Group 6 metal carbonyl complexes containing alkene ligands have been reported, including some mixed alkene-diene (bicyclo[2.2.1]hepta-2,5-diene, norbornadiene, NBD) complexes, such as $[M(CO)_3(\eta^2\text{-ethene})(\eta^4\text{-NBD})]$ [12]. Recently a series of new vinylsilane complexes of the type $[W(CO)_5(\eta^2\text{-}H_2C{=}CHSiR_3)]$ and *trans*-$[W(CO)_4(\eta^2\text{-}H_2C{=}CHSiR_3)_2]$ (R = Me, OMe, OCH_2CH_2OMe, and Cl) have been synthesized photochemically, and an interesting effect of substituents at the silyl groups on the structure and reactivity of the η^2-coordinated vinyl group in compounds of tungsten(0) has been observed [63].

2. Photochemical substitution of CO by alkene in $M(CO)_6$ (M = Cr, Mo, W)

2.1. Complexes of the type $[M(CO)_5(\eta^2\text{-alkene})]$

Photolysis of an alkane solution of $M(CO)_6$ and alkene leads first to the formation of a thermally unstable $[M(CO)_5(\eta^2\text{-alkene})]$ complex and on further irradiation to a much more stable *trans*-$[M(CO)_4(\eta^2\text{-alkene})_2]$ complex (Scheme 1).

Even prolonged irradiation of $M(CO)_6$ in the presence of alkene gives a mixture of penta- and tetra-carbonyl compounds. Separation of these two compounds can be achieved due to their different stability. In a slowly evaporated alkane solution, the pentacarbonyl compound decomposes, leaving a stable enough tetracarbonyl species [22,26]. Only in a few cases has it been possible to isolate and fully characterize the pentacarbonylalkene complexes [17,25,33]. The first one to be isolated and stable enough to be handled at room temperature was the *cis*-cyclooctene (*c*-COE) complex $[Cr(CO)_5(\eta^2\text{-}c\text{-COE})]$ [5]; subsequently $[W(CO)_5(\eta^2\text{-}c\text{-COE})]$ [17] and $[W(CO)_5(\eta^2\text{-}(t\text{-COE})]$ (*t*-COE = *trans*-cyclooctene) [25] were also synthesized in pure crystalline form. Recently, the pentacarbonyl complex of bicycloolefin (bicyclo[2.2.1]hepta-2-ene, norbornene, NBE) has been obtained and its separation has been achieved by fractional sublimation in vacuum. During the latter process light yellow crystals of $[W(CO)_5(\eta^2\text{-NBE})]$ were grown, suitable for X-ray analysis [33]. Later, a very labile in solution ethene pentacarbonyl complex of tungsten was synthesized in reaction of $[(\mu\text{-GeCl}_2)\{W(CO)_5\}_2]$ with ethene and its molecular structure determined by single crystal X-ray diffraction studies [64]. The pentacarbonyl complexes of other olefin were characterized mainly in solution by IR (Table 1) and/or ^1H and ^{13}C NMR spectroscopy (Tables 2 and 3). In photochemical reaction of $W(CO)_6$ with vinylsilane, $H_2C{=}CHSiR_3$ (R = Me, OMe, OCH_2CH_2OMe, and Cl), the formation of pentacarbonyl compounds $[W(CO)_5(\eta^2\text{-}H_2C{=}CHSiR_3)]$ was observed by IR and NMR spectroscopy [63].



Scheme 1. Photochemical synthesis of alkene–carbonyl complexes of Group 6 metal.

Table 1
Selected IR data for $[M(CO)_5(\eta^2\text{-alkene})]$ complexes at room temperature unless otherwise indicated

Metal	Olefin	ν(C≡O), cm^{-1} (relative intensity)	Medium	Reference
Cr	Ethene	2078 (w), 1967 (s), 1961.5 (vs)	Pentane	[11]
Mo	Ethene	2086 (w), 1976 (s), ∼1960 (vs)	Pentane	[11]
W	Ethene	2085.5 (w), 1974 (s), 1955.5 (vs)	Pentane	[11]
Mo	Propene	2085 (w), 1969 (ms), 1959 (s)	*n*-Hexane	[1]
W	Propene	2085 (w), 1966 (ms), 1951 (s)	*n*-Hexane	[1]
W	1-Butene	2083 (w), 1965 (vs)	*n*-Hexane[a]	[24]
W	*trans*-2-Butene	2084 (w), 1962 (ms), 1947 (s)	*n*-Hexane	[1]
W	*cis*-2-Butene	2083 (w), 1960 (ms), 1946 (s)	*n*-Hexane	[1]
Cr	1-Pentene	2074 (m), 1957.5 (s), 1951 (sh)	1-Pentene	[5]
W	1-Pentene	2082 (vw), 1965 (s), 1951 (vs)	*n*-Hexane	[22]
W	Cyclopentene	2078 (w), 1957 (s), 1946 (vs)	Methylcyclohexane[b]	[6]
Cr	*cis*-Cyclooctene	2070.5 (m), 1953.5 (s), 1948 (sh)	*n*-Hexane/5% *cis*-cyclooctene	[5]
W	*cis*-Cyclooctene	2078.4 (m), 1959.3 (s), 1946.0 (vs)	*n*-Hexane	[17]
Cr	*trans*-Cyclooctene	2070.5 (m), 1960 (s), 1954.5 (s)	*n*-Hexane	[5]
W	*trans*-Cyclooctene	2079.5 (3.6×10^4), 1999.2 (vw), 1966.1 (2.1×10^5), 1954.3 (10×10^3), 1947.4 (2.2×10^4)	*n*-Hexane	[25]
W	Norbornene	2078 (w), 1951 (vs)	*n*-Heptane	[33]
W	Methyl acrylate	2093 (m), 1986 (s), 1975 (s), 1961 (s)	*n*-Hexane	[4]
W	Dimethyl fumarate	2100 (m), 1999.5 (s), 1987.5 (s), 1979.5 (s), 1972.5 (s)	*n*-Hexane	[4]
W	Trimethylvinylsilane	2083 (w), 1971 (vs), 1950 (vs)	*n*-Heptane	[63]
W	Trichlorovinylsilane	2093 (w), 1967 (vs)	*n*-Heptane	[63]

[a] At 233 K.
[b] At 77 K.

Table 2
^1H NMR data (room temperature, toluene-d_8) for $[M(CO)_5(\eta^2\text{-alkene})]$ complexes

Metal	Olefin, $H^aH^bC{=}CH^cR$	δ (ppm)			$\Delta\delta$ (ppm)			Reference
		H^a	H^b	H^c	H^a	H^b	H^c	
Cr	Ethene*	2.67			2.61			[18]
W	Ethene	2.84			2.44			[27]
W	Propene	2.82	2.94	3.96	2.17	2.00	1.76	[26]
W	1-Butene	2.75	2.89	4.06	2.21	2.01	1.71	[26]
W	Methyl acrylate	3.36	2.66	3.69	2.99	2.69	2.26	[4]
W	Dimethyl fumarate*	4.37			2.49			[4]
W	Trimethylvinylsilane**	3.69	4.14	3.60	1.96	1.76	2.54	[63]
W	Trichlorovinylsilane**	3.54	3.87	3.27	2.71	2.45	2.98	[63]
W	*trans*-Cyclooctene	3.54			2.02			[25]
W	*cis*-Cyclooctene**	4.58			0.98			[17]
W	*cis*-Cyclooctene	3.91			1.65			[25]
W	Norbornene	4.13			1.81			[33]

* In benzene-d_6.
** In $CDCl_3$.

Table 3
Selected ^{13}C NMR data for $[M(CO)_5(\eta^2\text{-alkene})]$ complexes

Metal	Olefin	δ (ppm) ($^1J_{W\text{–}C}$, Hz)				$\Delta\delta$ (ppm)		Solvent (T, K)	Reference
		$H_2C{=}$	$HC{=}$	1CO	4CO	$H_2C{=}$	$HC{=}$		
W	Propene	63.42	85.31	200.71	196.37 (127)	50.4	52.0	Toluene-d_8 (293)	[26]
W	1-Butene	61.47	91.82	200.94 (157)	196.28 (127)	51.9	48.7	Toluene-d_8 (293)	[26]
W	Dimethyl fumarate		58.0	202.9	196.3		75.5	Benzene-d_6 (298)	[4]
W	Trimethylvinylsilane	66.94	73.96	199.82 (149)	195.24 (126)	63.9	63.3	$CDCl_3$ (298)	[63]
W	Trichlorovinylsilane	56.57	54.51	199.32 (141)	193.33 (124)	82.7	74.5	$CDCl_3$ (298)	[63]
Cr	*trans*-Cyclooctene		87.9	224.6	217.1		46.0	Toluene-d_8 (273)	[5]
Cr	*cis*-Cyclooctene		90.9	224.7	216.5		39.4	Toluene-d_8 (213)	[5]
W	*trans*-Cyclooctene		83.9	201.71	196.9		50.0	Toluene-d_8 (r.t.)	[25]
W	*cis*-Cyclooctene		88.0	201.3	197.4		42.3	Toluene-d_8 (r.t.)	[25]
W	*cis*-Cyclooctene		86.33	201.94	196.9		44.0	Cyclohexane-d_{12} (r.t.)	[17]
W	Norbornene		87.95	199.99 (155)	196.88 (126)		47.2	Toluene-d_8 (263)	[33]

