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High Oxidation State Multiple Metal−Carbon Bonds

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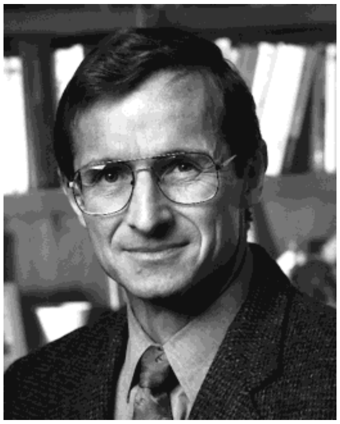

Richard R. Schrock received his Ph.D. degree in inorganic chemistry from Harvard in 1971 under the tutelage of John Osborn. After spending 1 year as an NSF postdoctoral fellow at Cambridge University working for Lord Jack Lewis and 3 years at the Central Research and Development Department of E. I. duPont de Nemours and Company, he moved to Massachusetts Institute of Technology in 1975. He became full professor in 1980 and the Frederick G. Keyes Professor of Chemistry in 1989. His interests include the inorganic and organometallic chemistry of high oxidation state, early metal complexes (especially those that contain an alkylidene or alkylidyne ligand), catalysis and mechanisms, the chemistry of high oxidation state dinitrogen and related complexes, and the controlled polymerization of olefins and acetylenes. He has received the ACS Award in Organometallic Chemistry (1985), the Harrison Howe Award of the Rochester ACS section (1990), the ACS Award in Inorganic Chemistry (1996), and an ACS Cope Scholar Award (2001). He has been elected to the American Academy of Arts and Sciences and the National Academy of Sciences. He was Associate Editor of *Organometallics* for 8 years, has published more than 370 research papers, and has supervised over 100 Ph.D. students and postdocs. (Photograph is reprinted with permission from Richard R. Schrock and L. Barry Hetherington. Copyright 1999 L. Barry Hetherington.)

1. Introduction

The first "high oxidation state" transition metal complexes that contain a multiple metal−carbon bond were discovered ∼25 years ago in the form of $(\eta^5\text{-}C_5H_5)_2Ta(CH_2)(CH_3)$[1] and $(Me_3CCH_2)_3Ta(CHCMe_3)$.[2] Since that time, interest in high oxidation state alkylidene ($M{=}CR_1R_2$) and alkylidyne ($M{\equiv}CR$) complexes has grown considerably. It could be argued that interest in the catalytic metathesis of alkenes and (to a lesser degree) alkynes was the driving force for the development of "high oxidation state" (d^0) alkylidene and alkylidyne chemistry. Interest in complexes in which the metal is not in its highest possible oxidation state (so-called carbene and carbyne complexes) has also grown considerably, especially with respect to the use of heteroatom-stabilized carbene complexes as stoichiometric reagents in organic synthesis, and in the use of non-heteroatom-stabilized ruthenium(II) carbene complexes as relatively oxygen-, water-, and functionality-tolerant olefin metathesis catalysts. Although comprehensive yearly surveys that cover metal−carbon double and triple bonds began to appear in 1999[3] (for 1997; see also surveys for 1998[4] and 1999[5]), there is good reason to separate high oxidation state species from the rest and review them here. The first comprehensive review of high oxidation state alkylidene chemistry appeared in 1986.[6] The second comprehensive article appeared in 1991,[7] while an article covering recent advances in high oxidation state alkylidene complexes appeared in 1994.[8] The only comprehensive review of high oxidation state alkylidyne complexes appeared in 1988,[9] although a review of all types of metal−carbon triple bonds was published in 1991[10] and a review of carbon−carbon and carbon-heteroatom coupling reactions involving carbyne complexes appeared in 1995.[11] In this review, I

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Table 1. Tabulation of Isolated Alkylidene Complexes[a]

compound		ref
Group 4		
(η^5-C$_5$H$_4$R)$_2$Ti(CHCMe$_3$)(PMe$_3$)	R = H, Me	32
Cp$_2$(PMe$_3$)Ti=C=C=TiCp$_2$(PMe$_3$)		34
CpTi(CHCMe$_3$)[OCR$_2$(CH$_2$PMe$_2$)]	CR$_2$ = C(t-Bu)$_2$ or C[1,2-(CMe$_2$)$_2$C$_6$H$_4$]	35, 36
[η^5-C$_5$H$_4$(CH$_2$CH$_2$N−t-Bu)]Ti(CHCMe$_3$)(PMe$_3$)		37
CpITi[C(Ph)C(Me)=CHNR][Li(ether)]	R = i-Pr, Cy	38
[Et$_2$AlOC(C$_5$H$_{10}$)C(C$_5$H$_{10}$)O]$_2$Ti=CHCH$_3$		39
TaCp*(CHSiMe$_3$)(CH$_2$SiMe$_3$){η^2-C(CH$_2$SiMe$_3$)=NAr}		78
[(i-PrN−*o*-C$_6$H$_4$)$_2$O]Ti(CHCMe$_3$)(PMe$_3$)$_2$		40
Zr[η^5-1,3-(i-Pr$_2$PCH$_2$SiMe$_2$)$_2$C$_5$H$_3$](CHR)Cl	R = Ph or SiMe$_3$	42, 43
Hf[η^5-1,3-(i-Pr$_2$PCH$_2$SiMe$_2$)$_2$C$_5$H$_3$](CHPh)Cl		45
Group 5		
VCp(N−2,6-i-Pr$_2$C$_6$H$_3$)(PMe$_3$)(CHPh)		52
[(TMS)$_2$N]V=CPhCPh=CPhCPhCH$_2$SiMe$_2$N(TMS)		54
[(η^5-t-BuC$_5$H$_4$)$_2$Nb(CHPh)(THF)]$^+$		55
[(η^5-Me$_3$SiC$_5$H$_4$)$_2$(CO)Nb=C=CMe]$_2^{2+}$		56
NbCp*(N−2,6-i-Pr$_2$C$_6$H$_3$)(PMe$_3$)(CHPh)	Cp* = η^5-C$_5$Me$_5$	58
NbCp*(CHSiMe$_3$)(CH$_2$SiMe$_3$)$_2$		60
Tp*ClNb=C(Ph)C(Ph)=CHCH(Me)	Tp* = tris(3,5-dimethylpyrazolyl)borate	62
Tp*(OMe)Nb=C(Ph)C(R)=CR′O]		63
Cp′$_2$(X)Nb=CSCR=CRS	X = Cl, Et, CH$_2$CH$_2$Ph; R = CF$_3$, CO$_2$Me, CO$_2$(t-Bu)	64
(calix[4]arene)Nb(CRR′)	CRR′ = C(Cp$_2$Fe)Me, CHPh	65
(silox)$_3$Nb=CH−CH=CH−CH=CH−N=Nb(silox)$_3$		66
(silox)$_3$Nb(alkylidene)	alkylidene = cyclohexylidene or butylidene	67
Ta(CHCMe$_3$)Cl$_2$[OC(Me)(CH$_2$PPh$_2$)$_2$]		35
Ta(CHSiMe$_3$)(CH$_2$SiMe$_3$)$_3$		68
Ta[C(SiMe$_3$)(SiHPhR′)](CH$_2$SiMe$_3$)$_3$	R′ = Me, Ph	90
Cp$_2$Ta(I)(CHCH$_3$)		70
Cp$_2$Ta(CHR)(R′)	R = Si−t-Bu$_2$H, R′ = H; R = H, R′ = Ph; R = H, R′ = Si−t-Bu$_2$H	72
Cp$_2$Ta(CH$_2$)Cl		74
Cp*$_2$TaH[C=C(R)H]	R = Me, Et	76
TaCp(NEt$_2$)$_2$(cyclopentadienylidene)		77
TaCp′(CHSiMe$_3$)(CH$_2$SiMe$_3$)$_2$	Cp′ = η^5-C$_5$Me$_5$; η^5-Me$_3$SiC$_5$H$_4$, η^5-1,3-(Me$_3$Si)$_2$C$_5$H$_3$	60
TaCp*(η^4-C$_4$H$_6$)(PMe$_3$)(CHPh)		81, 82
TaCp*(η^4-C$_4$H$_4$−*o*-C$_6$H$_4$)(CHPh)		81, 82
Cp*MeTa=CH(Ph)C(Ph)=C(Me)X	X = O, N−t-Bu	83
Cp*(Me$_2$NCH$_2$-o−C$_6$H$_4$)Ta=CHN(Me)CH$_2$−*o*-C$_6$H$_4$		84
TaTp*(CH−t-Bu)X$_2$	X = Cl, Br	86
TaTp*(CH−t-Bu)(Cl)Y	Y = OMe, O−i-Pr, NMe$_2$	86
(t-BuCH)(t-BuCH$_2$)Ta−N(t-Bu)=B(CH$_2$−t-Bu)N(t-Bu)SiMe$_2$CH$_2$		87
CpClTa=C(t-Bu)B(i-Pr)N(i-Pr)		88
Cp*Ta(N=P−t-Bu)(CHPh)(CH$_2$Ph)		85
Ta(CH$_2$SiMe$_3$)(PMe$_3$)$_2$[C(SiMe$_3$)SiPhRC(SiMe$_3$)]	R = Me, Ph	89
Ta(CH$_2$SiMe$_3$)$_3$[C(SiMe$_3$)(SiPhRH)]	R = Me, Ph	89
Ta(CHSiMe$_3$)$_2$(CH$_2$SiMe$_3$)(PMe$_3$)$_2$		91
Ta(CHR)(CH$_2$R)$_2$[Si(SiMe$_3$)$_3$]	R = t-Bu, SiMe$_3$	93, 94
Ta(CHSiMe$_3$)(CH$_2$SiMe$_3$)(O−2,6-Ph$_2$−3,5-X$_2$C$_6$H)	X = H, Me, Ph	95
Ta(O−2,6-Ph$_2$−3,5-X$_2$C$_6$H)$_2$(CH$_2$SiMe$_3$)$_2$(CHSiMe$_3$)	X = H, Ph, Me, i-Pr, t-Bu	96
[(Me$_3$SiNCH$_2$CH$_2$)$_3$N]Ta=CHR	R = Me, t-Bu, CH$_2$CHMe$_2$, CH$_2$CMe$_3$, Ph, SiMe$_3$	99
[(Et$_3$SiNCH$_2$CH$_2$)$_3$N]Ta=CHR	R = Me, Et, CH$_2$CHMe$_2$, SiMe$_3$, Ph, 0.5CH$_2$CH$_2$ (dimer)	100
Ta[2-(CH$_2$NMe$_2$)C$_6$H$_4$](CH−t-Bu)Cl$_2$		101
Ta(CHR)[2,6-(CH$_2$NMe$_2$)$_2$C$_6$H$_3$](X)(Y)	X = Y = Cl; X = Y = O−t-Bu; X = Cl, Y = O−t-Bu; R = CMe$_3$, SiMe$_3$	101−103
Ta(CHCMe$_3$)X[2-(CH$_2$NMe$_2$)−6-(CH$_2$NMeCH$_2$)C$_6$H$_3$]	X = Cl, O−t-Bu	105
Ta[C(t-Bu)(2,6-(CH$_2$NMe$_2$)$_2$C$_6$H$_3$)]Cl$_2$[2-(CH$_2$NMe$_2$)C$_6$H$_4$]		105
Ta(CH−t-Bu)[C$_6$H$_4$−2-CH$_2$N(Me)CH$_2$CH$_2$NMe$_2$)]X$_2$	X = Cl, O−t-Bu	105
Ta(CH−t-Bu)[2,4-(CH$_2$NMe$_2$)$_2$C$_6$H$_3$](X)(Y)	X = Y = O−t-Bu; X = Cl, Y = O−t-Bu	107
Ta(CH−t-Bu)[*o*-C$_6$H$_4$(CH$_2$(Me)CH$_2$CH$_2$NMe$_2$)]X$_2$	X = Cl, O−t-Bu	108
[PhP(CH$_2$SiMe$_2$NSiMe$_2$CH$_2$)$_2$PPh]Ta(CH$_2$)Me		109
Ta(CHR)(CH$_2$R)$_2$[PhC(NTMS)$_2$]$_2$	R = H, Ph	111
Ta(CHSiMe$_3$)(CH$_2$SiMe$_3$)(NAr)[(N−i-Pr)$_2$(CH$_2$CH$_2$)$_3$NLi]		112, 113
[{(i-Pr)$_2$NCH$_2$SiMe$_2$}$_2$N]Ta(CHR)Cl$_2$	R = Ph, t-Bu	115
{[{(i-Pr)$_2$NCH$_2$SiMe$_2$}$_2$N]Ta(CHR)}$_2$(μ-N$_2$)	R = Ph, t-Bu	115

Table 1 (Continued)

compound		ref
Group 6		
Cr(CH−t-Bu)(NAr)$_2$(PMe$_3$)		119
Mo(CHR)(NR′)(OTf)$_2$(dme)	R = CMe$_3$ or CMe$_2$Ph; R′ = 4-Br−2,6-i-Pr$_2$C$_6$H$_2$, 2,6-Me$_2$C$_6$H$_3$, 3,5-Me$_2$C$_6$H$_3$, 2-i-PrC$_6$H$_4$, 2-CF$_3$C$_6$H$_4$, 2-t-BuC$_6$H$_4$, and 1-adamantyl	122
Mo(CHR)(NR′)(OR″)$_2$	R = t-Bu or CMe$_2$Ph; R′ = 2,6-i-Pr$_2$−C$_6$H$_3$, 4-Br−2,6-i-Pr$_2$C$_6$H$_2$, 2,6-Me$_2$C$_6$H$_3$, 3,5-Me$_2$C$_6$H$_3$, 2-t-Bu-C$_6$H$_4$, 2-i-PrC$_6$H$_4$, 2-CF$_3$C$_6$H$_4$, 2-PhC$_6$H$_4$, or 1-adamantyl, and OR″ = OCMe$_3$, OCEt$_3$, O−1-adamantyl, OCHMe$_2$, OCMe$_2$(CF$_3$), OCMe(CF$_3$)$_2$, OC(CF$_3$)$_3$, or OC(CF$_3$)$_2$(CF$_2$CF$_2$CF$_3$)	122
Mo(CHR)(NAr)(OR″)$_2$(PMe$_3$)	R = H, t-Bu, SiMe$_3$; OR″ = OC(CF$_3$)$_2$Me, OC(CF$_3$)Me$_2$	124
Mo(CHR)(NAr)(OR″)$_2$(quin)	R = t-Bu, CH═CHMe; OR″ = OC(CF$_3$)$_2$Me, OC(CF$_3$)Me$_2$	124
Mo(CHCMe$_2$Ph)(NAr)(O−2,6-C$_6$H$_3$Cl$_2$)$_2$(py)		124
Mo[CHCH$_2$CH(OMe)CH$_2$Me](NAr)(OR$_{F6}$)$_2$		130
[(R$_{F6}$O)$_2$(ArN)MoCHCH$_2$CH$_2$CH(OMe)CH$_2$]$_2$C$_6$H$_4$	OR$_{F6}$ = OCMe(CF$_3$)$_2$	130
Mo(CHPh)(NAr)X$_2$(dme)	X = OR$_{F6}$, OTf	130
Mo(CHR)(NAr)(OR$_{F6}$)$_2$(dme)	R = 4-(NMe$_2$)C$_6$H$_4$, 2,4,6-C$_6$H$_2$(OMe)$_3$	130
(L)(R$_{F6}$O)$_2$(ArN)Mo(CH)$_6$Mo(NAr)(OR$_{F6}$)$_2$(L)	L = dme, ether, THF	130
(quin)(*t*-BuO)$_2$(ArN)Mo(CH)$_6$Mo(NAr)(O−*t*-Bu)$_2$(quin)		130
1,4-{(L)(R$_{F6}$O)$_2$(ArN)MoCH}$_2$C$_6$H$_4$	L = dme or THF	130
Mo(CH$_2$)(NAr)(OR$_{F6}$)$_2$(bpy)		130
Mo(CHCMe$_2$Ph)(NR′)(diolate)	R′ = Ar, Ar′, 2-t-Bu−C$_6$H$_4$; diolate = 3,3′-disubstituted binaphtholate or 3,3′,5,5′-tetra-t-Bu−6,6′-dimethyl-diphenolate	131
Mo(CHR)(NR′)(diolate)	R = CMe$_3$, CMe$_2$Ph; R′ = 2,6-X$_2$C$_6$H$_3$ (X = Me, Et, i-Pr, Cl), 2-CF$_3$C$_6$H$_4$, 2,4-t-Bu−6-MeC$_6$H$_2$; see text for diolates	132, 138, 140, 141, 143, 145, 274
Mo(CHCMe$_2$Ph)(NAr){(*R*,*R*)-1,2-[OC(CF$_3$)$_2$CH$_2$]$_2$C$_5$H$_8$}		136
Mo(CHCMe$_2$Ph)(NAd)[OCH(CF$_3$)$_2$]$_3$[M(dme)]	M = Li or K	148
Mo(CHCMe$_2$Ph)(NAd)[OCH(CF$_3$)$_2$]$_2$(L)	L = 2,4-lutidine, py, 3-pentylpyridine, quin	148
Mo(CHCMe$_2$Ph)(NAr)[OCH(CF$_3$)$_2$]$_2$(2,4-lutidine)		148
Mo(CRR′)(NAd)[OCH(CF$_3$)$_2$]$_2$(2,4-lutidine)	R = R′ = Ph; R = Me, R′ = Ph	148
Mo(CRR′)(NAd)[OCH(CF$_3$)$_2$]$_2$	CRR′ = C(*o*-TMSC$_6$H$_4$)(CH═CHCMe$_2$Ph)	148
Mo(CRR′)(NAd)[OCH(CF$_3$)$_2$]$_2$(2,4-lutidine)	CRR′ = C(Ph)[C(Ph)═CHCMe$_2$Ph]	148
Mo(CHCMe$_2$Ph)(NAr′)(OC$_6$F$_5$)$_2$(quin)		148
Mo(CHCMe$_2$Ph)(NAr)(OC$_6$F$_5$)$_2$(H$_2$N−t-Bu)		149
Mo(CHCMe$_2$Ph)(NAr)[2,6-(OCPh$_2$CH$_2$)$_2$C$_5$H$_3$N]		150
Mo(CHCMe$_2$Ph)(NAr)(silsesquioxane)		151
Mo(CHR)(NR′)(O$_2$CPh$_3$)$_2$	R′ = 2-t-BuC$_6$H$_4$, 2,6-i-Pr$_2$C$_6$H$_3$, 1-adamantyl; R = CMe$_3$, CMe$_2$Ph	153
Mo(CHCMe$_2$Ph)(NAr)[BINA(NR)$_2$]	R = i-Pr or TMS	154
Mo(CHR)(NR′)[BINA(NTs)$_2$]	R′ = Ar or 2-CF$_3$C$_6$H$_4$; R = CMe$_2$Ph or t-Bu	154
$\mathrm{(ArN)(R''O)}\overline{\mathrm{Mo{=}C(t\text{-}Bu)P(OR'')C}}\mathrm{H(t\text{-}Bu)}$		155
MoTp(CHCMe$_2$Ph)(NAr)X	X = Me, OMe	157
[MoTp(CHCMe$_2$Ph)(NAr)(S)]$^+$	S = ether, acetonitrile, PMe$_3$	157
[Mo(CHCMe$_2$Ph)(NAr)Tp(L)]A	A$^-$ = B(C$_6$F$_5$)$_4^-$ or triflate; L = CH$_3$CN, PMe$_3$	157
Mo(CHCMe$_2$Ph)(NAr)Tp(X)	X = NMe$_2$, O−tol, OPh, OMe	157
Mo(O)(SAr)$_3$[C(Ph)CH═C(Ph)CH$_2$PMe$_2$Ph]		158
Mo(CH−t-Bu)(NPh)[[*o*-(Me$_3$SiN)$_2$C$_6$H$_4$]		160
MoTp(CHCMe$_2$Ph)(NAr)(OTf)		168
W(CH−t-Bu)(NAr)(OR)$_2$L	R′ = t-Bu, CH═CHMe; OR = OC(CF$_3$)$_2$Me, OC(CF$_3$)Me$_2$; L = PMe$_3$, quin	124
W(CHR)(X){(*R*,*R*)-1,2-[OC(CF$_3$)$_2$CH$_2$]$_2$C$_5$H$_8$}[P(OMe)$_3$]	R = CHCHCPh$_2$, CHC(O$_2$C$_3$H$_6$); X = O, NAr (see text)	136
W(CHCMe$_2$Ph)(NAr)(silsesquioxane)		151
WCp*(NPh)(CH$_2$Ph)(CHPh)		161

Table 1 (Continued)

compound		ref
Group 6 (continued)		
WCp*(NPh)(Cl)(CHSiMe$_3$)		161
W(η^5-C$_5$R′$_5$)(N−t-Bu)(CHR)(CH$_2$R)	R = Me, Et; R′ = H, Me	162
WCp*(CHR)(CH$_2$R)(N−t-Bu)	R = Me, Et	162
CpW(NCMe$_3$)(CHAd)Cl		238
WTp*(CH−t-Bu)(O)X	X = Cl, Br	164, 166
Tp*W(CHPh)(NPh)Br		165
WTp*(CHCMe$_2$Ph)(NAr)(3,5-dimethylimidazole)]$^+$		167
WTp*(CHCMe$_2$Ph)(NAr)(3,5-dimethylimidazolate)		167
Tp*(I)(O)W═C═C(R)Me	R = H, Me	170
WTp(X)(CHPh)Br	X = N−t-Bu, NAd, NAr′, O	172
WTp(CHR)(CH$_2$R)(NR′)	R = t-Bu, CMe$_2$Ph; R′ = Ph, N−2,6-i-Pr$_2$C$_6$H$_3$	171
[WTp(CH−t-Bu)(NPh)L]$^+$	L = Et$_2$O, i-Pr$_2$O, CH$_3$CN	171
WTp(CH−t-Bu)(NPh)Cl		171
WTp(CHMe$_2$Ph)(NAr)(OTf)		167
L$_{\mathrm{OMe}}$(Cl)W(CHTol)(X)	X = O, NPr	174
W(CHCHCPh$_2$)(O)(OR$_{\mathrm{F6}}$)$_2$L	L = PPh$_2$Me, P(OMe)$_3$, THF	175
W(CHCMe$_3$)(O)(O−2,6-Ph$_2$C$_6$H$_3$)$_2$L	L = PPh$_2$Me, PMe$_3$	177
W(CHCHCPh$_2$)(NR)Cl$_2$L$_2$	R = 2,6-Me$_2$C$_6$H$_3$, 2,6-i-Pr$_2$C$_6$H$_3$; L = PEt$_2$Ph, P(OMe)$_3$	178
W(CHCHCPh$_2$)(N−2,6-i-Pr$_2$C$_6$H$_3$)(OR)$_2$[P(OMe)$_3$]	OR = O−2,6-i-Pr$_2$C$_6$H$_3$; OC(CF$_3$)$_2$Me	178
W[CHCHC(O$_2$C$_3$H$_6$)](NR)Cl$_2$L$_n$	R = 2,6-Me$_2$C$_6$H$_3$, 2,6-i-Pr$_2$C$_6$H$_3$; L = PEt$_2$Ph, P(OMe)$_3$; n = 1 or 2	178
W[CHCHC(O)(OC$_3$H$_6$Cl)](NR)(Cl)L$_2$	R = 2,6-Me$_2$C$_6$H$_3$, 2,6-i-Pr$_2$C$_6$H$_3$; L = PEt$_2$Ph, P(OMe)$_3$	178
W(CH−t-Bu)(NPh)[1,2-(NSiMe$_3$)$_2$C$_6$H$_3$](PMe$_3$)		179
W[CH−2-(OMe)C$_6$H$_4$](NR)(OR$_{\mathrm{F6}}$)$_2$	R = 2,6-Me$_2$C$_6$H$_3$, 2,6-i-Pr$_2$C$_6$H$_3$	183
W(CHR)(NPh)Cl$_2$(PPh$_2$Me)$_2$	R = Ph, *p*-tolyl, *p*-CF$_3$C$_6$H$_4$, 2-naphthyl, C$_6$F$_5$, CHCMe$_2$, 0.5(C$_6$H$_4$)$_2$	183
W(CHR)(NR′)(OR$_{\mathrm{F6}}$)$_2$L	R = Ph, 2-(OMe)C$_6$H$_4$; R′ = Ph, 2,6-Me$_2$C$_6$H$_3$, 2,6-i-Pr$_2$C$_6$H$_3$; L = THF, PMe$_3$	183
W[2-(CH$_2$NMe$_2$)C$_6$H$_3$](CHSiMe$_3$)(NPh)(CH$_2$SiMe$_3$)		184
W[2-(CH$_2$NMe$_2$)C$_6$H$_4$](CHSiMe$_3$)(OSiPh$_3$)(NPh)		184, 185
(PhN)(Me$_3$SiCH$_2$)W═CHN(Me)CH$_2$−1,2-C$_6$H$_3$−3-CH$_2$NMe$_2$		188
W(OCRR′C$_5$H$_4$N)(CHSiMe$_3$)(CH$_2$SiMe$_3$)(NPh)	R = R′ = Ph; R = H, R′ = t-Bu	186
W[2-(OCPh$_2$)C$_5$H$_4$N](CHSiMe$_3$)(NPh)(CH$_2$SiMe$_3$)		187
{[calix]W═C(R′)CRR″}$_2$	R = R′ = R″ = Me; R′ = Ph, R = Me, R″ = H	190
[calix]W═C(X)(R)	R = Ph, Pr, SiMe$_3$, X = H, Me, I, C$\equiv$CPh	191,194, 195
W(O)[C(t-Bu)(Si−t-BuPh$_2$)](CH$_2$−t-Bu)$_2$		196
W(CHPh)(Me$_2$BINO)$_2$		197
W(CHR)(R′$_2$BINO)(O−t-Bu)$_2$	R = Ph, i-Pr; R′ = Me, Ph, Br	197
[W(CPh$_2$)(OCH$_2$−t-Bu)(OEt)$_2$(*m*-OEt)]$_2$		199
(2,6-Ph$_2$C$_6$H$_3$O)(OEt$_2$)Cl(t-BuCH)W−O−2-PhC$_6$H$_3$−6-C$_6$H$_4$		200
[(Me$_3$SiNCH$_2$CH$_2$)$_3$N]W(H)(cyclopentylidene)		202
{(Me$_3$SiNCH$_2$CH$_2$)$_3$N]W═CHCH$_2$CH$_2$CH$_2$		202
Group 7		
ReO$_2$(CH−t-Bu)(CH$_2$−t-Bu)(quin)$_x$	x = 0 or 1	203
Re(NAr)(CH−t-Bu)(OAr′)	OAr′ = OC$_6$F$_5$, O−2,6-C$_6$H$_3$Cl$_2$, OC$_6$Cl$_5$	204
Re(NAr)(C−t-Bu)(OAr′)$_2$(py)	OAr′ = O−2,6-C$_6$H$_3$Cl$_2$, OC$_6$Cl$_5$	204
Re(NAr)(CH−t-Bu)(OAr′)Cl$_2$	OAr′ = O−2,6-C$_6$H$_3$R$_2$; R = Cl, Me, i-Pr, OMe	204
ReO$_2$(CHCMe$_2$Ph)(CH$_2$CMe$_2$Ph)		206
Re(O)(NAr)(CH−t-Bu)(CH$_2$−*t*-Bu)		206
Re(NR)$_2$(CHCMe$_2$Ph)(CH$_2$CMe$_2$Ph)	R = NAr, t-Bu	206
[Re(CCMe$_2$R′)(CHCMe$_2$R′)(RNH$_2$)Cl$_2$]$_2$	R = Ar, Ar′; R′ = Me, Ph	206
Re(C−t-Bu)(CH−t-Bu)L$_x$Cl$_2$	L = t-BuNH$_2$, py, $^1/_2$ TMEDA; x = 0 or 2	206
Re(CCMe$_2$R′)(CHCMe$_2$R′)(OR)$_2$L$_x$	R′ = Me, Ph; OR = O−t-Bu, OSi(t-Bu)$_3$, OCMe$_2$(CF$_3$), OAr′, OCMe(CF$_3$)$_2$; L = PMe$_3$, t-BuNH$_2$, ArNH$_2$, py; x = 0 or 1	206
Re(C−t-Bu)(CHR)(OR$_{\mathrm{F6}}$)$_2$(dme)	R = Me, Et, Ph, *p*-C$_6$H$_4$NMe$_2$	207
Re(C−t-Bu)(CHEt)(OR$_{\mathrm{F6}}$)$_2$(TMEDA)		207
Re(C−t-Bu)(CHR)(OR$_{\mathrm{F6}}$)$_2$(THF)$_2$	R = OEt, OSiMe$_3$, SPh	207
Re(C−t-Bu)(CHSPh)(OR$_{\mathrm{F6}}$)$_2$(*t*-BuNH$_2$)$_2$		207
Re(C−t-Bu)[CH−2-pyrrolidinone](OR$_{\mathrm{F6}}$)$_2$		207
Re(C−t-Bu)(CHFerrocenyl)(OR$_{\mathrm{F6}}$)$_2$		207

Table 1 (Continued)

compound		ref
Group 7 (continued)		
$Re(C{-}t\text{-}Bu)(CH_2{-}t\text{-}Bu)_3X$	$X = OTf, OC_6F_5$	213
$[Re(C{-}t\text{-}Bu)(CH_2{-}t\text{-}Bu)_3S_n]^+X^-$	S = ether, water; $n = 0$ or 1; $X^- = [BAr_F]^-$, $[BF_4]^-$	213
$Re(C{-}t\text{-}Bu)(CH{-}t\text{-}Bu)(CH_2{-}t\text{-}Bu)L_nX$	L = methanol, THF, py, water; $X = BF_4$, O_3SCF_3, BAr_F; $n = 2$ or 3	213
$Re(L_{OEt})(C{-}t\text{-}Bu)(CH{-}t\text{-}Bu)Cl$		213
$ReCp(C{-}t\text{-}Bu)(CH{-}t\text{-}Bu)(CH_2{-}t\text{-}Bu)$		213
$Re(X)(C{-}t\text{-}Bu)(CH{-}t\text{-}Bu)X'$	$X = L_{OEt}$, $HBpz_3$, Cp; $X' = CH_2\text{-}t\text{-}Bu$, O_3SCF_3	213
$Re(C{-}t\text{-}Bu)(CH{-}t\text{-}Bu)(CH_2{-}t\text{-}Bu)(S)(OTf)$	S = trithiacyclononane, py	213
$[ReCp(C{-}t\text{-}Bu)(CH{-}t\text{-}Bu)(py)]^+[OTf]^-$		213
$[Re(L_{OEt})(C{-}t\text{-}Bu)(CH{-}t\text{-}Bu)(Et_2O)]^+[BAr_F]^-$		213
$[Re(S_3C_6H_{12})(C{-}t\text{-}Bu)(CH{-}t\text{-}Bu)(OTf)]^+[OTf]^-$		213
$Re(C{-}t\text{-}Bu)(CHR)(CH_2{-}t\text{-}Bu)L_2(OTf)$	R = H, C_6H_5, OEt; L = py, $^1/_2$ bipy	213
$\{Re(C{-}t\text{-}Bu)(CH{-}t\text{-}Bu)(CH_2{-}t\text{-}Bu)L_3\}[BAr_F]$	L = pyridine or acetonitrile	213
$Re(CHCH{=}CPh_2)(O)(OR_{F6})_3(THF)$		209

[a] Not all combinations may be represented. See text for special abbreviations.

include alkylidyne complexes with the more numerous alkylidene complexes, in part because alkylidyne complexes are often formed from alkylidene complexes by α hydrogen abstraction reactions (or vice versa), and also because alkylidyne and alkylidene ligands are found in similar environments and sometimes bound to the same metal center. In general, I will discuss only compounds that are well-characterized, although some reference to compounds identified in solution or generated in situ will be made from time to time. I will not cover in any comprehensive manner the various reactions of alkylidene and alkylidyne complexes and the still-expanding use of high oxidation state species in various types of metathesis reactions[12-19] and stoichiometric reactions (e.g., olefinations of the carbonyl groups) except when a new alkylidene or alkylidyne complex thereby is prepared and characterized. I also will not cover complexes in any detail in which an alkylidene or alkylidyne ligand is bridging between two metals. However, vinylidenes will be included and heteroatom-substituted alkylidenes will be mentioned occasionally. The literature will be covered from the beginning of 1991 for both alkylidene and alkylidyne complexes. I will add comments where appropriate in an attempt to put some aspect of high oxidation state multiple metal−carbon bond in perspective. The vast majority of high oxidation state compounds that contain a multiple metal−carbon bond contain Ta, Mo, W, or Re. Nevertheless, the review will include all metals within groups 4−7. Tables of reported alkylidene complexes (Table 1) and alkylidyne complexes (Table 2) will serve as quick reference guides to the literature and to location of the compound within the text. An attempt has been made to be comprehensive. Any omissions are the fault of the author and entirely unintentional.