Table 4
Selected IR data for *cis*-[$M(CO)_4(\eta^2\text{-alkene})_2$] and [$M(CO)_4(\eta^4\text{-diene})$] complexes

Metal	Olefin	ν(C≡O), cm^{-1} (relative intensity)	Medium	*T* (K)	Reference
Cr	Ethene	2036.8, 1954.3, 1949.3, 1913.4	Liquid Xe	195	[7]
Mo	Ethene	2050, 1958, 1914	Liquid Xe	195	[7]
W	Ethene	2050, 1957, 1910	Liquid Xe	195	[7]
W	Propene	2042 (1), 1900 (2)[a]	*n*-Hexane	213	[24]
W	1-Butene	2041 (1), 1901 (1.5)[a]	*n*-Hexane	263	[24]
W	1-Pentene	2052.5 (w), 1949.3 (m), 1942.1 (m), 1897.7 (m)	Ar	16	[23]
W	Cyclopentene	2036 (1), 1955 (s), 1945 (vs), 1891 (1.6)	*n*-Pentane/4% cyclopentene	203	[24]
W	*trans*-Cyclooctene	2037 (s), 1950 (s), 1934 (vs), 1930 (m, sh), 1914 (w), 1894 (m)	*n*-Hexane	r.t.	[25]
Cr	2,4-Hexadiene	2035 (m), 1962 (m), 1942 (s), 1927 (s)	*n*-Pentane	r.t.	[40]
W	1,4-Ph_2-1,3-BD[b]	2030, 1972, 1946, 1932	Toluene	r.t.	[72]
Mo	1,5-Cyclooctadiene	2032, 1950, 1906	*n*-Hexane	r.t.	[69]
W	1,5-Cyclooctadiene	2043 (s), 1952 (vs), 1907 (vs)	Cyclohexane	r.t.	[55]
Cr	Norbornadiene	2030.2, 1955.7, 1944.2, 1913.2	*n*-Hexane	r.t.	[41]
Mo	Norbornadiene	2044.0, 1959.4, 1914.2	*n*-Hexane	r.t.	[41]
W	Norbornadiene	2042.0, 1956.0, 1909.2	*n*-Hexane	r.t.	[41]

[a] Only two external bands were detected, other bands obscured.
[b] *trans*,*trans*-1,4-Diphenyl-1,3-butadiene.

2.2. Synthesis of [$M(CO)_4(\eta^2\text{-alkene})_2$] complexes

As was predicted by theoretical studies and observed in all photochemical substitution reactions of CO by alkene ligands, the thermodynamically most stable bis(alkene) compounds contain two mutually *trans* alkene ligands [1–14,16–34,63]. However, in 1985 Pope and Wrighton observed that UV photolysis of [$M(CO)_5(\eta^2\text{-alkene})$] isolated in a methylcyclohexane matrix at 77 K resulted in the loss of the CO ligand that was *cis* to the alkene ligand [6]. That experiment showed that further replacement of alkene should afford the *cis*-[$W(CO)_4(\eta^2\text{-alkene})_2$] complex, the product predicted under kinetic control. Accordingly, *cis*-bis(alkene) complexes have been observed only at low temperatures [6,7,23,24,26] or as transient species in the gas phase [20] (Table 4). Thus, UV photolysis of a liquid xenon solution of Group 6 metal hexacarbonyls in the presence of ethene at 195 K has been shown to result in the formation of *cis*-[$M(CO)_4(\eta^2\text{-ethene})_2$], along with the *trans* isomer [7]. The *cis* isomer of the bis(ethene) complex of tungsten has also been detected using time-resolved infrared absorption techniques following pulsed laser photolysis of the respective hexacarbonyl in the presence of ethene [20]. Later, the *cis*-[$W(CO)_4(\eta^2\text{-ethene})_2$] complex was detected by IR at room temperature and observed by ^1H NMR spectroscopy down from 290 K [27] (Table 5). However, other *cis*-bis(alkene) complexes are more unstable, and their observation has been possible in an argon matrix or in low-temperature alkane solution as a result of photochemical isomerization of the *trans*-bis(alkene) complex [23,24]. During broad-band photolysis, *cis*-to-*trans* isomerization takes place, precluding isolation of the *cis*-bis(alkene) complex. That is probably the reason why only *trans*-[$W(CO)_4(\eta^2\text{-NBE})_2$] has been isolated in photochemical reaction of $W(CO)_6$ in the presence of norbornene and the *cis*-bis(norbornene) complex has

Table 5
Selected ^1H NMR data for *cis*-[$M(CO)_4(\eta^2\text{-alkene})_2$] and [$M(CO)_4(\eta^4\text{-diene})$] complexes

Metal	Olefin $H^aH^bC{=}CH^cR$	δ (ppm)			$\Delta\delta$ (ppm)			Solvent (*T*, K)	Reference
		H^a	H^b	H^c	H^a	H^b	H^c		
W	Ethene	2.39			2.89			Toluene-d_8 (293)	[27]
W	Propene*	2.82	1.46	3.47	2.17	3.48	2.25	Toluene-d_8 (263)	[26]
		2.74	2.00	3.25	2.25	2.94	2.47		
W	1-Butene*	2.75	1.39	3.63	2.21	3.51	2.14	Toluene-d_8 (263)	[26]
		2.69	1.97	3.40	2.27	2.93	2.37		
W	1,4-Ph_2-1,3-BD**	5.85, 3.56			1.17, 3.11			CD_2Cl_2 (293)	[72]
W	*trans*-Cyclooctene*	3.47			2.09			Benzene-d_6	[25]
		3.42			2.14				
W	1,5-Cyclooctadiene	4.45			1.11			CS_2	[55]
Mo	Norbornadiene	5.00			1.65			$CDCl_3$	[49]
W	Norbornadiene	4.63			2.02			CS_2	[55]

* Two isomers.
** *trans*,*trans*-1,4-Diphenyl-1,3-butadiene.

Table 6
Selected ^{13}C NMR data for *cis*-$[M(CO)_4(\eta^2\text{-alkene})_2]$ and $[M(CO)_4(\eta^4\text{-diene})]$ complexes

Metal	Olefin	δ (ppm) ($^1J_{W-C}$, Hz)			$\Delta\delta$ (ppm)	Solvent (T, K)	Reference
		HC=	2CO	2CO	HC=		
W	*trans*-Cyclooctene[a]	81.63	206.83	201.55	52.3	Toluene-d_8 (253)	[25]
		86.69	208.28	204.95	47.8		
W	1,4-Ph_2-1,3-BD[b]	78.67, 72.32	210.93	203.26, 202.09	53.8, 56.5	CD_2Cl_2 (233)	[72]
Mo	1,5-Cyclooctadiene	94.4	216.5	216.4	34.7	Toluene-d_8	[69]
W	1,5-Cyclooctadiene	87.56	207.87 (117)	207.70 (162)	41.3	$CDCl_3$ (298)	[70]
Cr	Norbornadiene	74.7	228.6	225.5	68.5	$CDCl_3$	[41]
Mo	Norbornadiene	78.5	217.7	213.8	64.7	$CDCl_3$	[41]
W	Norbornadiene	68.9	209.3	203.3	74.3	$CDCl_3$	[41]
W	Norbornadiene	68.78	209.74 (118)	204.31 (163)	74.4	Toluene-d_8 (298)	[12]

[a] Two isomers.
[b] *trans*,*trans*-1,4-Diphenyl-1,3-butadiene.

never been observed [33]. In 1999 Grevels et al. described an unusual thermal synthesis of *cis*-$[W(CO)_4(\eta^2\text{-}(trans\text{-cyclooctene})_2]$ starting from $[W(CO)_5(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)]$ or $[W(CO)_4(\eta^4\text{-}trans,trans\text{-}PhCH{=}CHCH{=}CHPh)]$ [25]. This was the first example of a *cis*-bis(alkene) complex whose structure has been fully characterized in solution by IR, ^{1}H, and ^{13}C NMR spectroscopy (Tables 4–6). A very good model of *cis*-bis(alkene)tetracarbonyl complexes is provided by diene complexes. Many octahedral diene-tetracarbonyl complexes containing such chelating ligands as norbornadiene [12,39–44,55,65–68], 1,5-cyclooctadiene (1,5-COD) [55,69,70], 1,3-butadiene [71], 1,3-pentadiene [71], and 1,4-diphenyl-1,3-butadiene [72] are known, and their photoreactivity has been investigated. Recently, the first octahedral tetra(carbonyl) complex containing dimethylfurane as an η^4-chelating ligand has been synthesized [73]. The compound, $[W(CO)_4(\eta^4\text{-}Me_2Fur)]$ (Me_2Fur = 2,5-dimethylfuran), was obtained in photochemical reaction of $[W(CO)_5(\eta^1\text{-}Me_2Fur)]$, in which dissociation of CO ligands is followed by η^1-to-η^4 rearrangement of the Me_2Fur ligand [73].

Although metal carbonyl derivatives have been demonstrated to readily lose carbonyl ligands upon photolysis, Platbrood and Wilputte-Steinert observed that during the photolysis of $[Cr(CO)_4(\eta^4\text{-NBD})]$ the primary photochemical process involves a metal–olefin bond rupture [39,40].

2.3. *Formation of $[M(CO)_3(\eta^2\text{-alkene})_3]$ complexes*

Octahedral tris(olefin)-tri(carbonyl) complexes are rather unstable, and for that reason the first such compounds were prepared in photochemical reaction of a chelating diene complex, $[W(CO)_4((\eta^4\text{-NBD})]$, with ethene or *cis*-cyclooctene [12]. The first two tri(carbonyl) compounds were isolated and their investigation revealed a *mer* configuration of the carbonyl ligands (Tables 7–10). Later, during the irradiation of *trans*-$[W(CO)_4(\eta^2\text{-alkene})_2]$ complexes (alkene = propene, 1-butene, cyclopentene) at low temperature (123–263 K) in an alkane solution containing ca. 5% of alkene, the formation of *mer* as well as *fac* isomers of tri(carbonyl) compounds was detected by IR spectroscopy [24] (Table 7). The very unstable *fac* isomer transforms

Table 7
Selected IR data for *mer* and *fac*-$[M(CO)_3(\eta^2\text{-alkene})_3]$ complexes

Configuration	Metal	Olefin	ν(C≡O), cm^{-1} (relative intensity)	Medium	T (K)	Reference
mer	W	Propene	2020 (1), 1938 (5.2), 1928 (3)	*n*-Hexane/propene	203	[24]
mer	W	Cyclopentene	2020 (vw), 1928 (s)	*n*-Pentane/4% cyclopentene	203	[24]
mer	Mo	Norbornadiene, ethene	2026.1, 1954, 1943.3	Liquid Xe	182	[16]
mer	W	Norbornadiene, ethene	2028 (w), 1951.5 (vs,br)	*n*-Hexane	r.t.	[12]
mer	W	Norbornadiene, *cis*-cyclooctene	2019.5 (w), 1942.5 (s), 1932.5 (m)	*n*-Hexane	r.t.	[12]
mer	Mo	η^4-Norbornadiene, η^2-norbornadiene	2014.5, 1938.1, 1932.0	*n*-Heptane	r.t.	[16]
mer	W	η^4-Norbornadiene, η^2-norbornadiene	2017.5, 1943.7, 1933.4	*n*-Heptane	r.t.	[16]
mer	W	η^4-Norbornadiene, η^2-norbornene	2014.5, 1938, 1931	*n*-Heptane	r.t.	[16]
fac	W	Propene	1974 (1), 1909 (0.9), 1873 (0.9)	*n*-Hexane	203	[24]
fac	W	Cyclopentene	1966 (1), 1909, 1863 (1)	*n*-Pentane/4% cyclopentene	203	[24]
fac	W	Norbornadiene, ethene	1992, 1929, 1887	Ar/ethene	12	[16]
fac	Cr	η^4-Norbornadiene, η^2-norbornadiene	1990, 1930, 1885	Liquid Xe	182	[16]
fac	Mo	Norbornadiene, ethene	1988.1 1920.1, 1891.2	Liquid Xe	182	[16]
fac	W	η^4-Norbornadiene, η^2-norbornadiene	1993.6, 1926.5, 1900.2	*n*-Heptane	r.t.	[16]
fac	Mo	*trans*-Cyclooctene, iprop-dab[a]	1958.0 (vs), ~1956 (sh), 1893.4 (m), 1886.4 (m), 1854.7 (s), ~1850 (sh)	*n*-Hexane/5% *trans*-cyclooctene	r.t.	[28]
fac	W	*trans*-Cyclooctene, iprop-dab[a]	1963.0 (vs), 1899.2 (m), 1859.4 (s)	Cyclohexane	r.t.	[28]

[a] 1,4-Diisopropyl-1,4-diazabuta-1,3-diene.

Table 8
Selected ^{1}H NMR data (room temperature, toluene-d$_8$) for *mer* and *fac*-[W(CO)$_3$(η^2-alkene)$_3$] complexes

Configuration	Olefin	δ, ppm	$\Delta\delta$, ppm	Reference
mer	One ethene	2.73	2.55	[27]
	Two ethenes	1.56	3.52	
mer	Norbornadiene	4.10, 2.88	2.55, 3.72	[12]
	Ethene	1.55	3.73	
mer	Norbornadiene	4.08, 2.93	2.57, 3.72	[12]
	cis-Cyclooctene	1.90	3.66	
fac	Ethene[a]	2.45	2.83	[27]
fac	*trans*-Cyclooctene[b]	3.05	2.45	[28]
	iprop-dab[c]			

[a] At 213 K.
[b] At 300 K.
[c] 1,4-Diisopropyl-1,4-diazabuta-1,3-diene.

into the more stable *mer* isomer. Similar photoreactivity was revealed by the *trans*-[W(CO)$_4$(η^2-ethene)$_2$] compound. However, in that case, ^{1}H NMR spectroscopy was used for identification of the tris(ethene)tri(carbonyl) species [27] (Table 8). During the photolysis of W(CO)$_6$ or *trans*-[W(CO)$_4$(η^2-ethene)$_2$] in an ethene-saturated toluene-d$_8$ solution at ca. 200 K, ^{1}H resonances originating in bis(ethene) and tris(ethene) derivatives were observed (Table 8). Raising the temperature of the solution causes the ^{1}H signals of *fac*-tris(ethene) to decay very fast, while *mer*-tris(ethene) species can be observed much longer and even at room temperature [27]. Recently, during the photolysis of [M(CO)$_4$(iprop-dab)] (M = W, Mo; iprop-dab = 1,4-diisopropyl-1,4-diazabuta-1,3-diene) in the presence of *trans*-cyclooctene, *fac*-tricarbonyl compounds of the type [M(CO)$_3$(iprop-dab)(η^2-*t*-COE)] were isolated, more stable than compounds obtained before [28].

3. Structural characterization and spectroscopic properties of alkene–carbonyl complexes

In recent years, many Group 6 metal–olefin complexes have been prepared and considerable insights have been gained into the metal-olefin geometry from X-ray structure analysis, spectral investigations, and theoretical studies.

3.1. X-ray crystallography

The molecular structure of three pentacarbonyl compounds containing cycloolefin ligands (*cis*-cyclooctene, *trans*-cyclooctene, and norbornene) has been established by single-crystal X-ray diffraction studies [17,25,33]. All three compounds represent distorted octahedral arrangement of the ligands around the tungsten atom. The C–W–C angles in the *trans*-W(CO)$_2$ units are 178.3° and 173.4° in the norbornene complex [33] and the *cis*-cyclooctene complex [17], while for the *trans*-cyclooctene complex these angles are 177.0° and 175.4°. As has been proved by the calculation of torsion angles, the C=C bond of the norbornene ligand is staggered with the respective CO–W–CO axes of an almost square-planar W(CO)$_4$ moiety (Scheme 2).

A similar staggered orientation of the alkene ligand has been observed for [W(CO)$_5$(η^2-*c*-COE)] [17], while the theoretically predicted [21,31] eclipsed structure has been found for [W(CO)$_5$(η^2-*t*-COE)] [25] and [W(CO)$_5$(η^2-ethene)] [64]. The W–CO bond length falls in the range of 1.96(1)–2.08(2) Å, but the shorter W–CO bond distance, in the range of 1.96(1)–2.01(1) Å, is always observed for CO in the *trans* position to the olefin ligand (Table 10).