2. Alkylidene Complexes

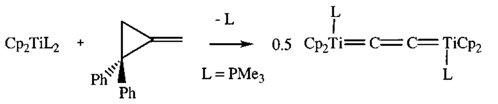
2.1. Group 4 Metals

2.1.1. Titanium

Stable alkylidene complexes of group 4 metals are rare, although titanium alkylidene complexes have been proposed as intermediates in a variety of reactions, according to products obtained upon reaction in the presence of olefins, ketones, solvent CH bonds, alkynes, etc. For example, titanium alkylidene complexes have been generated by treating dithioacetals with $Cp_2Ti(II)$ reagents,[20-22] by decomposing Cp_2TiRR' species,[23-26] by thermolyzing tetraalkyls (neopentyl[27,28] or trimethylsilylmethyl[29]), or by thermolyzing $Cp^*{}_2Ti$(diazoalkane) complexes.[30,31] The reader is referred to comprehensive reviews for details.[3-5] The few new examples of group 4 complexes, like many high oxidation state alkylidene complexes, often are formed by α hydrogen abstraction in a sterically crowded environment.

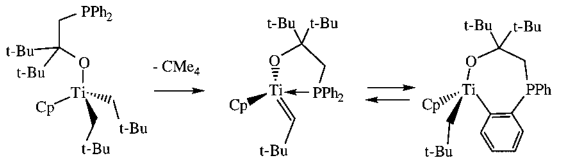
The dineopentyl complex $(\eta^5\text{-}C_5H_4R)_2Ti(CH_2CMe_3)_2$ (R = H, Me) has been found to be unstable above 0 °C. It decomposes readily in the presence of trimethylphosphine to yield $(\eta^5\text{-}C_5H_4R)_2Ti(CHCMe_3)(PMe_3)$, which shows an H_α resonance at 12.32 ppm and a C_α resonance at 313 ppm with $J_{CH} = 110$ Hz.[32] In the absence of trimethylphosphine in C_6D_6, the product of decomposition is $(\eta^5\text{-}C_5H_4R)_2Ti(CHDCMe_3)(C_6D_5)$, an example of addition of a CH bond across a metal−carbon multiple bond. This type of reaction is rare for any metal−carbon double bond, whatever the oxidation state of the metal.[33]

A stable biscyclopentadienyl complex that contains a Ti=C=C=Ti core[34] is formed via the reaction shown in eq 1. A monophosphine olefin adduct is formed initially, but the mechanism of its subsequent conversion to the Ti=C=C=Ti species is not known. The product is also formed in low yield (∼20%) by reducing $Cp_2(Cl)Ti{-}C{\equiv}C{-}TiCp_2Cl$ with magnesium in the presence of trimethylphosphine. The α carbon atom resonance was found at 258.1 ppm, and the Ti=C bond length was found to be 2.051(2) Å.



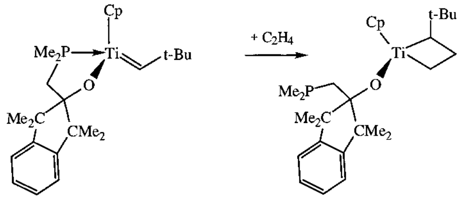
(1)

The dineopentyl complex, $CpTi(CH_2CMe_3)_2[OC(t\text{-}Bu)_2(CH_2PPh_2)]$, was found to decompose readily to give the neopentylidene complex shown in eq 2.[35] It could be identified in solution only, since it was



(2)

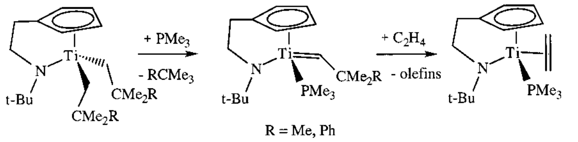
transformed into the neopentyl complex by CH activation. The latter was isolated in pure form in one instance and shown to revert to the neopentylidene complex (an α abstraction reaction), and an equilibrium between the two was reestablished. In a subsequent paper[36] it was reported that the neopentylidene complex shown in eq 3 could be isolated



(3)

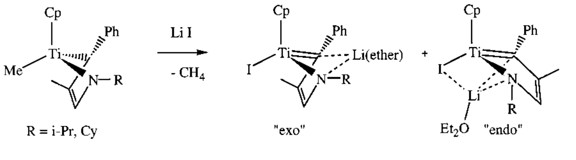
because CH activation did not take place in a PMe_2 group. An X-ray structure showed that Ti=C = 1.911(3) Å and Ti=C−C = 158.7(2)°. The neopentylidene complex was shown to react with ethylene to give a titanacyclobutane complex, which upon heating decomposed to yield an ethylene complex and organic products from rearrangement of titanacyclobutane rings by a β hydride process. No sustained olefin metathesis activity was found.

α Hydrogen abstraction has been induced in the dineopentyl and dineophyl complexes that contain the amido/Cp ligand shown in eq 4.[37] The neopentylidene and neophylidene complexes are inactive for ring-opening metathesis polymerization (ROMP) of norbornene, although they do react with ethylene to give olefinic products that result from rearrangement of an intermediate titanacyclobutane complex and an ethylene complex.



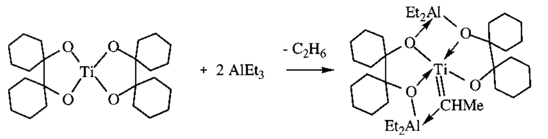
(4)

The α hydrogen abstraction reaction shown in eq 5 is probably induced by coordination of iodide to the metal.[38] Two isomers are formed that were shown in X-ray studies to be the "exo" and "endo" LiI adducts of the TiC_3N metallacycle (Ti=C = 1.958(3) and 1.979(3) Å, respectively).



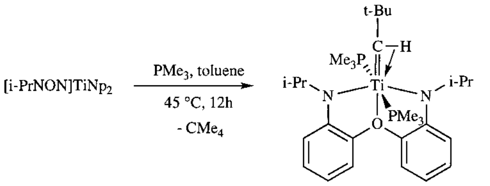
(5)

Several titanium alkylidene complexes have been isolated that do not contain a cyclopentadienyl ring.[39] The reaction shown in eq 6 yielded the first noncyclopentadienyl titanocene alkylidene complex, which is stabilized by coordination of the alkylidene to aluminum. It is interesting to note that α hydrogen abstraction takes place in the presence of β protons. Two isomers are observed in solution. The reaction of this species with 3,3-diphenylcyclopropene yields a new alkylidene (identified in solution only) that is formed by addition of the cyclopropene to the metal and subsequent opening of the titanacyclobutane ring. An X-ray study of the ethylidene complex showed Ti=C = 1.933(6) Å and Ti=C−C = 134.5(5)°.



(6)

Heating [i-PrNON]Ti$(CHCMe_3)_2$ ([i-PrNON]$^{2-}$ = [(i-PrN−*o*-$C_6H_4)_2O]^{2-}$) in the presence of excess PMe_3 produced the neopentylidene complex shown in eq 7 as green-black crystals in ~50% yield.[40] The alkylidene proton appears at ~3 ppm, which is characteristic of an alkylidene in which there is a significant agostic $CH_α$ interaction. The value for J_{CH} (80 Hz) is also consistent with a significant agostic interaction, as is the relatively short Ti=C bond (1.884(4) Å) and essentially linear Ti=C−C angle (179.3(3)°). NMR spectra are characteristic of a molecule that contains two mirror planes, so the alkylidene must rotate freely about the Ti−C bond.

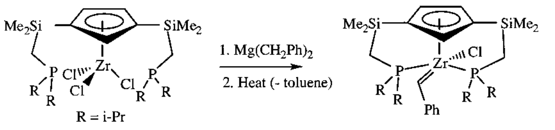


(7)

A dimeric complex that contains a *meso*-octaethylporphyrinogen tetraanion ($[Et_8N_4]^{4-}$) on each metal and a Ti=C=C=Ti core has been prepared by reduction of $Ti[Et_8N_4](THF)_2$ with lithium in the presence of ethylene.[41] Two lithiums are coordinated to the carbon atoms in the core of $\{[Et_8N_4]Ti{=}C{=}C{=}Ti[Et_8N_4]\}^{4-}$. There is some ambiguity as to the exact nature of the two-carbon bridging unit, i.e., whether it is a Ti=C=C=Ti or a Ti−C≡C−Ti species.

2.1.2. Zirconium

Alkylidene complexes of Zr have been prepared by treating $(CpP_2)ZrCl_3$ (where the CpP_2 is $[\eta^5\text{-}1,3\text{-}(i\text{-}Pr_2PCH_2SiMe_2)_2C_5H_3]^{2-}$) with alkylating agents (benzyl, neopentyl, trimethylsilylmethyl). The first alkylidene to be isolated was a benzylidene complex in 85% yield (eq 8).[42] NMR data and an X-ray study suggest that the benzylidene ligand is distorted through an agostic interaction with the metal. The α hydrogen was located in the X-ray structure, and the Zr=C−H angle was found to be 79.8(23)° (Zr=C = 2.024(4) Å). The reaction was shown to proceed via decomposition of $(CpP_2)Zr(CH_2Ph)_2Cl$ with $\Delta H^{\ddagger} = 19(1)$ kcal/mol and $\Delta S^{\ddagger} = -22(5)$ eu. Analogous reactions between $(CpP_2)ZrCl_3$ and $LiCH_2EMe_3$ (E = C or Si) led to analogous trimethylsilylmethylene and neopentylidene complexes in increasingly slower reactions.[43] Only the trimethylsilylmethylene complex could be isolated (Zr=C = 2.015(9) Å, Zr=C−C = 164.3(6)°). The ease with which the alkylidenes form follows the trend benzyl > trimethylsilylmethyl > neopentyl, the reverse of the trend in all other known circumstances involving α hydrogen abstraction. These alkylidene complexes were shown to react with ethylene to yield the products of rearrangement of intermediate zirconacyclobutane complexes.[44] They also react with acetone in a Wittig-like manner and with CO and t-BuNC.



(8)

2.1.3. Hafnium

The first example of a hafnium alkylidene complex has appeared recently.[45] The reaction between $(CpP_2)HfCl_3$ and benzyl potassium yielded a mixture of species, among them $(CpP_2)Hf(CH_2Ph)_3$ and $(CpP_2)Hf(CH_2Ph)Cl_2$. Although $(CpP_2)Hf(CH_2Ph)_2Cl$ could not be identified in the mixture, it is likely to be formed and to decompose to $(CpP_2)Hf(CHPh)Cl$ upon heating the mixture to 95 °C for 6 days. An X-ray study showed $(CpP_2)Hf(CHPh)Cl$ to be analogous to the zirconium species above with a Hf═C bond length of 1.994(4) Å and a Hf═C−C angle of 170°, characteristic of an α agostic interaction. The α hydrogen in the benzylidene ligand was found at 7.33 ppm and the α carbon at 210 ppm.

Although the bis(iminodiphenylphosphorano)methylene species of all three group 4 metals have been prepared, these carbenoid derivatives contain two phosphorus nuclei directly bound to the carbenoid carbon.[46−48] Therefore, they are heavily stabilized and do not fall in the same category as alkylidenes with which we are concerned here.

2.1.4. Theory of Group 4 Metals

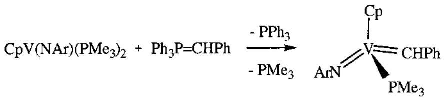
Several theoretical studies have addressed some aspect of the decomposition of group 4 metal alkyl complexes. The unimolecular and bimolecular decompositions of $TiMe_4$ and $Ti(CH_2CMe_3)_4$ have been addressed using ab initio molecular orbital theory.[49] A high barrier for unimolecular elimination of methane from $TiMe_4$ was found, while a low barrier toward bimolecular elimination of methane was found. For $Ti(CH_2CMe_3)_4$ intramolecular α hydrogen abstraction was favored over γ abstraction. The analogous Zr and Hf tetraalkyls were studied by similar methods.[50] $HfMe_4$ was found to be the most likely of the three to decompose intramolecularly, while $ZrMe_4$ had the lowest barrier of the three toward bimolecular elimination of methane. Intramolecular abstraction of a γ hydrogen was found to be relatively facile for Zr and Hf. An experimental study of the decomposition of $Zr(CD_2CMe_3)_4$ supported a mechanism in which γ hydrogen abstraction is the first step of the thermolysis.

Local and nonlocal DFT theory was used to study olefin metathesis by $Cp_2Ti{=}CRR'$ species.[51] The predicted geometries of metallacyclobutane complexes and barriers for olefin exchange in general agreed with experimental results. No compelling evidence was found for a local minimum corresponding to a titanium/alkylidene/olefin complex, consistent with all prior calculations on metal-assisted 2 + 2 insertions.

2.2. Group 5 Metals

2.2.1. Vanadium

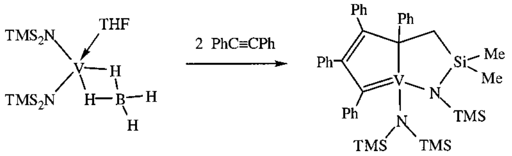
Transfer of a benzylidene from phosphorus to vanadium(III) proved to be a successful route to the first V(V) alkylidene complex (eq 9; Ar = 2,6-i-$Pr_2C_6H_3$).[52] An X-ray study showed the benzylidene



(9)

ligand to be relatively undistorted (V═C = 1.922(6) Å, V═C−C = 136.9(4)°), as one might expect from the 18-electron count in this V(V) species. (In comparison, the V═C−C angle in $CpV(CHCMe_3)(dmpe)$[53] was found to be 173.3(3)°, which is characteristic of a significant α agostic interaction in this reduced species.) No reaction between $CpV(CHPh)(NAr)(PMe_3)$ and norbornene or acetone was observed.

The reaction between the V(III) borohydride complex shown in eq 10 and diphenylacetylene yielded a



(10)

V(V) species in which there is a V═C double bond formally.[54] An X-ray structure showed the V═C bond length to be 1.876(7) Å. A mechanism for this reaction was not offered, but probably at some stage it involves a relatively common coupling of two diphenylacetylene units on V(III) to give a V(V) species.

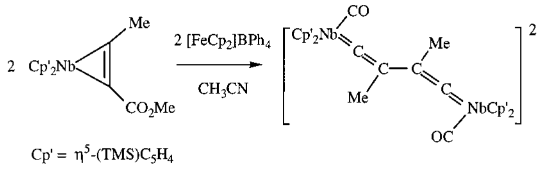
2.2.2. Niobium

One-electron oxidation of the biscyclopentadienyldibenzylniobium(IV) complex shown in eq 11 with silver ion led to a cationic Nb(V) benzylidene complex.[55] Presumably the cationic Nb(V) dibenzyl com-

$$[\eta^5\text{-(t-Bu)}C_5H_4]_2Nb(CH_2Ph)_2 \xrightarrow[-\text{Ag}\,-\,\text{toluene}]{+\text{Ag}^+/\text{THF}} \{[\eta^5\text{-(t-Bu)}C_5H_4]_2Nb(CHPh)(THF)\}^+ \quad (11)$$

plex is the intermediate species in which α hydrogen abstraction takes place, perhaps induced by coordination of THF.