X-ray crystallographic studies performed on *trans*-[M(CO)$_4$(η^2-alkene)$_2$] (alkene = methyl acrylate, ethene, *cis*- and *trans*-cyclooctene) complexes indicate that in these

Table 9
Selected ^{13}C NMR data (toluene-d$_8$) for *mer* and *fac*-[M(CO)$_3$(η^2-alkene)$_3$] complexes

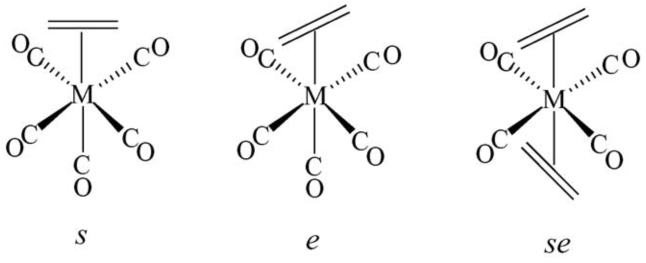
Configuration	Metal	Olefin	δ (ppm) ($^1J_{\text{W–C}}$, Hz)		$\Delta\delta$ (ppm)	T (K)	Reference
			HC=	CO	HC=		
mer	W	η^4-Norbornadiene	72.43, 37.98[a]	209.75, 1CO[a]	70.7, 105.4	353	[12]
		η^2-Ethene	32.09[a]	204.60, 2CO	91.2		
mer	W	η^4-Norbornadiene	76.26, 39.74[a]	213.52, 1CO (157)[a]	66.9, 103.5	363	[12]
		η^2-*cis*-Cyclooctene	56.58[a]	204.60, 2CO (137/124)	73.8		
mer	W	η^4-Norbornadiene	79.08, 44.74[a]	212.32, 1CO[a]	64.1, 98.5	243	[16]
		η^2-Norbornadiene	65.56	204.80, 2CO	77.6		
mer	W	η^4-Norbornadiene	78.65, 44.28[a]	213.29, 1CO[a]	64.5, 98.9	243	[16]
		η^2-Norbornene	61.76[a]	205.07, 2CO	73.4		
fac	Mo	η^2-*trans*-Cyclooctene	81.96	230.78, 1CO	43.4	300	[28]
		iprop-dab[b]		228.63, 1CO 216.42, 1CO[a]			
fac	W	η^2-*trans*-Cyclooctene	91.51	224.10, 1CO (147)	51.9	300	[28]
		iprop-dab[b]		223.86, 1CO (150) 213.16, 1CO (149)[a]			

[a] *trans* to C=C.
[b] 1,4-Diisopropyl-1,4-diazabuta-1,3-diene.

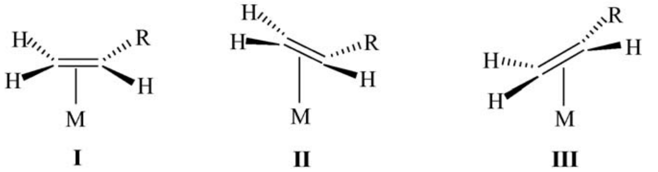
Table 10
Selected structural data for the octahedral alkene–carbonyl complexes

Compound	Space group	Bond lengths (Å)						Bond angles (°)	Reference
		M—(C=C)	C=C	M—CO *trans* to C=C	C≡O *trans* to C=C	M—CO *cis* to C=C	C≡O *cis* to C=C	*trans*-OC—M—CO	
[W(CO)$_5$(η^2-*c*-COE)]	$P2_1/c$ (No. 14)	2.49(1) 2.51(1)	1.38(2)	1.96(1)	1.16(1)	2.02(1) 2.01(1) 2.00(1) 1.97(1)	1.15(1) 1.16(1) 1.17(1) 1.20(1)	178.3(5) 173.4(4)	[17]
[W(CO)$_5$(η^2-*t*-COE)]	$P2_1/c$ (No. 14)	2.451(5) 2.425(4)	1.384(2)	2.011(5)	1.150(6)	2.047(5) 2.069(5) 2.050(5) 2.031(4)	1.141(6) 1.136(6) 1.134(6) 1.148(6)	177.0(2) 175.4(2)	[25]
[W(CO)$_5$(η^2-NBE)]	$P1$ (No. 2)	2.497(16) 2.510(15)	1.37(3)	1.983(14)	1.164(19)	2.049(16) 2.077(19) 2.042(19) 2.071(19)	1.14(2) 1.14(2) 1.14(2) 1.12(2)	178.3(7) 173.4(6)	[33]
[W(CO)$_5$(η^2-ethene)]	$P2_1/c$	2.434(6) 2.420(6)	1.339(9)	2.007(6)	1.146(7)	2.042(6) 2.044(5) 2.044(6) 2.049(5)	1.150(7) 1.141(6) 1.145(7) 1.150(7)	174.9(2) 173.4(2)	[64]
[W(CO)$_4$(η^4-NBD)]	$P2_1/c$	2.409(5) 2.403(6) 2.419(5) 2.412(6)	1.380(8) 1.399(8)	2.006(5) 1.971(6)	1.124(7) 1.185(8)	2.032(5) 2.045(5)	1.143(7) 1.139(7)	167.6(2)	[12]
[Mo(CO)$_4$(η^4-1,5-COD)]	$Pbca$	2.476(6) 2.497(6) 2.462(6) 2.496(6)	1.360(8) 1.348(8)	1.952(6) 1.954(6)	1.166(8) 1.156(7)	2.030(7) 2.032(6)	1.151(9) 1.156(7)	165.4(2)	[69]
[W(CO)$_4$(η^4-1,5-COD)]	$P2_1/c$ (No. 14)	2.424(5) 2.443(4) 2.445(5) 2.436(5)	1.386(7) 1.391(7)	1.986(5) 1.978(5)	1.147(6) 1.146(6)	2.044(5) 2.048(5)	1.139(6) 1.145(6)	166.5(2)	[70]
fac-[W(CO)$_3$(η^2-*t*-COE)(iprop-dab)][a]	$Pna2_1$ (No. 33)	2.402(8) 2.406(8)	1.35(1)	1.973(7)		1.95(2) 1.99(2)			[28]
trans-[W(CO)$_4$(η^2-*c*-COE)$_2$]	$P2_1/c$ (No. 14)	2.36(1) 2.38(1)	1.39(1)			2.03(1) 2.01(1) 2.04(1) 2.03(1)	1.14(1) 1.15(1) 1.16(1) 1.14(1)	174.8(3) 173.9(3)	[17]
trans-[W(CO)$_4$(η^2-*t*-COE)$_2$]	$C2/c$ (No. 15)	2.328(3) 2.327(3)	1.39(1)			2.026(5) 2.049(4)	1.150(6) 1.134(6)	176.6(1) 176.2(1)	[25]
trans-[W(CO)$_4$(η^2-ethene)$_2$]	$Aba2$	2.315(9) 2.299(9)	1.413(13)			2.033(10) 2.045(9)	1.151(11) 1.142(10)	171.8(7)	[27]
trans-[W(CO)$_4$(η^2-methyl acrylate)$_2$]	$Pbca$	2.292(8) 2.310(7) 2.306(9) 2.292(9)	1.416(11) 1.396(13)			2.062(9) 2.043(10) 2.039(8) 2.034(8)	1.128(11) 1.170(11) 1.170(10) 1.149(11)	172.5(3)	[4]
mer-[W(CO)$_3$(η^2-ethene)(η^4-NBD)]	$P2_1/n$	2.303(7) 2.303(6) 2.306(8) 2.228(8) 2.405(7) 2.404(7)	1.39(1) 1.41(1) 1.48(1)	2.033(7)	1.13(1)	2.014(7) 2.045(7)	1.158(9) 1.14(1)	171.6(3)	[12]

[a] 1,4-Diisopropyl-1,4-diazabuta-1,3-diene.



Scheme 2. Staggered (s), eclipsed (e), and staggered-eclipsed (se) orientation of olefin C=C bonds in penta- and tetracarbonyl alkene complexes.



Scheme 3. Deviations (**II**) and (**III**) from ideal symmetrical (**I**) η^2-coordination of monosubstituted olefin to the transition metal atom.

complexes the two *trans* oriented alkene ligands are mutually staggered, but each eclipses one of the OC–M–CO vectors [4,17,25,27] (Scheme 2). A similar orientation of two mutually *trans* olefin bonds has been found for the X-ray-analyzed compound *mer*-[W(CO)$_3$)(η^2-ethene)(η^4-NBD)] [12]. A *fac*-tricarbonyl orientation was detected by X-ray diffraction studies for only one compound containing 1,4-diisopropyl-1,4-diazabuta-1,3-diene and a *trans*-cyclooctene ligand, [W(CO)$_3$(η^2-*t*-COE)(iprop-dab)] [28]. In this compound, the η^2-*t*-COE ligand takes up a position *trans* to the CO group and *cis* to the two N atoms, with its C=C bond eclipsed to one of the N–W–CO vectors.

In all X-ray-investigated alkene complexes, both the C=C and the W–C bond lengths are in the normal range observed for related carbonyl complexes containing the η^2-alkene ligand (Table 10). However, the M–C(olefin) bond lengths in the *trans* position to carbonyl ligands are ca. 0.1 Å longer than in the position *trans* to another olefin. The same effect is observed for *mer*-[W(CO)$_3$(η^2-ethene)(η^4-NBD)] [12], where the position of an ethene ligand is *trans* to one of the olefin bonds of the NBD ligand. The C=C bonds of the coordinated alkene molecules are ca. 0.1 Å longer compared with the free molecule. The longest C=C bond, 1.48(1) Å, was detected for η^2-ethene in the *mer*-[W(CO)$_3$(η^2-ethene)(η^4-NBD)] complex [12] (Table 10).