Attempts to oxidize niobium alkyne complexes led to the unusual bimetallic vinylidene complex shown in eq 12.[56] The reaction is proposed to involve

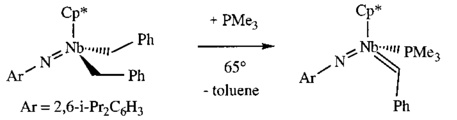


(12)

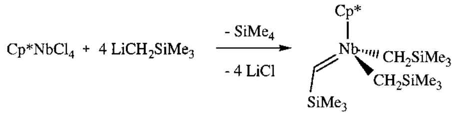
formation of the intermediate acetylide complex [Cp′2-

Nb(C≡CMe)(CO)]$^+$ (after loss of “MeO” in some manner; Cp′ = η^5-$Me_3SiC_5H_4$), which undergoes a coupling through the β carbon atoms, the metal being oxidized from Nb(IV) to Nb(V) in the process. An X-ray study established that Nb=C = 2.001(2) Å and Nb=C−C = 173.0(2)°.

A niobium complex analogous to the vanadium complex shown in eq 9 was prepared by a trimethylphosphine-induced α hydrogen abstraction reaction (eq 13).[57−59] Monocyclopentadienylniobium trimethylsilylmethylene complexes also have been prepared via α hydrogen abstraction reactions such as that shown in eq 14.[60]

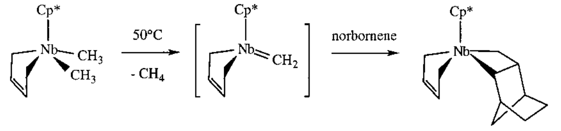


(13)



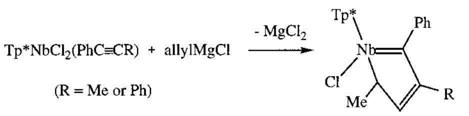
(14)

The dimethyl complex Cp*(η^4-C_4H_6)$NbMe_2$ was found to be thermally unstable.[61] It decomposed at 50 °C to give a transient methylene species, which could be trapped with norbornene to give a metallacyclobutane complex in 32% isolated yield (eq 15). It was characterized in an X-ray study and shown to initiate the polymerization of norbornene. The methylene species was also trapped with acenaphthylene. Unlike the corresponding Ta dibenzyl system (see later), trimethylphosphine was not an adequate trap for the alkylidene intermediate, perhaps because trimethylphosphine is too labile to prevent further intermolecular decomposition.



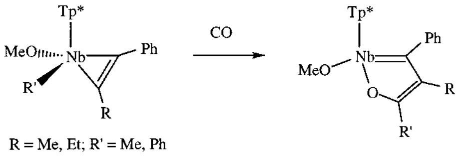
(15)

The reaction between Tp*$NbCl_2$(PhC≡CR) (R = Me or Ph; Tp* = tris(3,5-dimethylpyrazolyl)borate) and allylMgCl was shown to give a low yield (∼25%) of compounds of the type shown in eq 16, as shown in an X-ray study of that in which R = Ph (Nb=C = 1.993(4) Å).[62] The reaction was proposed to proceed via regioselective allyl/alkyne coupling followed by a rearrangement involving a 1,3 hydrogen shift.



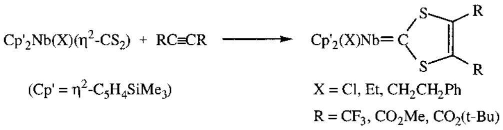
(16)

The reaction between the Nb(III) alkyne complexes shown in eq 17 and carbon monoxide led to a cyclic alkylidene species.[63] A plausible mechanism involves an acyl alkyne intermediate followed by the regioselective coupling of the acyl and alkyne ligands. An X-ray study showed the Nb=C double bond length to be 1.983 Å.



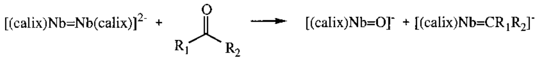
(17)

Reactions between Nb(III) carbon disulfide adducts and various alkynes yielded the dithiocarbene species shown in eq 18.[64] It is not clear whether this type of carbene in this circumstance should be viewed as a dianionic “alkylidene” ligand bound to Nb(V) or as a neutral carbene bound to Nb(III). These are rare examples of what could be called heteroatom-substituted carbenes bound to a d^2 metal center.



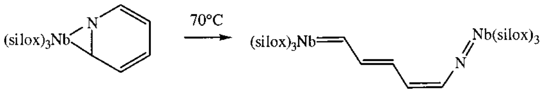
(18)

Significant progress has been made in the chemistry of (calix[4]arene)$^{4-}$ complexes of niobium, which are proposed models for organometallic chemistry on silica surfaces.[65] Anionic Nb(V) complexes were prepared by the unusual bimetallic cleavage of a carbon−oxygen bond in $R_1R_2C{=}O$ (R_1/R_2 = Ph/Ph, Ph/Me, Ph/CH_2Ph, Pr/H, Cp_2Fe/Me, or $(CH_2)_4$), as shown in eq 19. An analogous [(calix)Nb(CHPh)]$^-$ species was prepared by deprotonation of (calix)Nb(CH_2Ph). X-ray structures of [(calix)Nb(CHPh)]$^-$ and [(calix)Nb[C(Cp_2-Fe)Me)]$^-$ confirmed their proposed nature (Nb=C = 1.965(3) and 1.954(2) Å, respectively).



(19)

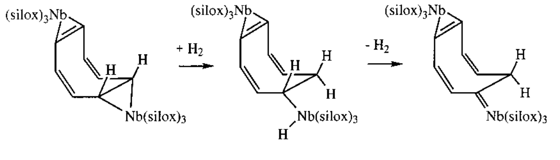
Decomposition of the Nb(III) η^2-pyridine complex shown in eq 20 at 70 °C yields a bimetallic alkylidene/imido complex in modest yield.[66] Several isomers were observed and found to interconvert with time through isomerization of the double bonds. The bonds that isomerized most readily were those nearest Nb. An X-ray study of the trans and cis derivatives showed Nb=C = 1.945(10) Å and Nb=C−C = 128.8(8)°.



(and isomers)

(20)

Further study of the niobium silox system revealed that the bimetallic alkene/alkyne complex shown in eq 21 rearranges to the bimetallic alkylidene/alkyne complex upon heating.[67] The reaction was shown to be catalyzed by molecular hydrogen, and the intermediate alkyl hydride complex could be isolated. An X-ray study confirmed the nature of the final product (Nb=C = 1.971(10) Å). It was also found that



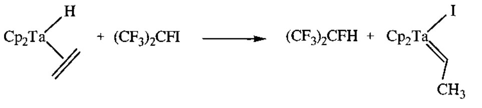
(21)

(silox)$_3$Nb(cyclohexene) rearranged to (silox)$_3$Nb(cyclohexylidene) after 13 days at 85 °C and that (silox)$_3$Nb(1-butene) rearranged to (silox)$_3$Nb(1-butylidene) in 8.5 h at 155 °C. The mechanism or mechanisms are not yet known, and it is also not known what factor or factors tip the energetic balance in favor of the alkylidene. These unusual findings lend credence to the possibility that alkylidene complexes might be able to form directly from olefin complexes and reduced metal complexes under some circumstances.

2.2.3. Tantalum

The reaction between Ta(CH$_2$SiMe$_3$)$_3$Cl$_2$ and 2 equiv of Me$_3$SiCH$_2$MgCl was found to give Ta(CH$_2$SiMe$_3$)$_5$, which could be isolated as yellow crystals from hexane at −78 °C.[68] At a concentration of 0.06 M, Ta(CH$_2$SiMe$_3$)$_5$ was found to decompose in hexane (52 °C, 45 min) to give (Me$_3$SiCH$_2$)$_3$Ta(CHSiMe$_3$), which could be identified in solution by NMR. Solutions of (Me$_3$SiCH$_2$)$_3$Ta(CHSiMe$_3$) ($<$0.06M) were found to be stable at −20 °C for 1 month. The conversion of Ta(CH$_2$SiMe$_3$)$_5$ to (Me$_3$SiCH$_2$)$_3$Ta(CHSiMe$_3$) was found to be first order with $\Delta H^{\ddagger} = 21.6(1.4)$ kcal/mol and $\Delta S^{\ddagger} = -5(5)$ eu. Decomposition of (Me$_3$SiCH$_2$)$_3$Ta(CHSiMe$_3$) to [(Me$_3$SiCH$_2$)$_2$Ta(CSiMe$_3$)]$_2$ was found to be bimolecular with $\Delta H^{\ddagger} = 6.2(0.3)$ kcal/mol and $\Delta S^{\ddagger} = -61.6\ (0.8)$ eu. NMR evidence was obtained for Ta(CH$_2$CMe$_3$)$_5$, one of the possible intermediates in the original synthesis of (Me$_3$CCH$_2$)$_3$Ta(CHCMe$_3$).[2] It is believed that Ta(CH$_2$CMe$_3$)$_5$ rapidly decomposes to (Me$_3$CCH$_2$)$_3$Ta(CHCMe$_3$) after a relatively slow reaction (for steric reasons) between Ta(CH$_2$CMe$_3$)$_3$Cl$_2$ and an alkylating agent (even LiCH$_2$CMe$_3$) that leads to its formation. The thermochemistry of the decomposition of Ta(CH$_2$SiMe$_3$)$_5$ to give (Me$_3$SiCH$_2$)$_3$Ta(CHSiMe$_3$) by α hydrogen abstraction has been quantified.[69] After some necessary assumptions, the Ta=C bond dissociation energy was found to be 126(4) kcal/mol, which is almost twice the average Ta−C bond dissociation energy in Ta(CH$_2$SiMe$_3$)$_5$ (67(1) kcal/mol), which was also determined by thermochemical methods. Any Ta=C bond strength would include any α agostic interaction between the alkylidene and the metal, which may be significant in view of the value for J_{CH} (99.6 Hz) in (Me$_3$SiCH$_2$)$_3$Ta(CHSiMe$_3$). Despite the high Ta=C bond strength, the authors find that reaction of the alkylidene with ethylene to give a metallacyclobutane complex is almost a thermoneutral process, as is the reaction of the alkylidene with acetone to give an oxymetallacyclobutane intermediate.

The reaction between Cp$_2$Ta(H)(C$_2$H$_4$) and (CF$_3$)$_2$CFI gave the result shown in eq 22.[70] The analogous Nb compound could be observed by proton NMR (δH$_\alpha$ = 13.15 ppm), but it was too unstable to isolate. This result is related to the reaction between {Cp$_2$W(H)(C$_2$H$_4$)}$^+$ and iodine to give {Cp$_2$W(I)(CHMe)}$^+$.[71] An X-ray structure showed this complex to be similar to a variety of other alkylidene complexes in this general class; i.e., the plane of the alkylidene ligand lies perpendicular to the I−Ta−C plane with Ta=C = 2.024(11) Å and Ta=C−C = 140.9(12)°.



(22)

The reaction of Cp$_2$Ta(CH$_2$)(CH$_3$) with silanes has been reported (eq 23).[72] The reaction with t-Bu$_2$SiH$_2$

$$\mathrm{Cp_2Ta(CH_2)(CH_3) + t\text{-}Bu_2SiH_2 \xrightarrow{-CH_4} Cp_2Ta(H)[CHSi(H)(t\text{-}Bu)_2]} \quad (23)$$

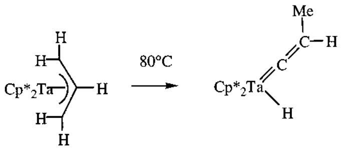
is believed to proceed via decomposition of Cp$_2$Ta(CH$_2$)(CH$_3$) to yield Cp$_2$Ta(CH$_2$CH$_2$)(CH$_3$) and "Cp$_2$Ta(CH$_3$)",[73] which then acts as a catalyst for formation of the product by reacting with (t-Bu)$_2$SiH$_2$ to give "Cp$_2$Ta[Si(H)(t-Bu)$_2$]". This intermediate then accepts a methylene from Cp$_2$Ta(CH$_2$)(CH$_3$), as shown in eq 24. Smaller silanes do not give analogous

$$\begin{aligned}&\mathrm{Cp_2Ta[Si(H)(t\text{-}Bu)_2] \xrightarrow[-\text{“}Cp_2Ta(CH_3)\text{”}]{+Cp_2Ta(CH_2)(CH_3)}}\\ &\qquad \mathrm{Cp_2Ta[Si(H)(t\text{-}Bu)_2](CH_2) \rightarrow}\\ &\qquad \mathrm{\text{“}Cp_2Ta[CH_2Si(H)(t\text{-}Bu)_2]\text{”} \rightarrow}\\ &\qquad\qquad \mathrm{Cp_2Ta(H)[CHSi(H)(t\text{-}Bu)_2]} \quad (24)\end{aligned}$$

alkylidene products. It was also shown that the reaction between Me$_3$P=CH$_2$ and Cp$_2$Ta(PMe$_3$)Ph or Cp$_2$Ta(PMe$_3$)[(Si(H)(t-Bu)$_2$] gave Cp$_2$Ta(CH$_2$)Ph or Cp$_2$Ta(CH$_2$)[Si(H)(t-Bu)$_2$], respectively, by methylene transfer. A qualitative comparison of the rate of migration of X groups in Cp$_2$Ta(CH$_2$)X to the methylene was argued to be H $>$ t-Bu$_2$SiH $\gg$ Ph $>$ Me. (Migration of a carbon-based group to a high oxidation state alkylidene is rarely observed.)

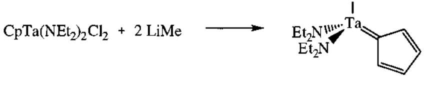
A convenient synthesis of Cp*$_2$TaCl(THF) has been reported.[74] Cp*$_2$TaCl(THF) reacts with LiCH$_3$ to give the previously known Cp*$_2$Ta(CH$_2$)(H)[75] and with Me$_3$P=CH$_2$ to give Cp*$_2$Ta(CH$_2$)Cl.

Heating Cp*$_2$Ta(η^3-C$_3$H$_5$) to 80 °C for 6 days led to formation of a single isomer of the propenylidene complex shown in eq 25.[76] The α carbon resonance of the propenylidene complex is found at 348 ppm. The reaction between Cp*$_2$TaH$_3$ and butadiene leads to several products, among them a single isomer of the analogous complex Cp*$_2$TaH[C=C(Et)H]. Cp*$_2$TaH[C=C(Me)H] was also formed in the reaction between Cp*$_2$TaH(C=CH$_2$) and Me$_3$P=CH$_2$ at 110 °C for 2 days, presumably via intermediate Cp*$_2$Ta(CH$_2$)(CH=CH$_2$).



(25)

The reaction shown in eq 26 gave rise to an unusual cyclopentadienylidene complex in low yield



(26)

(~10%).[77] No mechanism was offered. An X-ray study showed Ta=C = 2.037(4) Å.

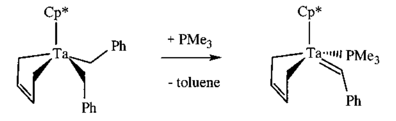
The reaction between $Cp'TaCl_4$ and 4 equiv of $LiCH_2SiMe_3$ (Cp' = Cp*, η^5-$(Me_3Si)C_5H_4$, or η^5-1,3-$(Me_3Si)_2C_5H_3$) produced complexes of the type $Cp'Ta(CHSiMe_3)(CH_2SiMe_3)_2$.[60] In the TaCp* complex the Ta=C and Ta−C bond lengths were found to be 1.920(6) and 2.165(7) Å, respectively, while Ta=C−C = 169.6(5)° and Ta−C−C = 126.9(3)°. Several reactions of $Cp^*Ta(CHSiMe_3)(CH_2SiMe_3)_2$ have been reported, among them a reaction with ArNC (Ar = 2,6-$Me_2C_6H_3$) to give the η^2-iminoacyl derivative $TaCp^*(CHSiMe_3)(CH_2SiMe_3)\{\eta^2\text{-}C(CH_2SiMe_3)=NAr\}$.[78]

Imido and alkylidene ligands were found to scramble intermolecularly, as shown in eq 27.[79] (A similar

$$CpTaCl_2(CHCMe_2Ph) + Cp^*TaCl_2(NAr) \rightleftarrows CpTaCl_2(NAr) + Cp^*TaCl_2(CHCMe_2Ph) \quad (27)$$

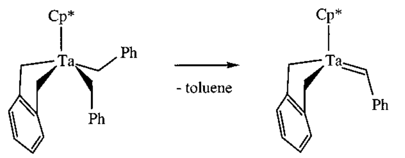
scrambling took place between Mo and W complexes.) The ability of an alkylidene ligand on Ta to migrate to another metal has been known since the original synthesis of high oxidation state group 6 oxo alkylidene complexes using $Ta(CHCMe_3)(PMe_3)_2Cl_2$ as the source of the alkylidene ligand.[80]

Benzylidene complexes that contain an η^4-C_4H_6 ligand (a tantalacyclo-3,4-pentene) could be prepared by trimethylphosphine-induced α hydrogen abstraction (eq 28).[81,82] The analogous Cp complex could be



(28)

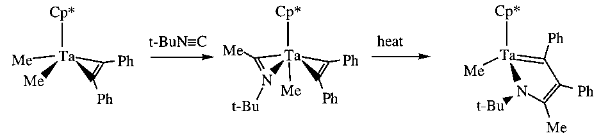
observed (δH_α = 10.52), but it was much less stable and could not be isolated. The analogous tantalacycle that contains a phenylene ring (eq 29) decomposed to yield a stable benzylidene complex in the absence of trimethylphosphine. The trimethylphosphine com-



(29)

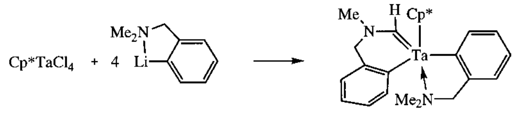
plex was found to be inactive for ROMP of norbornene at 65°, while the phosphine-free complex would readily polymerize norbornene. Several tantalacyclobutane products of reactions between $TaCp^*(\eta^4\text{-}C_4H_4\text{-}o\text{-}C_6H_4)(CHPh)$ and olefins were isolated, and one, the product formed upon adding acenaphthalene, was structurally characterized. For $TaCp^*(\eta^4\text{-}C_4H_4\text{-}o\text{-}C_6H_4)(CHPh)$, Ta=C = 2.180(9) Å and Ta=C−C = 164.8(7)°.

The reaction between the diphenylacetylene complex shown in eq 30 and *tert*-butylisonitrile yields the monomethyl species shown, which upon heating rearranges to the cyclic species containing a Ta=C bond.[83] An analogous reaction of the diphenylacetylene complex with carbon monoxide yielded an analogous species in which oxygen is found in place of the t-BuN moiety. The Ta=C bond length in the latter species was found to be 1.972(8) Å.



(30)

The reaction between Cp^*TaCl_4 and 4 equiv of Li[2-$(CH_2NMe_2)C_6H_4$] yielded the cyclic alkylidene complex shown in eq 31.[84] Intermediate species could be



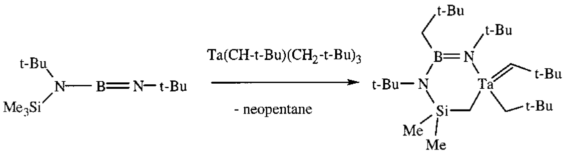
(31)

identified that supported the double stepwise CH activation of a methyl group on nitrogen by the tantalum aryl species. The chemical shifts of the proton (7.83) and carbon (227.8) seem normal, but J_{CH} is unusually large (170 Hz), perhaps as a consequence of the direct attachment of a nitrogen to the alkylidene carbon atom, which is a rare circumstance in a high oxidation state species.

The reaction between $Cp^*Ta(N=P\text{-}t\text{-}Bu)Cl_3$ and 3 equiv of $PhCH_2MgCl$ yielded the structurally characterized benzylidene complex, $Cp^*Ta(N=P\text{-}t\text{-}Bu)(CHPh)(CH_2Ph)$ in which Ta=C = 1.957(7) Å.[85] Two isomers are observed in solution (δH_α = 9.13 and 8.40 ppm; δC_α = 213.1 and 222.9 ppm). Addition of methyl iodide to $Cp^*Ta(N=P\text{-}t\text{-}Bu)(CHPh)(CH_2Ph)$ yielded the Ta(III) styrene complex $Cp^*Ta(N=P\text{-}t\text{-}Bu)(CH_2=CHPh)(CH_2Ph)$ in 19% yield presumably as a consequence of nucleophilic attack by the benzylidene ligand on methyl iodide followed by β hydride elimination.

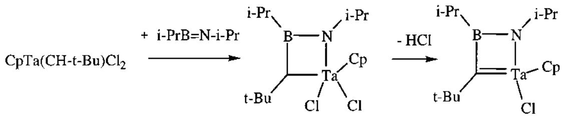
Tris(3,5-dimethylpyrazolyl)borate derivatives, $Tp^*Ta(CH\text{-}t\text{-}Bu)X_2$, can be prepared straightforwardly by adding KTp* to $Ta(CH\text{-}t\text{-}Bu)X_3(THF)_2$ (X = Cl or Br).[86] One of the chlorides can be substituted by OMe, O−i-Pr, or NMe_2 (Y) to yield derivatives of the type $TaTp^*(CH\text{-}t\text{-}Bu)Cl(Y)$. All are inert toward olefins and substituted alkynes.

Some new complexes have turned up in reactions between tantalum alkylidene complexes and iminoboranes. The reaction shown in eq 32 involves migration of a neopentyl group to boron followed by CH activation in a methyl group of the TMS group.[87] (An



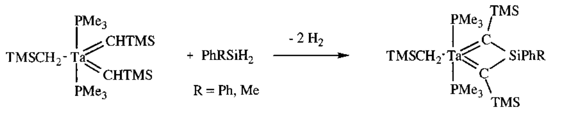
(32)

X-ray structure revealed Ta=C = 1.891(4) Å and Ta=C−C = 166.8(3)°.) In a related study shown in eq 33 dehydrohalogenation of the initial metallacycle formed by addition of the B=N bond to the Ta=C bond yields a cyclic alkylidene species in which Ta=C = 1.903(7) Å.[88]



(33)

Several new tantalum alkylidene complexes have been prepared in reactions involving silanes. Reactions between bisalkylidene complexes and silanes proceed as shown in eqs 34 and 35.[89,90] The reaction in eq 34 is essentially a double deprotonation by a hydridic reagent, while that in eq 35 overall involves addition of an Si−H bond across the Ta=C bond, followed by loss of trimethylphosphine and dihydrogen. These species could not be isolated. An X-ray study of the compound in eq 34 in which R = Me revealed Ta=C bond lengths of 1.947(12) and 1.962(12) Å. Deuterium labeling and kinetic studies were consistent with addition of Si−H across the Ta=C bond after initial loss of trimethylphosphine. More than one mechanism appeared to be operative after that point. An analogous reaction involving $PhH_2SiCH_2SiPhH_2$ yielded a bisalkylidene complex having a $SiCH_2Si$ link between the two alkylidene carbon atoms.[90]



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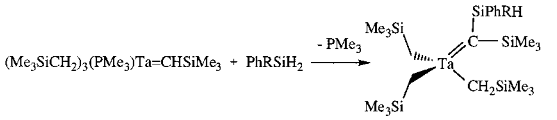
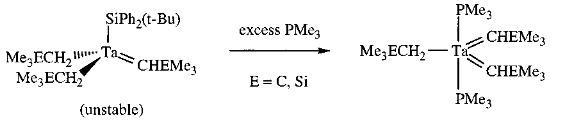


(35)

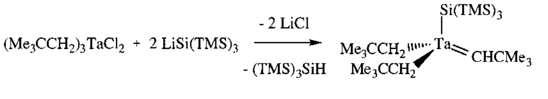
The reaction between $Ta(CH_2ECMe_3)_3Cl_2$ (E = C or Si) and $LiSiPh_2(t\text{-}Bu)$ gave unstable alkylidene complexes, which upon addition of trimethylphosphine yielded bisalkylidene complexes (eq 36).[91]



(36)

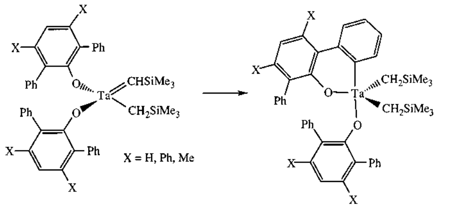
These are two of the few bisalkylidene complexes known to date.[6] An X-ray study of $Ta(CHSiMe_3)_2(CH_2SiMe_3)(PMe_3)_2$ (Ta=C = 1.998(8) Å and 1.95(2) Å; Ta=C−C = 133.7(5)° and 142.0(12)°) showed it to be similar to that of $Ta(CHCMe_3)_2(CH_2CMe_3)(PMe_3)_2$.[92]

The reaction between $LiSi(TMS)_3$ and $Ta(CH_2CMe_3)_3Cl_2$ was found to lead to the neopentylidene silyl complex shown in eq 37.[93] The reaction was proposed to proceed via formation of $(Me_3CCH_2)_3TaCl[Si(TMS)_3]$ followed by loss of $HSi(TMS)_3$ to give unobservable $(Me_3CCH_2)_2Ta(CHCMe_3)Cl$ and then further reaction with $LiSi(TMS)_3$ to give the observed product. Similar results were obtained upon treatment of $(Me_3SiCH_2)_3TaCl_2$ with $LiSi(TMS)_3$.[94] Addition of HCl to $Ta(CHSiMe_3)(CH_2SiMe_3)_2[Si(SiMe_3)_3]$ gave $Ta(CH_2SiMe_3)_3[Si(SiMe_3)_3]Cl$, a proposed intermediate. An X-ray structure of $Ta(CHCMe_3)(CH_2CMe_3)_2[Si(SiMe_3)_3]$ revealed a Ta=C distance of 1.97(5) Å and a Ta=C−C angle of 149(3)°. An X-ray structure of $Ta(CHSiMe_3)(CH_2SiMe_3)_2[Si(SiMe_3)_3]$ revealed a Ta=C distance of 2.03(4) Å and a Ta=C−C angle of 131.8(13)°.



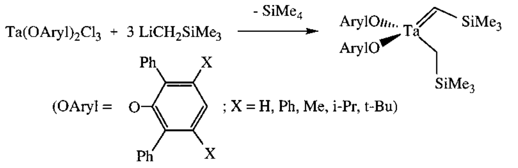
(37)

The reaction between $Ta(CH_2SiMe_3)_3Cl_2$ and 2 equiv of lithium aryloxide, $LiO{-}2,6\text{-}Ph_2{-}3,5\text{-}X_2C_6H$ (X = H, Ph, Me) gave $Ta(CH_2SiMe_3)_3(OAr'')_2$, which upon photolysis yields the alkyl alkylidene complex shown in eq 38.[95] The stability of the alkylidene complex varies dramatically with the nature of X. When X = H the half-life is ~11 h at 25 °C. The stability increases in the order X = Ph < Me, with the relative half-lives being 15 and 75 min, respectively, at 105 °C; the conversion at 105 °C when X = H is too fast to measure. Therefore, there is an increase in the stability of the alkylidene toward CH activation of about 2 orders of magnitude upon going from X = H to Me, which seems unusual given the fact that the X groups are in the 3 and 5 positions on the ring.



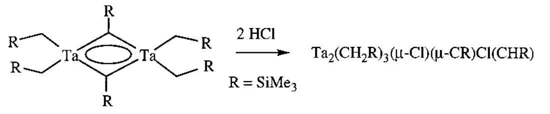
(38)

Trimethylsilylmethylenetantalum aryloxide complexes were prepared by the reaction shown in eq 39 or by photolysis of $Ta(OAryl)_2(CH_2SiMe_3)_3$.[96] Interestingly, in one case (OAr = $2,6\text{-}Ph_2C_6H_3$) photolysis of $Ta(OAryl)_3(CH_2SiMe_3)_2$ gave $Ta(OAryl)_2(CH_2SiMe_3)(CHSiMe_3)$, a rare example of α hydrogen abstraction by a heteroatom.



(39)

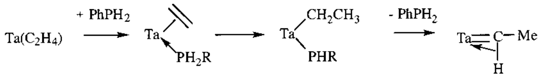
The reaction shown in eq 40 led to formation of an unstable dimeric species that was proposed to contain a bridging alkylidyne and a terminal alkylidene.[97] It was characterized by NMR methods only ($\delta H_\alpha = 4.68$; $\delta C_\alpha = 237.4$; $J_{CH} = 104$ Hz).



(40)

Several alkylidene complexes of tantalum that contain the $[(Me_3SiNCH_2CH_2)_3N]^{3-}$ ($[N_3N]^{3-}$) ligand have been prepared either by dialkylation of $[N_3N]TaCl_2$ (alkyl = CH_2SiMe_3, $CH_2CH_2CH_3$, $CH_2CH_2CHMe_2$, $CH_2CH_2CMe_3$, CH_2Ph) or by addition of $Li_3[N_3N]$ to $Ta(alkyl)_2Cl_3$ (alkyl = CH_2CMe_3, CH_2Ph).[98,99] The dialkyl complexes, $[N_3N]TaR_2$, are the presumed intermediates. When the alkyl is an ethyl, only $[N_3N]Ta(C_2H_4)$ is formed by β hydride abstraction; $[N_3N]Ta(CHMe)$ is not observed. As the alkyl group increases in size and as the β proton becomes less accessible, the yield of the alkylidene complex increases steadily until it reaches 75% for $[N_3N]Ta$-

($CHCH_2CHMe_2$). It was proposed that as the alkyl becomes larger and the β proton less accessible sterically, α abstraction becomes the favored process in the crowded coordination pocket. The ethylidene complex can be prepared by the phenylphosphine-catalyzed process shown in eq 41. This is a rare example of rearrangement of an olefin to an alkylidene ligand. In this case it is most likely favorable because of the strong α agostic interaction in all alkylidene complexes of this type, as suggested by the dramatically low values for J_{CH} (~75 Hz).



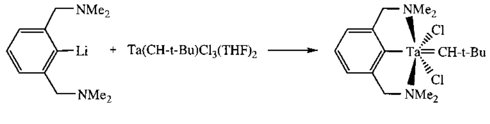
(41)

When the substituent in the triamidoamine ligand is $SiEt_3$ instead of $SiMe_3$ ($[N_3N^*]^{3-}$), then dialkylation of $[N_3N^*]TaCl_2$ yields alkylidene complexes in high yield as a consequence of even more sterically restricted β hydride abstraction versus α hydride abstraction.[100] $[N_3N^*]Ta(CHMe)$ can be observed in ~10% yield but could not be isolated, while other $[N_3N^*]Ta(CHR)$ species were formed in high yields (R = Et, Pr, i-Bu, Ph, $SiMe_3$). Attempts to prepare a divinyl species led to the mixture shown in eq 42,

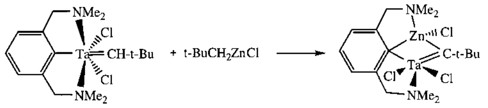
$$[N_3N^*]TaCl_2 \xrightarrow[\text{tol, 80 °C}]{2H_2C{=}CHMgBr} [N_3N^*]Ta(HC{\equiv}CH) + \{[N_3N^*]Ta{=}CHCH_2\}_2 \quad (42)$$

the first being the product of β abstraction and the second the product of proposed vinyl coupling in an intermediate Ta(IV) species, $[N_3N^*]Ta(CH{=}CH_2)$, which presumably is formed by reduction of intermediate $[N_3N^*]Ta(CHCH_2)Cl$. An X-ray structure of $\{[N_3N^*]Ta{=}CHCH_2)\}_2$ confirmed the short Ta=C bonds (1.947(12) and 1.962(12) Å) and large Ta=C−C angles (172.1(12)° and 173.1(12)°) typical of alkylidenes with a significant α agostic interaction.