The experimental bond lengths detected by X-ray analysis are in excellent agreement with the degree of electron back-donation from the dπ orbitals of metal with a d^6 electronic configuration to the π-acceptor ligands. Hence, the alkene ligands have poorer π-acid properties than CO; the coordination of the alkene ligand *trans* to the CO ligand leads to an increase in dative overlap of a filled dπ metal orbital with an empty pπ^* orbital of the C≡O bond. As a result the M–C(carbonyl) bond becomes shorter and the C≡O bond becomes longer (Table 10). For the same reason two mutually *trans* alkene ligands are closer to the tungsten atom than in compounds in which alkene ligands compete with carbonyl ligands for the dπ orbitals of the metal atom. The olefin ligands in *trans*-bis(alkene) complexes with strong M–C(olefin) bonds and high amounts of back-bonding can be thought of as metallacyclopropane with sp^3-hybridized olefin carbons [3]. A similar conclusion can be drawn from IR and NMR data (*vide infra*).

Monosubstituted olefins are bonded to the metal atom asymmetrically with the deviation degree depending on the substituents at the olefin carbon (Scheme 3). For a bis(methyl acrylate) complex of tungsten this asymmetry leads to the M–CH bond being 0.018 and 0.014 Å longer than the M–CH$_2$ bond [4]. It should be noted that asymmetrical η^2-coordination of vinyl ligands was theoretically predicted more than 20 years ago [3] and then experimentally observed for vinylsilane, vinylamine, and vinyl ether complexes [4,63,74,75].

3.2. IR spectroscopy

In agreement with the Cotton and Kraihanzel analysis of phosphine-substituted Group 6 metal carbonyls [76], the infrared spectra of the [M(CO)$_5$L] molecules with a local $C_{4\mathrm{v}}$ symmetry in the C≡O stretching region are characterized by three absorptions (two A_1 and one E) of weak, very strong, and strong intensity. In all IR spectra of pentacarbonylalkene compounds, the CO stretching vibration patterns are almost identical with respect to frequencies as well as relative intensities and in an agreement with a local $C_{4\mathrm{v}}$ symmetry of the M(CO)$_5$ moiety. The appearance of five ν(C≡O) absorptions, instead of typical three-band pattern reflects the reduction in symmetry to $C_{2\mathrm{v}}$ ($3A_1$, B_1, B_2) [25] (Table 1).

For *cis*-[M(CO)$_4$(η^2-alkene)$_2$] with a local $C_{2\mathrm{v}}$ symmetry, four ν(C≡O) stretching fundamentals should be infrared-active: $A_1^{(1)}$, $A_1^{(2)}$, B_1, and B_2. However, the *cis*-bis(alkene) complexes have mostly been identified as intermediate species at low temperatures [6,7,11,23,24,26,27] or in the gas phase [20]. The only compound stable enough to be isolated is *cis*-[W(CO)$_4$(η^2-*c*-COE)$_2$] [25]. Its IR spectrum is very close to those of chelating η^4-diene compounds (Table 4).

In accord with their local $D_{2\mathrm{d}}$ symmetry, *trans*-[M(CO)$_4$(η^2-alkene)$_2$] complexes show a strong band due to the single allowed E_u vibration alongside one or two very weak bands. These weak bands have been attributed to the Raman active $A_{1\mathrm{g}}$ and $B_{1\mathrm{g}}$ modes and to ^{13}C bands [14,74] (Table 11). The strong E_u band has been observed in the region between 2031.5 cm^{-1} for dimethyl fumarate [4] and 1928 cm^{-1} for *trans*-3-hexene [22]. The W–C–O deformation mode has been found between 600 and 560 cm^{-1}. The weak bands in the region 1300–1200 cm^{-1} can be assigned as the ν(C=C) stretching vibration, whose wavenumber is ca. 300 cm^{-1} lower than that observed for uncoordinated alkene [14,22,63]. This suggests substantial weakening of the olefinic bond due to rehybridization towards sp^3.

The *fac* structure of the W(CO)$_3$ moiety should give rise to three bands of nearly equal intensities, while for the *mer* geometry three bands of weak, strong, and medium intensity have been detected by IR spectroscopy (Table 7).

Table 11
Selected IR data for *trans*-$[M(CO)_4(\eta^2\text{-alkene})_2]$ complexes at room temperature

Metal	Alkene	ν(C≡O), cm^{-1} (relative intensity)	Medium	Reference
Cr	Ethene	1986 (vw), 1952.5 (vs)	*n*-Hexane	[11]
Mo	Ethene	1997.5 (vw), 1965 (vs)	*n*-Hexane	[11]
W	Ethene	1991 (vw), 1965 (vs)	*n*-Hexane	[11]
Mo	Propene	1952	*n*-Hexane	[1]
W	Propene	2058 (vvw), 1990 (w), 1954 (vs), 1928 (w), 1917 (w)	*n*-Hexane	[26]
W	1-Butene	2058 (vvw), 1990 (w), 1952 (vs), 1928 (w), 1919 (w)	*n*-Hexane	[26]
W	*cis*-2-Butene	1943	*n*-Hexane	[1]
W	1-Pentene	2056 (vw), 1986 (w), 1932 (vs)	KBr pellet	[22]
W	1-Hexene	2056 (vw), 1987 (w), 1936 (vs)	KBr pellet	[22]
W	*trans*-3-Hexene	2046 (vw), 1978 (w), 1928 (vs), 1916 (s)	KBr pellet	[22]
W	Cyclopentene	2047 (1), 1980 (3.6), 1936 (24), 1916 (1.9), 1907 (1.7)	*n*-Pentane	[24]
W	Cyclohexene	2042 (vw), 1966 (w), 1926 (vs)	KBr pellet	[22]
Cr	*trans*-Cyclooctene	2024 (vw), 1973 (vw), 1937 (s), 1908 (w)	*n*-Hexane	[5]
W	*trans*-Cyclooctene	1983.8 (vw), 1949.9 (3×10^4)	*n*-Hexane	[25]
W	*cis*-Cyclooctene	1939.7	*n*-Hexane	[17]
W	Norbornene	1940 (vs)	*n*-Heptane	[33]
Mo	Methyl acrylate[a]	2089.5 (w), 2043 (m), ~1997 (s), ~1994 (w)	*n*-Hexane	[4]
W	Methyl acrylate[a]	2092 (w), 1939.7 (m), ~1997 (s), 1992 (w)	*n*-Hexane	[4]
W	Dimethyl fumarate	2055 (w), 2031.5 (s), 2020 (w)	*n*-Hexane	[4]
W	Trimethylvinylsilane[a]	2062 (vvw), 2018 (vvw), 1995 (w), 1962 (vs)	*n*-Heptane	[63]
W	Trichlorovinylsilane[a]	2066 (vvw), 2031 (w), 2000 (vs)	*n*-Heptane	[63]

[a] One of the isomers.

3.3. ^{1}H and ^{13}C NMR spectroscopy

3.3.1. Structures of $[M(CO)_5(\eta^2\text{-alkene})]$, $[M(CO)_4(\eta^2\text{-alkene})_2]$, and $[M(CO)_3(\eta^2\text{-alkene})_3]$ complexes observed in solution by NMR studies

The η^2-coordination of alkene is confirmed by the observation of coordination shifts of olefin protons and carbons signals, $\Delta\delta = \delta$ (free alkene) − δ (coordinated alkene). Comparing the NMR data (Tables 2, 5, 8 and 12—^{1}H; Tables 3, 6, 9 and 13—^{13}C) for alkene compounds, one can see a relationship between the $\Delta\delta$ coordination shifts and the strength of interaction between the olefin ligand and the metal center. This correlation nicely illustrates the degree of back-donation from the dπ metal orbital to an empty pπ* orbital of the C≡O bond. However, it must be remembered that $\Delta\delta$ sometimes depends very strongly on temperature and the solvent. With toluene-d$_8$ as solvent, the chemical shifts of most proton signals due to the alkene ligands move to lower field as the temperature increases in the range from 190 to 295 K [4,22,26,27,33]. However, the temperature-dependent olefin proton signal changes are

Table 12
^{1}H NMR data (room temperature, toluene-d$_8$) for only one isomer of the *trans*-$[M(CO)_4(\eta^2\text{-alkene})_2]$ compound

Metal	Olefin $H^aH^bC{=}CH^cR$	δ (ppm)			$\Delta\delta$ (ppm)			Reference
		H^a	H^b	H^c	H^a	H^b	H^c	
Cr	Ethene	2.27			3.01			[11]
Mo	Ethene	2.33			2.95			[11]
W	Ethene	2.11			3.17			[11]
W	Propene	2.00	2.33	2.94	2.99	2.61	2.78	[26]
W	1-Butene	1.93	2.28	2.98	3.03	2.62	2.79	[26]
W	1-Pentene	2.31	1.96	2.99	2.59	2.90	2.68	[22]
W	1-Hexene	2.32	1.97	3.00	2.62	2.91	2.68	[22]
W	1-Heptene	2.33	1.99	3.04	2.56	2.85	3.04	[22]
Mo	Methyl acrylate	2.91	2.31	3.27	3.44	3.04	2.68	[4]
W	Methyl acrylate	2.65	1.99	3.07	3.70	3.36	2.88	[4]
W	Dimethyl fumarate*	3.74			3.12			[4]
W	Trimethylvinylsilane	2.28	2.73	1.80	3.18	3.37	4.34	[63]
W	Cyclopentene	3.53			2.14			[22]
W	Cyclohexene	3.41			2.20			[22]
W	Cycloheptene	3.10			2.41			[22]
W	*trans*-Cyclooctene	2.64			2.92			[25]
W	*cis*-Cyclooctene	3.14			2.42			[17]
W	Norbornene	3.07			2.87			[33]

* In benzene-d$_6$.