The octahedral complex shown in eq 43 is prepared straightforwardly from the aryllithium reagent and $Ta(CH{-}t\text{-}Bu)Cl_3(THF)_2$.[101,102] An X-ray study revealed that the neopentylidene ligand is distorted toward a linear Ta=C−C arrangement (Ta=C = 1.938(4) Å, Ta=C−C = 170.6(3)°), which is characteristic of an alkylidene having a significant α agostic interaction, a conclusion that is supported by NMR data. The α hydrogen was located, and the Ta=C−H angle was shown to be 71(3)°. This compound undergoes typical Wittig-like reactions with carbonyl compounds and imines and reacts with ethylene and propylene readily to give products formed by rearrangement of intermediate tantalacyclobutane complexes. Addition of *tert*-butoxide or methoxide gives TBP monoalkoxide derivatives, while a di-*tert*-butoxide derivative can be formed by treating $Ta(CH{-}t\text{-}Bu)Cl(O{-}t\text{-}Bu)_2(PMe_3)$ with the lithium aryl.[103] $Ta(CH{-}t\text{-}Bu)[NCN]Cl(O{-}t\text{-}Bu)$ (where $[NCN]^-$ is $[2,6\text{-}(CH_2NMe_2)_2C_6H_3]^-$) was found to react with vinyltrimethylsilane to yield $Ta(CHSiMe_3)[NCN]Cl(O{-}t\text{-}Bu)$, the product of a metathesis reaction. An X-ray structure of $Ta(CH{-}t\text{-}Bu)[NCN](O{-}t\text{-}Bu)_2$ showed that the alkylidene was significantly less distorted (Ta=C−C = 159.5(4)°; Ta=C = 1.914(4) Å) than in the dichloride compound, consistent with a less electrophilic metal center being present. Addition of neopentylzinc chloride to $Ta(CH{-}t\text{-}Bu)[NCN]Cl_2$ yielded a species having an alkylidyne and an aryl bridging between Ta(III) and zinc (eq 44).[104,105]

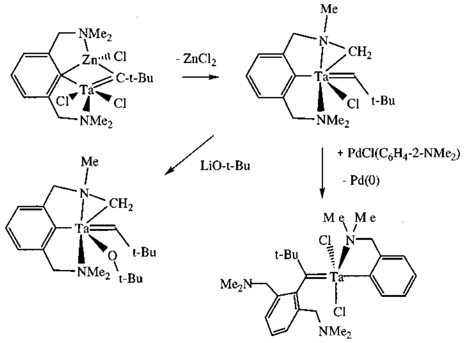


(43)



(44)

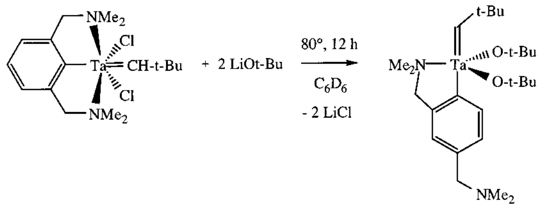
Removal of zinc chloride led to CH activation in a dimethylamido methyl group (eq 45). If $Pd(C_6H_4{-}2{-}CH_2NMe_2)Cl$ is also present, then an unusual disubstituted alkylidene is formed by migration of the aryl group to the neopentylidyne α carbon atom.



(45)

The reaction between $Ta(CH_2CMe_2Ph)(THF)_2Cl_3$ and $ClZnCH_2CMe_2Ph$ results in formation of *tert*-butylbenzene and $Ta(CCMe_2Ph)Cl_2(THF)_2[ZnCl_2(THF)]$, in which the "neophylidyne" ligand bridges between Ta and Zn.[106]

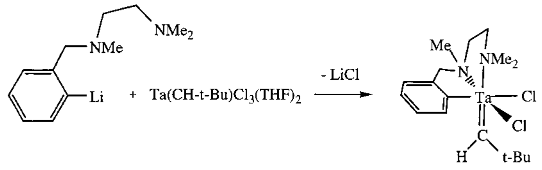
An attempt to add two *tert*-butoxides to the alkylidene complexes shown in eq 46 led to a rearrangement of the 2,6-disubstituted aryl ligand to a 2,4-disubstituted aryl ligand.[107] The rearrangement was proposed to proceed in the mono-*tert*-butoxide chloride complex (on the basis of labeling experiments) by α abstraction from the neopentylidene to give a neopentylidyne intermediate (not observable) followed by readdition of a comparable aryl CH bond across the Ta≡C bond. Two isomers of the mono-*tert*-butoxide complex were found, which were proposed to contain two different orientations of the alkylidene ligand. The two isomers were found to interconvert at a rate observable on the NMR time scale. In $Ta(CH{-}t\text{-}Bu)[2,4\text{-}(CH_2NMe_2)_2C_6H_3](O{-}t\text{-}Bu)Cl$ the Ta=



(46)

C bond length was found to be 1.962(7) Å and the Ta=C−C angle 140.7(5)°.

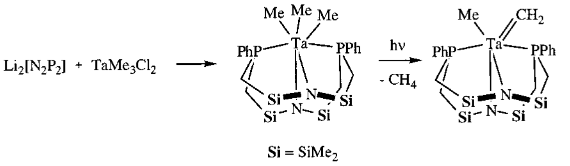
Success with the "NCN" ligand created an interest in the related "CNN" ligand shown in eq 47.[108] The



(47)

reaction produced three isomers, one of which could be isolated and crystallographically characterized. In the overall octahedral complex Ta=C = 1.860(11) Å, Ta=C−C = 168.9(9)°, and Ta=C−H = 77(5)°. The related dialkoxide complex, Ta(CH−t-Bu)[CNN](O−t-Bu)$_2$ could be prepared by treating Ta(CH−t-Bu)-Cl(O−t-Bu)$_2$(PMe$_3$) with LiCNN, although Ta(CH−t-Bu)[CNN](O−t-Bu)$_2$ could not be prepared by treating the dichloride complex with LiO−t-Bu. NMR spectra of both the dichloride and di-*tert*-butoxide species were complicated by the formation of isomers and by fluxional processes. For the major isomer of each, the value of J_{CH} for the alkylidene ligand was found to be quite low (~75 Hz), characteristic of an agostic interaction with the metal. Ta(CH−t-Bu)-[CNN]Cl$_2$ does not react readily with ethylene, but Ta(CH−t-Bu)[CNN](O−t-Bu)$_2$ reacts with ethylene to produce the tantalacyclobutane complex, Ta(C$_3$H$_6$)-[CNN](O−t-Bu)$_2$, and (at higher temperatures) the ethylene complex, Ta(C$_2$H$_4$)[CNN](O−t-Bu)$_2$. The bis-*tert*-butoxide complex is also active for ROMP. The higher reactivity of the bis-*tert*-butoxide complex can be attributed to the formation of a five-coordinate intermediate by dissociation of the dimethylamino group from the metal.

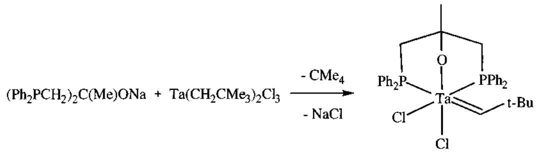
The bisamidobisphosphine ligand shown in eq 48 was employed in order to stabilize a trimethyltantalum species, which subsequently could be photolyzed to yield a methylene species.[109] A cationic dimethyl



(48)

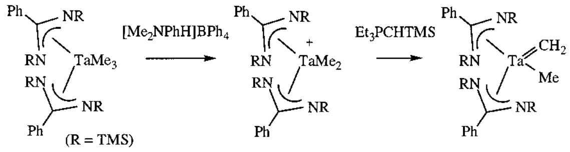
species, {[N$_2$P$_2$]TaMe$_2$}$^+$, could be prepared if a relatively unreactive anion (B(C$_6$F$_5$)$_4$]$^-$) is employed, but the cation could not be deprotonated successfully to yield [N$_2$P$_2$]Ta(CH$_2$)Me. It is relatively rare to find that a methylene species can be isolated at all in a thermal or photochemical α hydrogen abstraction reaction, since subsequent decomposition of the methylene complex is often relatively facile. An X-ray structure revealed Ta=C = 2.09(2) Å and Ta−C = 2.21(2) Å. The methylene complex decomposes in the presence of ethylene to [N$_2$P$_2$]Ta(C$_2$H$_4$)Et, with [N$_2$P$_2$]-Ta(C$_2$H$_4$)Me being observed as a minor product.[110] A mechanistic study suggests that the ethyl group in [N$_2$P$_2$]Ta(C$_2$H$_4$)Et forms by migration of the methyl to the methylene ligand, a relatively rare type of reaction for a high oxidation state species.

The reaction between the alkoxide shown in eq 49 and Ta(CH$_2$CMe$_3$)$_2$Cl$_3$ yielded the octahedral neopentylidene complex shown (Ta=C = 1.932(7) Å and Ta=C−C = 152.7(5)°).[35] A bisamidinate trimethyl com-



(49)

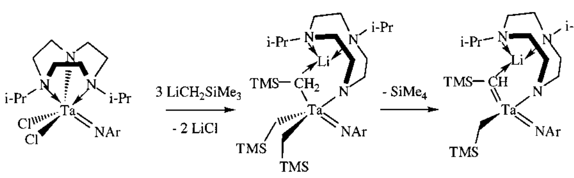
plex of tantalum was protonated to yield methane and a dimethyl cation, which was subsequently deprotonated to yield the methylene complex shown in eq 50.[111] The reaction between Ta(CH$_2$Ph)$_3$Cl$_2$ and



(50)

2 equiv of Li[PhC(NTMS)$_2$] yielded Ta(CH$_2$Ph)$_3$[PhC-(NTMS)$_2$]Cl only. This species could be dehydrohalogenated with LiN(TMS)$_2$ to give Ta(CH$_2$Ph)$_2$-(CHPh)[PhC(NTMS)$_2$].

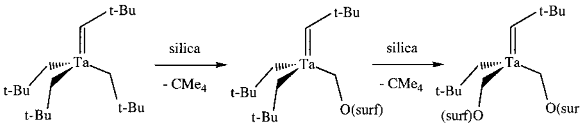
The addition of 3 equiv of LiCH$_2$SiMe$_3$ to the anionic triazacyclononanetantalum imido complex shown in eq 51 yielded an anionic trialkyl complex that decomposed upon heating to give the lithium adduct of the anionic alkylidene complex.[112] The



(51)

reaction was found to proceed in a unimolecular manner between 50 and 100 °C with $\Delta H^{\ddagger} = 109(2)$ kJ mol^{-1} and $\Delta S^{\ddagger} = -11.9(1)$ J mol^{-1} K^{-1}. An X-ray study showed the Ta=C bond length to be 1.93(3) Å, versus a Ta−C bond length of 2.24(3) Å. The alkylidene complex has been shown to react with a ketone in a Wittig-like fashion and with carbon monoxide to give a ketene complex.[113] Complexes also were prepared that contained the alkylidene bridging between Ta and Rh or Fe.

The addition of Ta(CH−t-Bu)(CH$_2$−t-Bu)$_3$ to a partially dehydroxylated silica surface has been shown through solid-state NMR studies to yield an alkylidene attached to the surface through one or two Si−O linkages (eq 52).[114] Labeling studies with



(52)

deuterated silica supported the proposal that Si−OH-(D) adds first across the Ta=C bond followed by random α hydrogen abstraction in the intermediate neopentyl species. The supported tantalum alkylidene species is hydrolyzed to give the expected amount of neopentane and reacts with acetone to give the expected amount of the Wittig-like product.

The addition of Li[NPN] ($[NPN]^- = [\{(i\text{-}Pr)_2NCH_2SiMe_2\}_2N]^-$) to dibenzyl and dineopentyltantalum trichloride yielded the benzylidene and neopentylidene complexes shown in eq 53.[115] Two-electron

$$\underset{R = Ph,\ t\text{-}Bu}{Ta(CH_2R)_2Cl_3} \xrightarrow[-\ LiCl]{+Li[NPN]} (NPN)Cl_2Ta{=}CHR \xrightarrow[\text{under } N_2]{2Na/Hg} 0.5[(NPN)Ta(CHR)]_2(\mu\text{-}N_2) \quad (53)$$

reduction of these species under dinitrogen yielded the alkylidene complexes that contain a μ-dinitrogen ligand that has been reduced to the $[N_2]^{4-}$ level. Although no X-ray structure was performed, these complexes could be identified by analogy with similar so-called hydrazido(4−) species in the literature.[116,117]

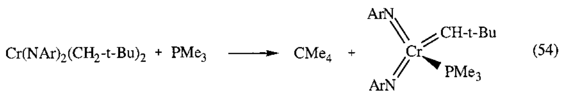
2.2.4. Theory of Group 5 Metals

Methane elimination in MMe_5 complexes (M = Nb or Ta) has been studied with the aid of ab initio quantum mechanics calculations.[118] The most favorable transition structure for unimolecular methane elimination is close to a trigonal bipyramid, although a bimolecular mechanism was found to be much more favorable than the unimolecular mechanism.

2.3. Group 6 Metals

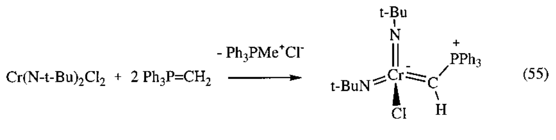
2.3.1. Chromium

The first stable chromium(VI) alkylidene complex was prepared via the α hydrogen abstraction reaction shown in eq 54.[119] In the absence of PMe_3, benzene-



d_6 adds across the Cr═C bond in proposed intermediate $Cr(NAr)_2(CH{-}t\text{-}Bu)$ to give $Cr(NAr)_2(CHD{-}t\text{-}Bu)(C_6D_5)$. None of the Cr(VI) neopentylidene complexes, including proposed intermediate $Cr(NAr)_2(CH{-}t\text{-}Bu)$, reacts with ethylene or norbornene to give metathesis-like products.

The compound shown in eq 55 is technically a deprotonated ylide complex rather than an alkylidene of the type we are reviewing here.[120] Related complexes of Mo, W, and Re are also known.[121]



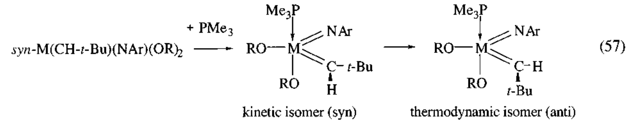
2.3.2. Molybdenum

Complexes of the type $Mo(CHR)(NR')(OR'')_2$ normally are synthesized via the sequence of reactions shown in eq 56. In a paper devoted to exploring

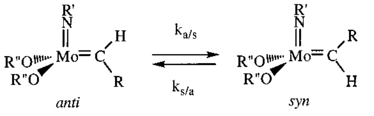
$$Mo(NR')_2(CH_2R)_2 \xrightarrow[-R'NH_3OTf\ -\ CH_3R]{3HOTf} Mo(NR')(CHR)(OTf)_2(dme) \xrightarrow[-2LiOTf\ -\ dme]{2LiOR''} Mo(NR')(CHR)(OR'')_2 \quad (56)$$

variations,[122] various $Mo(CHR)(NR')(OTf)_2(dme)$ (R = CMe_3, CMe_2Ph) complexes were prepared (Table 1) and from them various $Mo(CHR)(NR')(OR'')_2$ species. The synthesis of $Mo(CHCMe_2Ph)(NAr)[OCMe(CF_3)_2]_2$ has been published in a book devoted to synthetic methods of organometallic and inorganic chemistry.[123]

One paper was concerned with the formation of base adducts of imidoalkylidene complexes, syn and anti isomers, and alkylidene ligand rotation.[124] Trimethylphosphine was found to add to the CNO face of $M(CH{-}t\text{-}Bu)(NAr)[OCMe(CF_3)_2]_2$ complexes (M = Mo or W) to give a kinetic syn isomer first and with time, via dissociation of trimethylphosphine, the thermodynamic anti isomer (eq 57). The structures of the two Mo complexes were confirmed in X-ray studies, although the structure of the anti isomer could not be solved completely. (In *syn*-$Mo(CH{-}t\text{-}Bu)(NAr)[OCMe(CF_3)_2]_2(PMe_3)$, Mo═C = 1.878(9) Å and Mo═C−C = 156.3(8)°.) Analogous adducts could be isolated when OR = $OCMe_2(CF_3)$, but when OR = O−t-Bu, the adducts were too labile to isolate as a consequence of the metal not being electrophilic enough. Quinuclidine adducts and a pyridine adduct also were prepared (see Table 1). Reactions between $M(CH{-}t\text{-}Bu)(NAr)[OCMe(CF_3)_2]_2$ species and $CH_2{=}CHCH{=}CHMe$ produced $M(CHCH{=}CHMe)(NAr)[OCMe(CF_3)_2]_2$, quinuclidine adducts of which could be isolated. An X-ray structure of *syn*-W(*trans*-$CHCH{=}CHMe)(NAr)[OCMe(CF_3)_2]_2$(quinuclidine) was shown to contain the quinuclidine in the apical position in a trigonal bipyramid (TBP), with the imido and alkylidene ligands in equatorial positions (W═C = 1.942(6) Å and W═C−C = 126.3(5)°). A third isomer containing a mirror plane was also observed in several cases and was proposed to be the adduct formed by addition of quinuclidine to the COO or NOO face of the pseudotetrahedral complex. Barriers to rotation of the alkylidene about the M═C bond in several four-coordinate species (M = Mo or W; CHR = $CHSiMe_3$, $CHCMe_3$, or $CHCMe_2Ph$; OR = a phenoxide) were shown to lie in the range of $\Delta G^\ddagger$ (298) = 15−18 kcal/mol with $\Delta S^\ddagger$ usually being within 5 eu of 0. Alkylidene rotation in five-coordinate base adducts requires loss of base.

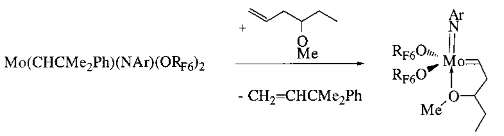


The interconversion of syn and anti alkylidene isomers and their relative reactivity has been explored.[125,126] Low-temperature (−85 °C) photolysis of complexes of a variety of Mo(usually) or W of the type *syn*-$M(CHR)(NR')(OR'')_2$ in THF-d_8, toluene-d_8, or methylcyclohexane-d_{14} generated significant quantities of the anti isomer (eq 58). Anti to syn isomerization rate constants ($k_{a/s}$) were then determined by NMR methods at higher temperatures and correlated with the nature of R, R′, R″, and the solvent. Values for $k_{a/s}$ were found to vary by up to 7 orders of magnitude (at 298 K), the smallest values for $k_{a/s}$ being found in complexes that contain the most electron-withdrawing alkoxides in THF as a solvent. Equilibrium constants ($K_{eq} = k_{a/s}/k_{s/a}$) at 25 °C were found to vary by up to 2 orders of magnitude. The anti isomer of $Mo(CHCMe_2Ph)(NAr)[OCMe(CF_3)_2]_2$ was estimated to be several orders of magnitude more reactive than the syn isomer toward bis(trifluoromethyl)norbornadiene (NBDF6) in THF-d_8 and in toluene-d_8. The anti isomer of every complex containing an arylimido ligand reacted with NBDF6 to yield a syn first insertion product that contained a trans C═C bond (anti → syn, trans), and the syn isomer produced a syn first insertion product that contained a cis C═C bond (syn → syn, cis). The result of bulk polymerizations suggested that high-cis polymers are formed when syn/anti isomerization rates are negligible on the time scale of polymerization, while high-trans polymers are obtained when syn/anti isomerization rates are fast on the time scale of polymerization. A mechanism was proposed that consists of olefin attack (through the exo face) on the CNO face of the syn isomer of the catalyst with C_7 of the monomer extending over the arylimido ring. The slow syn to anti conversion in $OCMe(CF_3)_2$ species was also proposed by others on the basis of ROMP results with a variety of monomers.[127−129]



(58)

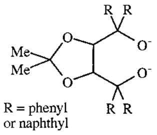
Five- and six-coordinate alkylidene complexes of the type $Mo(CHR)(NAr)[OCMe(CF_3)_2]_2S_x$ have been synthesized and explored as living ROMP initiators or Wittig reagents.[130] Addition of a variety of terminal monoolefins or diolefins to $Mo(CHCMe_2Ph)(NAr)(OR_{F6})_2$ or $Mo(CHCMe_3)(NAr)(OR_{F6})_2$ yielded the new species listed in Table 1. An example is shown in eq 59. (Only the anti isomer is formed in this and other cases when a donor is attached to the γ alkylidene carbon.) $Mo(CH_2)(NAr)(OR_{F6})_2(dme)$ could be generated and observed by ^1H NMR upon adding an excess of ethylene to a solution of $Mo(CHCMe_3)(NAr)(OR_{F6})_2$ in dme-d_{10}, and $Mo(CH_2)(NAr)(OR_{F6})_2(bpy)$ could be isolated upon addition of 2,2′-bipyridine (bpy). Addition of triflic acid to $Mo(NAr)_2(CH_2Ph)_2$ in dimethoxyethane yielded $Mo(CHPh)(NAr)(OTf)_2(dme)$, which is a precursor to complexes of the type $Mo(CHPh)(NAr)(OR)_2$. It is unusual to synthesize an alkylidene in this manner that is not a neopentylidene or neophylidene.



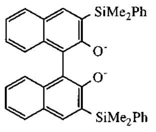
(59)

Several racemic or enantiomerically pure complexes of the general type Mo(CHR)(NR′)(diolate) that contain a 3,3′-disubstituted binaphtholate (substituent = $SiMe_2Ph$, Ph, 2-MeC_6H_4, 2,6-$Me_2C_6H_3$, 3,5-$Ph_2C_6H_3$) or biphenolate (3,3′,5,5′-tetra-*tert*-butyl-6,6′-dimethyl) ligands were prepared and employed to ring-open several achiral, racemic, or enantiomerically pure norbornenes and norbornadienes.[131] X-ray structures of $Mo(CHCMe_2Ph)(NAr')(t\text{-}Bu_4Me_2\text{−}biphenolate)$ showed it to be a base-free syn species in which Mo═C = 1.868(9) Å and Mo═C−C = 144.5(7)°, while an X-ray study showed $Mo(CHCMe_2Ph)(NAr')(3,3'\text{-}Ph_2binaphtholate)(THF)$ to be five-coordinate anti species in which Mo═C = 1.827(9) Å and Mo═C−C = 128.1(6)°. Variable-temperature X-ray studies suggested that the anti form of the binaphtholate species binds THF so strongly that only the THF adduct is observable, while the base-free syn form can be observed in solution. Several achiral, racemic, or enantiomerically pure norbornenes and norbornadienes were ring-opened with these initiators to give cis, isotactic polymers. A bimodal molecular weight distribution sometimes results from polymerization of an enantiomerically pure monomer with a racemic initiator as a consequence of a different rate of chain growth from enantiomeric metal centers, but polymerization of an enantiomerically pure monomer with an enantiomerically pure initiator containing (+)-3,3′-bisdimethylphenylsilyl-2,2′-diolate-1,1′-dinaphthyl yielded only a single polymer chain, as expected.

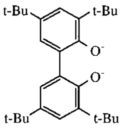
Molybdenum imidoalkylidene complexes of the type Mo(CHR)(NR′)(diolate) (R = CMe_3, CMe_2Ph; R′ = Ar or Ar′) were prepared that contain C_2-symmetric diolate ligands, either the enantiomerically pure “TADDOLS” ($[R_4tart]^{2-}$), racemic $[BINO(SiMe_2Ph)_2]^{2-}$, or racemic $[Bipheno(t\text{-}Bu)_4]^{2-}$ ligands and employed to control cis/trans content and tacticity of polymers prepared via ROMP of 2,3-disubstituted norbornadienes.[132,133] In a study involving the polymerization of enantiomerically pure norbornadienes and norbornenes, the all-cis polymer was proven to be isotactic.[134]



$[R_4tart]^{2-}$

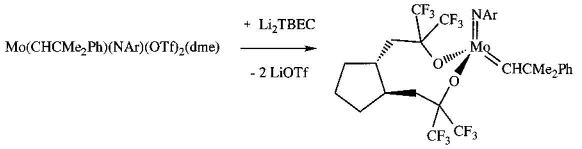


$[BINO(SiMe_2Ph)_2]^{2-}$



$[Bipheno(t\text{-}Bu)_4]^{2-}$

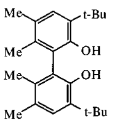
A molybdenum imidoalkylidene complex has been prepared that contains the enantiomerically pure diolate ligand, (*R*,*R*)-1,2-$(OC(CF_3)_2CH_2)_2C_5H_8$ (TBEC), as shown in eq 60.[135,136] The Mo complex was active for the ring-closing metathesis (kinetic resolution) of several substrates. The degree of kinetic resolution was modest, corresponding to a maximum k_{rel} for the



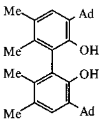
(60)

reaction of one enantiomer versus the other of approximately 2.5.[137]

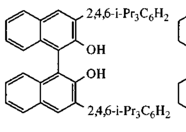
Two 3,3′-dialkyl-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diols, H_2Biphen or H_2Biad (Ad = 1-adamantyl), were prepared in two steps and resolved as menthol phosphate derivatives.[138,139] Addition of the dipotassium salt of each biphenolate to various Mo(CHR)(NAryl)(OTf)$_2$(dme) complexes produced racemic and enantiopure compounds of the type Mo(CHR)(NAryl)(biphenolate).[138,139] X-ray crystallographic studies of *syn*-Mo(CHCMe$_2$Ph)(NAr)[(*S*)-Biphen] (Mo=C = 1.885(10) Å and Mo=C−C = 143.8(7)°) and *syn*-Mo(CHCMe$_3$)(N−2-CF$_3$C$_6$H$_4$)[(*S*)-Biad](pyridine) (Mo=C = 1.90(2) Å and Mo=C−C = 148.0(13)°) proved the absolute stereochemistry of the biphenolate ligands in each case. Neophylidene and neopentylidene complexes were found to have predominantly the syn conformation in solution. The [syn]/[anti] equilibrium constant for Mo(CHR)(NAryl)[Biphen] complexes increases in magnitude with decreasing size of the arylimido ligand and decreases upon reduction of the steric bulk of the alkylidene substituent. The rates of exchange of syn and anti isomers, as determined by single-parameter line shape analysis and by spin-saturation transfer, were found to be of the order of ~1 s^{-1} at 22 °C. Addition of *trans*-3-hexene to Mo(CHCMe$_2$Ph)(NAr)[Biphen] at 22 °C generated a mixture of *syn*- and *anti*-Mo(CHCMe$_2$Ph)(NAr)[Biphen], *syn*- and *anti*-Mo(CHEt)(NAr)[Biphen], *cis*- and *trans*-PhMe$_2$CCH=CHEt, and *cis*- and *trans*-3-hexene. Enantiomerically pure Biphen catalysts have been employed in a variety of successful asymmetric metathesis reactions that include kinetic resolutions,[138] desymmetrization reactions,[140,141] ring-opening/ring-closing reactions,[142] and ring-opening/cross-coupling reactions.[143] Variations that contain the N−2,6-Cl$_2$C$_6$H$_3$ ligand[141] or the [Bitet]$^{2-}$ ligand[144] have also been prepared and employed for asymmetric metathesis reactions.



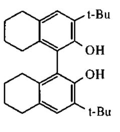
H_2Biphen



H_2Biad



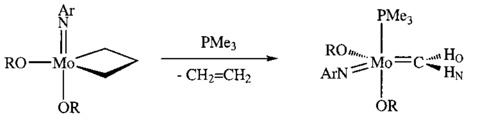
H_2TRIP



H_2Bitet

Molybdenum imidoalkylidene complexes that contain the (*R*)-(+)-3,3′-bis(2,4,6-triisopropylphenyl)-2,2′-dihydroxo-1,1′-dinaphthyl (TRIP) ligand have been prepared and employed in asymmetric metathesis reactions.[145] One advantage of a binaphtholate is that the parent binaphthol can be obtained in enantiomerically pure form commercially. The molybdenum complex Mo(CHCMe$_2$Ph)(NAr)(TRIP)(THF) only partially loses THF in vacuo in the solid state. Variable-temperature NMR studies suggest that THF binds relatively strongly to the anti isomer to give two diastereomers at low temperatures and binds relatively weakly to the syn isomer to give a single diastereomer at low temperatures. An X-ray study of *syn*-Mo(CHCMe$_2$Ph)(NAr)(TRIP)(py), which is relatively inactive for metathesis, shows the Mo=C distance to be 1.840(12) Å and the Mo=C−C angle to be 149.5(10)°, both of which are typical of syn isomers. Mo(CHCMe$_2$Ph)(NAr)(TRIP)(THF) has been shown to promote the asymmetric ring-closing metathesis of various dienes and trienes to afford six-membered carbo- and heterocycles efficiently and in high optical purity.[141,143,145] A short review covering asymmetric metathesis reactions has been published.[19]

Addition of ethylene or vinyltrimethylsilane to Mo imidoalkylidene complexes ultimately leads to reduction to Mo(IV), probably via bimolecular decomposition of intermediate methylene complexes.[146] In the case of ethylene, formation of unstable unsubstituted metallacyclobutane complexes was proposed (eq 61; OR = OCMe(CF$_3$)$_2$ or OCMe$_3$) that subsequently reacted with trimethylphosphine to give unstable methylene complexes; only one (OR = OCMe(CF$_3$)$_2$) was formed in good yield and was stable enough to characterize by NMR methods. The two H$_\alpha$ protons have significantly different values for J_{CH} (137 and 159 Hz), presumably as a consequence of one of them (H$_O$) being involved in an agostic interaction with Mo.



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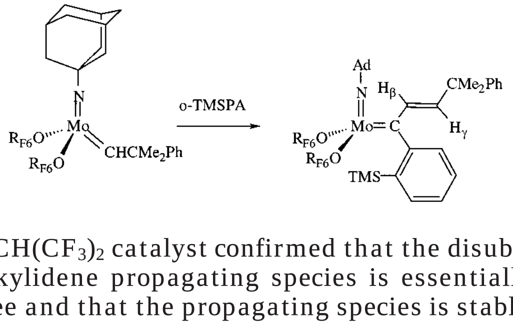
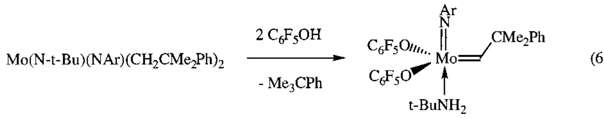


(62)

Molybdenum imidoalkylidene complexes that contain a “small” alkoxide can be isolated as five-coordinate base adducts.[147,148] Examples are Mo(CHCMe$_2$Ph)(N−1-adamantyl)[OCH(CF$_3$)$_2$]$_2$(2,4-lutidine) and Mo(CHCMe$_2$Ph)(NAr′)(OC$_6$F$_5$)$_2$(quinuclidine). Complexes can also be isolated that contain 1 equiv of lithium or potassium alkoxide, e.g., Mo(CHCMe$_2$Ph)(N−1-adamantyl)[OCH(CF$_3$)$_2$]$_3$[Li(dme)], as shown in an X-ray study (Mo=C = 1.87(2) Å). Addition of BF$_3$ etherate to Mo(CHCMe$_2$Ph)(N−1-adamantyl)[OCH(CF$_3$)$_2$]$_3$[K(dme)] followed by 2,4-lutidine yielded *syn*-Mo(CHCMe$_2$Ph)(NAd)[OCH(CF$_3$)$_2$]$_2$(2,4-lutidine), which was shown to be a distorted trigonal bipyramid in which lutidine occupies an axial position, a structure that results from addition of 2,4-lutidine to the CNO face of unstable pseudotetrahedral *syn*-Mo(CHCMe$_2$Ph)(NAd)[OCH(CF$_3$)$_2$]$_2$ (Mo=C = 1.880(4) Å). Complexes of this type were employed to polymerize *o*-trimethylsilylphenylacetylene (*o*-TMSPA). Solely the α-substituted metallacyclobutene intermediate forms and opens to give a disubstituted alkylidene complex, which can be isolated when *o*-TMSPA is added to Mo(CHCMe$_2$Ph)(NAd)[OCMe(CF$_3$)$_2$]$_2$ (eq 62; only one isomer is shown), since further polymerization is slow when the larger OCMe(CF$_3$)$_2$ ligand is present. Additional studies of the OCH(CF$_3$)$_2$ catalyst confirmed that the disubstituted alkylidene propagating species is essentially base-free and that the propagating species is stable under catalytic conditions (25 °C). Other versions of the Mo($CHCMe_2Ph$)(NAd)[$OCH(CF_3)_2$]$_2$(base) catalyst are either inactive (base = pyridine) or unstable (base = 2-(3-pentyl)pyridine). Mo(CRR′)(N−1-Ad)[$OCH(CF_3)_2$]$_2$(2,4-lutidine) (CRR′ = CPh_2 or CMe(Ph)) and Mo($CHCMe_2Ph$)(NAr′)(OC_6F_5)$_2$(quinuclidine) (Ar′ = 2,6-$Me_2C_6H_3$) were also prepared and shown to react smoothly with trimethylsilylphenylacetylene to give poly(*o*-TMSPA).