Table 13
Selected ^{13}C NMR data for one of the isomers of the *trans*-$[M(CO)_4(\eta^2\text{-alkene})_2]$

Metal	Olefin	δ (ppm)			$\Delta\delta$ (ppm)		Solvent	T (K)	Reference
		$H_2C{=}$	$HC{=}$	CO ($^1J_{W-C}$)	$H_2C{=}$	$HC{=}$			
Cr	Ethene	48.25		220.44	75.0		Toluene-d_8	r.t.	[11]
Mo	Ethene	41.89		208.74	81.4		Toluene-d_8	r.t.	[11]
W	Ethene	31.20		198.02 (119)	92.1		Toluene-d_8	293	[11,27]
W	Propene	37.35	50.20	200.00 (122)	78.1	85.5	Toluene-d_8	293	[26]
W	1-Butene	35.77	57.77	199.84 (122)	77.7	82.7	Toluene-d_8	293	[26]
W	1-Pentene	36.51	55.67	199.87 (122)	78.5	83.1	Toluene-d_8	273	[22]
W	1-Hexene	36.54	56.06	199.98 (122)	77.8	81.3	Toluene-d_8	273	[22]
W	3-Hexene		61.53	201.79 (124)		69.6	Toluene-d_8	273	[22]
Mo	Methyl acrylate	43.6	50.8	205.6	87.0	77.8	Benzene-d_6	298	[4]
W	Methyl acrylate	32.9	41.8	195.0	97.7	86.8	$CDCl_3$	298	[4]
W	Dimethyl fumarate		44.0	193.1		89.5	Benzene-d_6	298	[4]
W	Trimethylvinylsilane	38.46	36.33	198.37 (119)	92.4	104.0	$CDCl_3$	298	[63]
W	Trichlorovinylsilane	35.67	32.75	194.14 (118)	103.6	98.4	$CDCl_3$	298	[63]
W	Cyclopentene		62.20	201.82 (125)		68.5	Toluene-d_8	273	[22]
W	Cyclohexene		56.21	202.60		71.0	Toluene-d_8	273	[22]
W	Cycloheptene		56.60	201.74		74.9	Toluene-d_8	273	[22]
Cr	*trans*-Cyclooctene		71.9	221.70		62.2	Toluene-d_8	r.t.	[5]
W	*trans*-Cyclooctene		57.76	200.93		76.2	Toluene-d_8	r.t	[25]
W	*cis*-Cyclooctene		57.53	200.42		72.8	Cyclohexane-d_{12}	r.t.	[17]
W	Norbornene		60.40	201.50 (124)		74.8	Toluene-d_8	263	[33]

greater than for other proton signals. Most conspicuous are the shifts displayed by the protons of monoalkene, *cis*-bis(alkene), and *fac*-tris(alkene) compounds. With chloroform-d_1 as solvent, the proton signals vary little with temperature. However, in this solvent, chemical shifts displayed by the protons of all alkene compounds are shifted downfield (ca. 1 ppm) compared with their positions in toluene-d_8.

It is interesting to compare the NMR data, i.e. the $\Delta\delta$ coordination shifts of olefinic protons and carbons of mono, bis, and tris(alkene) compounds. For different ethene compounds, $\Delta\delta_H$ for the ethene ligand *trans* to a CO group increases from 2.44 (mono) to 2.55 (*mer*-tris), 2.60 (*fac*-tris), and 2.89 (*cis*-bis) [27]. For the mutually *trans* ethene ligands of *trans*-bis and *mer*-tris compounds, $\Delta\delta_H$ is substantially larger, viz. 3.16 and 3.72 ppm, respectively. This trend can be observed in NMR spectra of all alkene compounds, e.g. in chloroform-d_1 solution $\Delta\delta_H = 1.16$ and 2.70 ppm for mono and *trans*-bis(NBE), respectively. Similarly, $\Delta\delta_C$ of olefinic carbon is much lower ($\Delta\delta_C = 47.2$) for a mono than for a *trans*-bis(NBE) complex ($\Delta\delta_C = 74.3$) [33]. Another characteristic feature of NMR data for monoalkene compounds is a very high value of $^1J_{W-C}$ (ca. 150 Hz) for a carbonyl ligand *trans* to an olefin ligand, while for mutually *trans* carbonyl groups $^1J_{W-C} =$ ca. 120 Hz. The higher value of $^1J_{W-C}$ proves a stronger interaction between the tungsten atom and the CO ligand in the position *trans* to the olefin ligand. The four carbonyl ligands of the bis(ethene) compounds exhibited signals from 220.44 for a chromium to 208.74 for a molybdenum to 198.02 ($^1J_{W-C} = 120$ Hz) for a tungsten compound [11].

Analyzing the NMR data for the *trans*-bis(ethene) complexes of W, Mo, and Cr, one can see that the strongest $d\pi–p\pi^*$ interaction takes place between the ethene ligand and the tetracarbonyltungsten moiety, which is indicative of the $\Delta\delta_C$ value for the olefin carbons, which decreases in the order: W (92.1) > Mo (81.4) > Cr (75.1). The higher $\Delta\delta_C$ values (∼104 pm) for the olefin carbons are only detected for the vinylsilane complexes of tungsten (Table 13). A comparison of the NMR data for vinylsilane complexes of tungsten with those for their propene and 1-butene analogues reveals that $\Delta\delta_C$ values for vinylsilane carbons are more than 10 ppm larger. This suggests that the $d\pi–p\pi^*$ interaction of the tungsten atom with the trimethylvinylsilane ligand is stronger than with propene and 1-butene [26]. At the same time, for monosubstituted olefin compounds the values of the coordination shifts of the methine carbons are larger than those of the methylene carbons, while for vinylsilane complexes they depend upon the substituent at the silicon atom. The largest $\Delta\delta_C$ value, 105.5, has been obtained for the methylene carbon ($=CH_2$) of the trichlorovinylsilane compound. The smallest $\Delta\delta_C$ value of the methylene carbon (92.4 ppm) and the largest difference (11.6 ppm) between the coordination shifts for the vinyl $=CH_2$ and $=CH$ carbon has been found for a trimethylvinylsilane compound. This may suggest a very asymmetrical η^2-coordination of trimethylvinylsilane to the tungsten atom but with a deviation opposite to that observed for the trichlorovinylsilane compound. Tungsten satellites due to the coupling between the vinylsilane carbons and the ^{183}W nuclei have been detected only in the ^{13}C NMR spectra of the trichlorovinylsilane compound ($^1J_{W-CH} = 15.2$ Hz and $^1J_{W-CH_2} = 9.7$ Hz). That is in agreement with the description of the $W–\eta^2$ bond as metallacyclopropane [3], with a high component of the W–C σ-bond, attributable to the degree of increase in hybridization of the vinyl carbon toward sp^3. Although for the analogue bis(propene) compound the values of $^1J_{W-CH}$ (10.2 Hz) and $^1J_{W-CH_2}$ (12.7 Hz) lie in a similar range [26], the slightly greater value of $^1J_{W-CH_2}$ than $^1J_{W-CH}$ indicates that the asymmetry of metallacyclopropane in the bis(propene) compound is opposite to that in the trichlorovinylsilane compound.

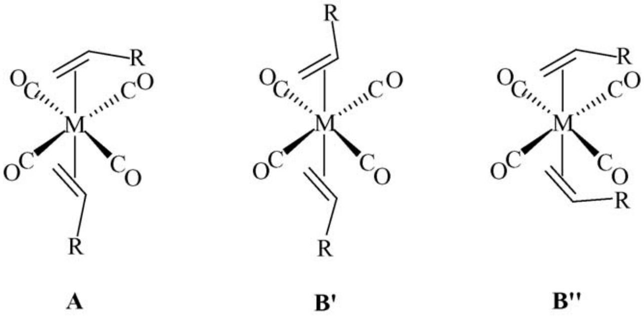
In the ^1H NMR spectra of metal carbonyl complexes with monosubstituted olefin, such as 1-propene, 1-butene [26], methyl acrylate [4], or vinylsilane $H_2C{=}CHSiR_3$ (R = Me, OMe, OCH_2CH_2OMe, and Cl) [63], three vinyl hydrogens give rise to three multiplets in the region about 1 ppm lower for monoalkenepentacarbonyl compounds than for *trans*-bis(alkene)tetracarbonyl complexes. Thus, for the trimethylvinylsilane complex all the three vinyl protons are observed as doublets of doublets with proton–proton coupling constants of 16.9, 11.9, and 2.7 Hz—considerably smaller than those observed for uncoordinated trimethylvinylsilane, viz. 20.3, 14.6, and 3.8 Hz, respectively. The highest coordination shift ($\Delta\delta_H = 4.34$) is observed for the proton that is at the methine carbon, which may indicate a greater degree of rearrangement around this carbon atom (=CH), involving partial rehybridization toward sp^3, and an increase in shielding compared with the methylene carbon. However, for 1-propene and 1-butene a higher $\Delta\delta_H$ value is detected for mutually *trans* vinyl protons than for the proton *trans* to the alkyl substituent (Table 12).

3.3.2. Dynamic NMR studies of *trans*-[W(CO)$_4$(η^2-alkene)$_2$] complexes

As was theoretically predicted a long time ago [8], for all X-ray-analyzed crystals of bis(olefin)tetracarbonyl complexes of tungsten(0), a characteristic *trans*-orthogonal orientation of the two olefin bonds, eclipsed to the respective OC–W–CO axes of the square-planar $W(CO)_4$ moiety (se), has been observed (Scheme 2) [4,17,25]. However, in solution, due to possible rotation of the olefin ligands around the W–(η^2-olefin) bond, such compounds show dynamic behavior, and their NMR spectra are temperature dependent [4,12,22,26,33,63,71]. The ^1H NMR spectra of *trans*-bis(alkene) complexes show sharp signals for all protons, suggesting relatively fast rotation around the W–(η^2-olefin) bond at room temperature. Lowering the temperature causes this process to be frozen. Variable-temperature spectra made it possible to observe the coalescence temperature T_c in the range from 243 to 191 K, from which the free energy barrier to olefin rotation and the other activation parameters: E_a, $\Delta G^\ddagger$, $\Delta H^\ddagger$, and $\Delta S^\ddagger$ have been calculated [4,12,22,26,33,71]. The lowest $\Delta G^\ddagger$ reported for *trans*-[W(CO)$_4$(η^2-alkene)$_2$] complexes is that calculated for a norbornene complex (38.9 kJ mol^{-1}) [33] and the highest for a methyl acrylate complex (75.3 kJ mol^{-1}) [4].

For *trans*-bis(monosubstituted olefin) complexes four diastereoisomers (*RS*, *SR*, *SS*, *RR*) isomers arising from different orientations of the unsymmetrical alkene ligands relative to the OC–M–CO vectors exist in solution (Scheme 4).

The presence of four isomeric forms, **A** (*RS*, *SR*), **B′** (*SS*), and **B″** (*RR*) results from different orientations of the vinyl group in one molecule of olefin with respect to the other molecule of olefin and the carbonyl ligands. These isomers give virtually identical IR spectra but are clearly distinguishable by ^1H and ^{13}C NMR spectroscopy. In the ^1H NMR spectrum of olefin complexes, two sets of vinyl proton signals for isomers **A** and **B** are sometimes observed at room temperature [63].



Scheme 4. Different orientations of the monosubstituted olefin ligands in molecules of *trans*-bis(alkene)tetracarbonyl complexes.

3.4. The effect of the metal electronic configuration on stability and reactivity of η^2-alkene ligands

The *cis*-bis(alkene) complexes have been identified as thermally unstable species at low temperatures [6,7,11,23,24,26,27] or in the gas phase [20]. Only one compound, *cis*-[W(CO)$_4$(η^2-*c*-COE)$_2$] [25], is stable enough to be isolated. The theoretically predicted structure for *cis*-[W(CO)$_4$(η^2-ethene$_2$] has a C_2 symmetry with two parallel ethene ligands [8,20,31]. DFT calculations of relative energies (ΔG) indicate that the *trans*-[W(CO)$_4$(η^2-ethene)$_2$] complex is more stable, by ca. 10 kJ mol^{-1}, than *cis*-[W(CO)$_4$(η^2-ethene$_2$]. In contrast, the stability of their one-electron oxidation products, the corresponding 17-electron cationic complexes, is reversed, the cationic form of the *cis* isomer being preferred by ca. 10 kJ mol^{-1} [31].

Two-electron chemical oxidation of stable *trans*-[W(CO)$_4$(η^2-NBE)$_2$] by $SnCl_4$ gives a very labile norbornene complex of tungsten(II), whose structure has been established by NMR spectroscopy in solution at low temperature (258 K) [33]. The latter compound decomposes in $CDCl_3$ solution to give chloronorbornane, whereas in benzene-d$_6$ or toluene-d$_8$ solution the products of norbornene hydroarylation are formed.

Photochemical oxidative addition reaction of $SnCl_4$ or $GeCl_4$ and a diene complex of the type [M(CO)$_4$(η^4-diene] (M = W, Mo) gives a seven-coordinate compound, very labile in solution, with a d^4 electronic configuration of the metal [70,77–80].

3.5. Compounds of metal in the second oxidation state (d^4)

Although the chemistry of octahedral alkenecarbonyl complexes of metal with a d^6 electronic configuration has been well studied, there are surprisingly few examples of d^4 Group 6 metal–olefin complexes. The first such pseudo-octahedral 16-electron compound [WBr$_2$(CO)$_2$(η^4-NBD)] was obtained in reaction of the tungsten(II) compound [{WBr$_2$(CO)$_4$}$_2$] with norbornadiene [81], and X-ray analysis showed that its two carbonyl ligands were *trans* to each other with an OC–W–CO angle of 172.9(8)°, and the norbornadiene ligand *trans* to the bromide ligands. Very short W–C(olefin) distances (2.28 Å av.) were detected in that arrangement. However, two-electron chemical oxidation of stable [M(CO)$_4$(η^4-diene)] (M = W, Mo) by $SnCl_4$ or $GeCl_4$ leads to the formation of seven-coordinate 18-electron compounds of metal in the second oxidation state,

$[MCl(M'Cl_3)(CO)_3(\eta^4\text{-diene})]$ (M′ = Sn, Ge; diene = NBD, 1,5-COD) [70,77–80]. The most significant feature of the latter diene compounds is an asymmetrical coordination of the diene ligand. The olefin bond of the diene ligand *trans* to the chloride ligand is ca. 0.1 Å closer to the metal atom than the olefin bond *trans* to the carbonyl ligand. This coordination asymmetry results in high lability of such compounds in solution and their smooth rearrangement to species initiating catalytic reaction of olefin [52,78].

4. Photochemical *trans* ↔ *cis* isomerization of bis(alkene) complexes

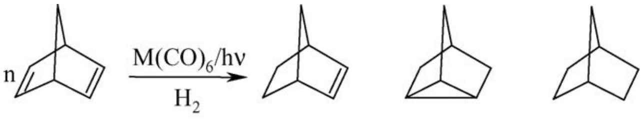
Reversible isomerization of *trans*- to *cis*-$[M(CO)_4(\eta^2\text{-alkene})_2]$ has been observed in argon matrices at low temperature under selective irradiation. UV photolysis ($\lambda \approx 313$ nm) of *trans*-$[M(CO)_4(\eta^2\text{-alkene})_2]$ (alkene = cyclopentene or 1-pentene) in an argon matrix at 16 K results in the formation of the *cis*-bis(alkene) complex. The isomerization is reversed under the action of visible light ($\lambda \approx 445$ nm) [23]. The *trans*-$[M(CO)_4(\eta^2\text{-alkene})_2]$ complexes have been found to undergo photoisomerization to the *cis*-$[M(CO)_4(\eta^2\text{-alkene})_2]$ derivatives via loss of alkene followed by subsequent rearrangement of the $[M(CO)_4(\eta^2\text{-alkene})]$ (C_{2v}) intermediate to its C_s analogue prior to recapture of alkene. A similar reversible *trans* ↔ *cis* isomerization has been observed for propene, 1-butene, and cyclopentene complexes of tungsten in an alkane solution at temperatures between 123 and 263 K [24]. Photochemical conversion of *cis*-$[W(CO)_4(t\text{-COE})_2]$ into *trans*-$[W(CO)_4(t\text{-COE})_2]$ was observed by Grevels et al. upon irradiation ($\lambda = 365$ nm) in *n*-hexane solution containing *trans*-cyclooctene [25].

5. Applications in transition-metal-catalyzed reactions

There are many reports in the literature of extraordinary catalytic activity of light-generated catalysts derived from Group 6 metal carbonyls [33,35–54,82–97]. Some η^2-alkene complexes have been detected in most homogeneous catalytic reactions of olefins, including hydrogenation, isomerization, hydrosilylation, oligomerization, polymerization, and metathesis.

5.1. Hydrogenation of olefins

Hydrogenation of dienes was one of the first examples of photocatalytic activity of Group 6 metal carbonyls [38–44]. Most of these studies have concentrated on the hydrogenation of norbornadiene, in which three possible hydrogenation products: norticyclene, norbornene, and norbornane can be formed (Scheme 5).



Scheme 5. Hydrogenation of norbornadiene catalyzed by photoactivated Group 6 metal carbonyls.

Chromium carbonyls lead mainly to the formation of nortricyclene as the product and are much better catalysts than the analogue molybdenum and tungsten compounds, which give predominantly norbornene. Detailed infrared (TR-IR and FT-IR) spectroscopic investigations have shown that a very important role during the catalytic process is played by *mer* and *fac* tricarbonyl compounds of the type $[M(CO)_3(\eta^4\text{-NBD})(\eta^2\text{-NBD})]$, which can be interconverted photochemically via loss of an η^2-alkene ligand [15,16]. The high catalytic activity of chromium compounds is the effect of the very low thermal stability of its *fac*-tris(alkene) species, which instead of losing an alkene ligand binds and thus activates the dihydride molecule during the catalytic process leading to the formation of nortricyclene.

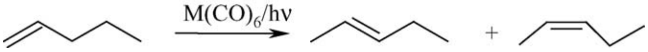
5.2. Isomerization of olefins

As was established by Wrighton et al. more than 30 years ego, photochemically activated Group 6 metal carbonyls catalyze double-bond migration (1,3 hydrogen shift) and *cis–trans* isomerization of olefins (Scheme 6) [35–38]. The catalytic activity of Group 6 metal hexacarbonyls with respect to olefin isomerization depends on the metal in the order W > Mo ≫ Cr. This order can be explained by a stronger interaction between the tungsten atom and olefin than between molybdenum or chromium atoms and olefin.

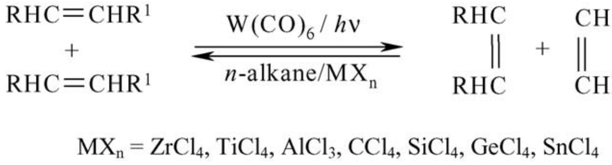
The catalytically important intermediates include coordinatively unsaturated 16-electron η^2-alkene complexes, whose transformation to π-allylmetal hydrides has been proposed to account for the observed isomerization. The formation of 16-electron complexes during photolysis of hexacarbonyls in the presence of olefin has been observed by IR spectroscopy in low-temperature investigations [6,15,16,23,24,27]. Monitoring of the photochemical reaction of *trans*-bis(alkene) complexes of tungsten by ^{1}H NMR spectroscopy and the detection of a hydride signal at ca. −3 ppm with the tungsten-183 satellite signals ($^1J_{W\text{–}H}$ = ca. 16 Hz) indicate that the initially formed product is indeed a hydride [26]. It is interesting to note that a terminal alkene, such as 1-butene bound to the tungsten atom in a thermodynamically stable *trans*-bis(1-butene) complex undergoes isomerization in solution to give *cis*- and *trans*-2-butene still in the coordination sphere of the metal [26].

5.3. Metathesis of acyclic and ring-opening metathesis polymerization (ROMP) of cyclic olefins

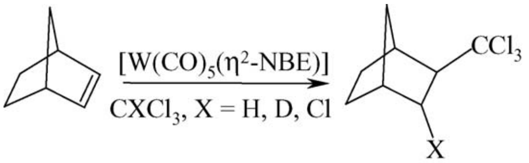
It was discovered in 1975 that the photolysis of tungsten hexacarbonyl in tetrachlorocarbon solutions affords an olefin metathesis catalyst (Scheme 7) [82–84]. Since then there has been much interest in this photochemical reaction, which produces a catalyst working in mild conditions without an organometallic component [51,85–97]. The same catalyst



Scheme 6. Isomerization of monosubstituted olefins catalyzed by photoactivated Group 6 metal carbonyls.



Scheme 7. Metathesis of olefins catalyzed by the photoactivated $W(CO)_6$.



Scheme 8. Addition of haloalkanes to norbornene catalyzed by the photochemically synthesized $[W(CO)_5(\eta^2\text{-norbornene})]$ complex.

induces the metathesis of acyclic alkenes and the ring-opening metathesis polymerization (ROMP) of cyclic olefins. During the investigation of a $W(CO)_6$-based photocatalytic system [51], it was observed that a more active and tractable catalyst for the metathesis of alkenes can be photogenerated in reaction of $W(CO)_6$ carried out in alkane solution containing catalytic amounts of Lewis acid, such as halides of Group 4, 13, and 14 elements [93]. In such a system even higher catalytic activity is achieved than in tetrachlorocarbon solution.

The above-mentioned photochemical reaction studies revealed that in reaction of tungsten and molybdenum hexacarbonyls with $SnCl_4$ and $GeCl_4$, bimetallic, binuclear seven-coordinate compounds of the type $[(CO)_4M(\mu\text{-}Cl)_3M(M'Cl_3)(CO)_3]$ (M = W, Mo; M′ = Sn, Ge) are formed [98–100]. In reaction of the latter compounds with norbornadiene, coordination of norbornadiene to the tungsten or molybdenum atom and initiation of ROMP of cyclic olefins have been observed [52,78]. As was established earlier, the ROMP polymer must be formed through interconversion of a complex with both a cyclic olefin and a carbene ligand via a metallacyclobutane intermediate [50]. In this particular case, the initiating carbene ligand must be formed due to the transformation of an η^4-NBD ligand. Such a transformation might occur in the case of the pentacarbonylnorbornene complex of tungsten(0), $[W(CO)_5(\eta^2\text{-NBE})]$, which in chloroform solution decays to give quantitatively the ROMP polymer, i.e. poly(1,3-cyclopentylenevinylene), and initiates the catalytic ROMP process in the presence of an excess of norbornene [33].

5.4. *Bis(alkene)-to-metallacyclopentane/alkylidene rearrangement—theoretical studies*

As has been very well documented [50], the true catalytic species in the metathesis reaction is a carbene complex. The question then arises about how the η^2-olefin is transformed to a carbene ligand in olefin metathesis initiated by tungsten carbonyls. DFT (B3LYP) calculations have shown that two-electron oxidation of *cis*-$[W(CO)_4(\eta^2\text{-ethene})_2]$ to its dicationic form enables the transformation of this complex to tungstacyclopentane at lower energy ($\Delta G = 36\,kJ\,mol^{-1}$) than in the case of the neutral compound ($\Delta G = 108\,kJ\,mol^{-1}$). The activation barriers for the formation of tungstacyclopentane and then its transformation to the butylidene complex $[W(CO)_4(=CHC_3H_7)]^{2+}$ have been found to be 48 and 87 kJ mol^{-1}, respectively. This result suggests a high probability of facile conversion of *cis*-bis(alkene) to tungstacyclopentane and next to alkylidene species initiating catalytic olefin metathesis [34].

5.5. *Addition of haloalkane to olefin*

1,2-Addition of haloalkane to olefin has been very well known since 1945 as the Kharasch addition reaction [53,101–105]. Catalytic activity in this reaction has been demonstrated for chromium and molybdenum carbonyls and recently for $Mo(CO)_6$ activated thermally in acetonitrile solution [53]. The photochemically synthesized $[W(CO)_5(\eta^2\text{-norbornene})]$ complex in chloroalkane, $CXCl_3$ (X = H, D, Cl), solution containing 1% of alcohol catalyzes selective conversion of norbornene to the NBE−$CXCl_3$ adducts (Scheme 8) [33].

It is clear that the coordination of olefin to the metal atom is also a very important step in reaction of haloalkanes with olefin.

6. Prospects and outlook

The work summarized in this survey shows that photochemical reactions of Group 6 metal carbonyls with alkenes have been attracting great abiding interest for the past 40 years. A photochemical reaction can be used not only in synthesis of new alkene complexes but also to generate very reactive coordinativelly unsaturated species or organometallic intermediates, the products of photochemical rearrangement of η^2-olefins. Even a very unstable alkene complex produced in photochemical reaction can be characterized by low-temperature spectroscopic investigations.

This survey presents several examples showing that alkene complexes of Group 6 metals are very reactive and may be used as precatalysts in reactions of alkenes proceeding under extremely mild conditions. The binding of olefin to metal is tantamount to its activation. For that reason the stability of the M–olefin bonds and the possibility to influence those bonds through other ligands are very important in catalysis. There is no doubt that alkene complexes have a considerable potential and further exploration of their reactivity is required.

Acknowledgements

I would like to thank all my co-workers who have been involved in studies of tungsten and molybdenum alkene–carbonyl complexes: B. Biernat, M. Górski, J. Handzlik, M. Jaroszewski, and K. Kern.

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