The mixed diamido complex shown in eq 63 was shown to react with pentafluorophenol to yield (after α hydrogen abstraction) the diisopropylphenylimido complex as a *tert*-butylamine adduct.[149] This method



(63)

is a potentially useful route to imidoalkylidene complexes if the alcohol has a low pK_a.

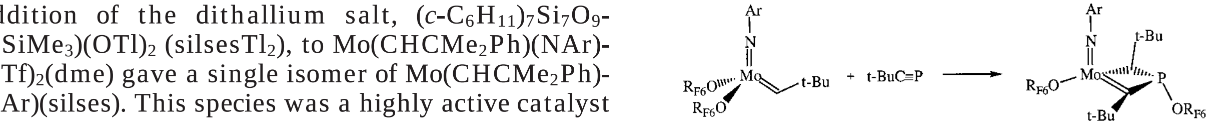
A complex that contains the tridentate [2,6-($OCPh_2CH_2$)$_2C_5H_3N$]$^{2-}$ ligand was prepared in order to compare the imido ligand in it with that in an analogous bisimido complex.[150] In Mo($CHCMe_2Ph$)(NAr)[2,6-($OCPh_2CH_2$)$_2C_5H_3N$] the Mo=C bond length was found to be 1.914(3) Å and the Mo=C−C angle was found to be 141.0(2)°. The imido ligand was a normal, relatively linear moiety.

A molybdenum imidoalkylidene complex that contains a silsesquioxane ligand was prepared in order to test the efficacy of a silsesquioxane as a substitute for two electron-withdrawing alkoxide ligands.[151] Addition of the dithallium salt, (*c*-C_6H_{11})$_7Si_7O_9$($OSiMe_3$)(OTl)$_2$ (silsesTl$_2$), to Mo($CHCMe_2Ph$)(NAr)(OTf)$_2$(dme) gave a single isomer of Mo($CHCMe_2Ph$)(NAr)(silses). This species was a highly active catalyst for the metathesis of terminal and internal olefins at room temperature, and the expected intermediate alkylidene complexes could be observed. Even metathesis of methyl oleate (400 equiv) was complete within 2 h. The relatively high activity suggests that the silsesquioxane is relatively electron-withdrawing. The structure of this species was established via double-pulsed field gradient spin−echo experiments along with an X-ray study that was adequate to establish connectivity (Mo−C = 1.891(16) Å, Mo=C−C = 144°).[152]

Addition of excess sodium triphenylacetate to Mo(CH−t-Bu)(N−2-*t*-BuC_6H_4)(OTf)$_2$(dme) gave yellow crystalline *syn*-Mo(CH−t-Bu)(N−2-*t*-BuC_6H_4)(O_2CCPh_3)$_2$.[153] An X-ray study showed it to be a monomeric species in which neither the Mo=C distance (1.884 Å) nor the Mo=C−C angle (145.8°) is unusual. The carboxylate ligands are both bound to the molybdenum asymmetrically in what can be said to be somewhere between an η^1 and an η^2 fashion. The electron count in *syn*-Mo(CH−t-Bu)(N−2-*t*-BuC_6H_4)(O_2CCPh_3)$_2$ is 18 if the carboxylato ligands are counted as bidentate ligands and π electron donation from the imido ligand is included. *syn*-Mo(CH−t-Bu)(N−2-*t*-BuC_6H_4)(O_2CCPh_3)$_2$ initiates the cyclopolymerization of diethyldipropargylmalonate in a living manner to give a polymer that contains exclusively six-membered rings. Related N(1-adamantyl) complexes are also active and regioselective initiators, while analogous complexes containing the N−2,6-*i*-$Pr_2C_6H_3$ ligand only extremely slowly polymerize diethyldipropargylmalonate.

Addition of the dipotassium salt of 2,2′-bis-*p*-tolylsulfonamido-1,1′-binaphthyl (K_2[BINA(NTs)$_2$]) to Mo($CHCMe_2Ph$)(NAr)(OTf)$_2$(dme) (Ar = 2,6-*i*-$Pr_2C_6H_3$; OTf = OSO_2CF_3), Mo($CHCMe_2Ph$)(N−2-$CF_3C_6H_4$)(OTf)$_2$(dme), and Mo(CH−t-Bu)(N−2-$CF_3C_6H_4$)(OTf)$_2$(dme) gave Mo($CHCMe_2Ph$)(NAr)[BINA(NTs)$_2$], Mo($CHCMe_2Ph$)(N−2-$CF_3C_6H_4$)[BINA(NTs)$_2$], and Mo(CH−t-Bu)(N−2-$CF_3C_6H_4$)[BINA(NTs)$_2$], respectively.[154] The X-ray crystal structure of Mo(CH−t-Bu)(N−2-$CF_3C_6H_4$)[BINA(NTs)$_2$] showed that one sulfonyl oxygen is coordinated to the molybdenum (Mo=C = 1.861(8) Å, Mo=C−C = 143.6(7)°). Related complexes Mo($CHCMe_2Ph$)(NAr)[BINA(N−i-Pr)$_2$] and Mo($CHCMe_2Ph$)(NAr)[BINA(NTMS)$_2$] were prepared similarly. The pseudotetrahedral nature of Mo($CHCMe_2Ph$)(NAr)[BINA(NTMS)$_2$] was confirmed in an X-ray study (Mo=C = 1.904(3) Å, Mo=C−C = 144.0(2)°). The planes of the two amido nitrogens in the [BINA(NTMS)$_2$]$^{2-}$ ligand are virtually perpendicular to one another. If π bonding from the amido ligands is included, then Mo($CHCMe_2Ph$)(NAr)[BINA(NTMS)$_2$] is an 18-electron species. None of these complexes reacts readily with ethylene, styrene, benzaldehyde, or diallyl ether.

Addition of *tert*-butylphosphaalkyne to Mo(CH−t-Bu)(NAr)(OR_{F6})$_2$ led to the unusual phosphamolybdacyclobutene shown in eq 64, as confirmed via an X-ray study (Mo=C = 1.894(6) Å).[155] When the alkoxide is trifluoro-*tert*-butoxide, the first product is a *neopentylidyne* complex formed by cleavage of the P−C triple bond and an amido ligand that contains phosphorus bound to N (eq 65).[156] This species then further rearranges at 80 °C to yield a phosphamolybdacyclobutene complex in which the original P−C bond has re-formed, as has the imido ligand. X-ray studies confirmed the nature of both species (Mo≡C = 1.739(6) Å, Mo≡C−C = 177.4(4)° in the former; Mo=C = 1.889(7) Å in the latter).



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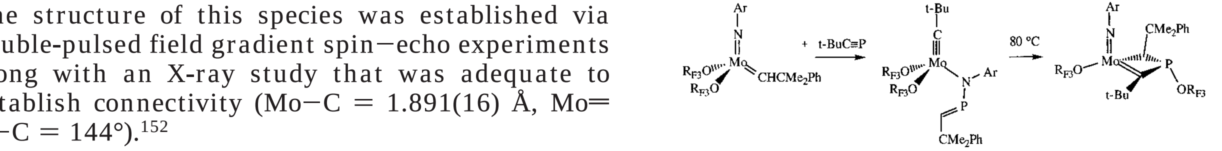
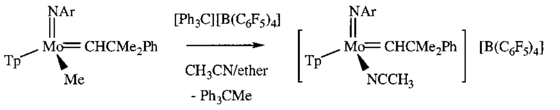


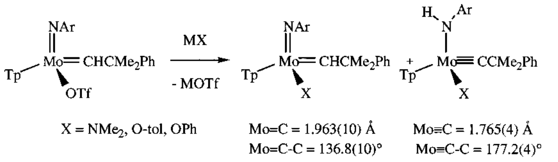
(65)

Trispyrazolylborate derivatives of molybdenum imidoalkylidene complexes have been reported.[157] TpMo($CHCMe_2Ph$)(NAr)(OTf) was converted into TpMo($CHCMe_2Ph$)(NAr)Me in order to prepare cationic complexes by protonation, addition of a trityl salt (eq 66), or abstraction of the methyl group with perfluorotriphenylboron. In all cases a solvent was retained in the cation. Addition of trimethylphosphine to TpMo($CHCMe_2Ph$)(NAr)(OTf) gave [TpMo($CHCMe_2Ph$)(NAr)(PMe_3)]OTf. The triflate could be



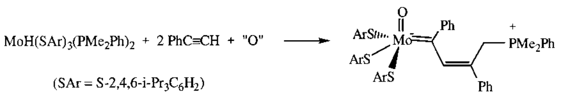
(66)

replaced by a methoxide by treatment with methanol in the presence of Florisil, but attempts to prepare the methoxide derivative employing KOMe led to an amidoalkylidyne tautomer. Attempts to prepare other derivatives (NMe_2, Otol, OPh) gave mixtures of imidoalkylidene and amidoalkylidyne complexes. Alkylidene and amido rotamers were observed, as well as restricted rotation about the aryl−N bond. All complexes were relatively inactive for metathesis reactions until activated by addition of $AlCl_3$. X-ray structures confirmed the nature of the methoxide derivatives of the alkylidene and alkylidyne complexes shown in eq 67.



(67)

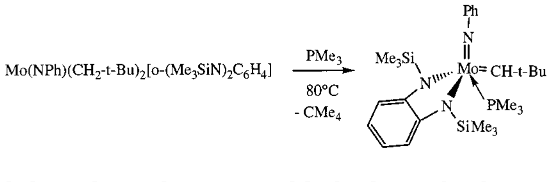
The reaction shown in eq 68 leads to the zwitterionic alkylidene species in high yield.[158,159] The origin



(68)

of the oxo group was not established. An X-ray structure established the nature of this product, and Mo=C = 1.990(5) Å.

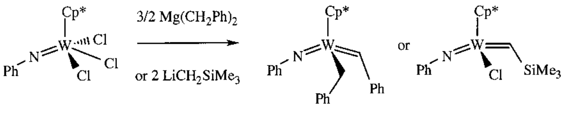
Dialkylation of $Mo(NPh)Cl_2[o\text{-}(Me_3SiN)_2C_6H_4](THF)$ yields several dialkyl species, $Mo(NPh)R_2[o\text{-}(Me_3SiN)_2C_6H_4]$ (R = Me, CH_2−t-Bu, CH_2Ph, CH_2SiMe_3). Upon heating the dialkyl in which R = CH_2−t-Bu to 80 °C in the presence of trimethylphosphine, the neopentylidene complex shown in eq 69 was obtained and could be isolated.[160] The presence of the neopentylidene ligand was established on the basis of its proton and carbon NMR spectra ($\delta H_\alpha = 12.13$ ppm (br), $\delta C_\alpha = 275.3$ ppm). The analogous trimethylsilylmethylidene complex could not be isolated in pure form.



(69)

2.3.3. Tungsten

Tungsten Cp* benzylidene and trimethylsilylmethylene complexes could be prepared as shown in eq 70.[161] Photolysis of isolated $WCp^*(NPh)Me_3$ yielded unstable $WCp^*(NPh)(CH_2)Me$ that could be identified only in solution (11.45 and 9.49 ppm). Other Cp* tungsten imidotrialkyl complexes could be prepared readily from the corresponding trichlorides, even when the alkyl contained β protons (e.g., Et or Pr). As shown in eq 71, the triethyl and tripropyl Cp* complexes decompose upon heating to yield ethylidene and propylidene complexes.[162] The cyclopentadienyl complexes behaved similarly. The alkylidene species were observed only in solution, and no in situ yields were measured. Selective or at least competitive α hydrogen abstraction (versus β hydrogen abstraction) is required for producing alkylidene catalysts in classical olefin metathesis systems.[163]



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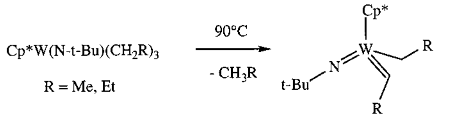
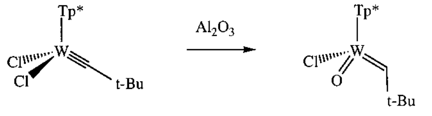


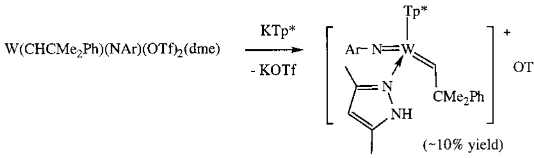
(71)

The addition of LiTp* to $W(C{-}t\text{-}Bu)Cl_3(dme)$ produced the neopentylidyne complex $WTp^*(C{-}t\text{-}Bu)Cl_2$.[164] Upon treatment with neutral alumina this species is transformed into the oxoalkylidene complex shown in eq 72. The alumina probably acts as a source of water, which yields intermediate $WTp^*(C{-}t\text{-}Bu)(OH)Cl$ and HCl. Proton migration from oxygen to carbon then yields the oxoalkylidene. Similar reactions involving $W(CPh)Br_3(dme)$ yielded $WTp^*(CH{-}t\text{-}Bu)(O)Br$, while the reaction between $W(CPh)Br_3(dme)$ and aniline yielded $Tp^*W(CHPh)(NPh)Br$.[165] The 18-electron oxoalkylidene complexes and the imidoalkylidene complex do not react readily with olefins. They can be activated by addition of aluminum trichloride, although under these circumstances the nature of the active species is not known. The analogous complex, $Tp^*Br_2W{\equiv}CPh$, was prepared similarly from $Br_3(dme)W{\equiv}CPh$ and shown to have a structure in which W≡C = 1.783(9) Å and to undergo a quasi-reversible reduction and oxidation.[166]

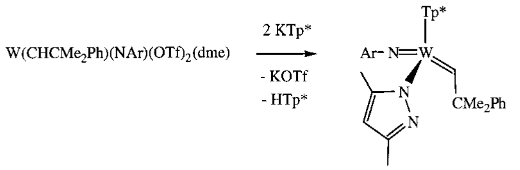


(72)

Related imidoalkylidene complexes can be prepared from $W(CHCMe_2Ph)(NAr)(OTf)_2(dme)$ as shown in eq 73.[167] The deprotonated form is obtained if 2 equiv of KTp* are employed (eq 74). Addition of KTp to $W(CHCMe_2Ph)(NAr)(OTf)_2(dme)$ gives $WTp(CHCMe_2Ph)(NAr)(OTf)$ in the form of two isomers of the



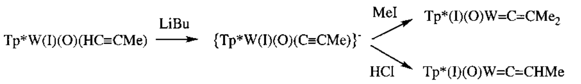
(73)



(74)

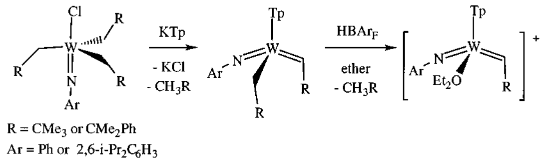
alkylidene. An analogous reaction between KTp and $Mo(CHCMe_2Ph)(NAr)(OTf)_2(dme)$ gives $MoTp(CHCMe_2Ph)(NAr)(OTf)$,[168] an X-ray study of which revealed Mo=C = 1.949(10) Å and Mo=C−C = 139.6(8)°.[169] All are inert toward cyclooctene but are activated by aluminum trichloride.

Addition of butyllithium at −78 °C to Tp*W(I)(O)(propyne) generates an anionic acetylide complex that is attacked by nucleophiles to yield the vinylidene complexes shown in eq 75.[170] An X-ray structure of the dimethylvinylidene complex shows the W=C bond length to be 1.909(7) Å. Two isomers for the methylvinylidene complex were observed in a ratio of ∼1:1 as a consequence of a preferred orientation of the plane of the vinylidene ligand so that it contains the N−W−O axis.



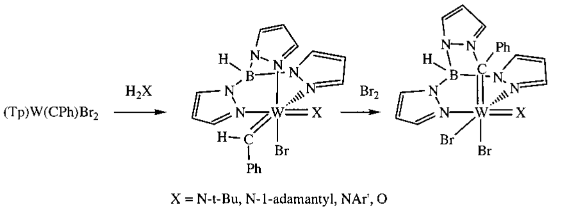
(75)

Other imidoneopentylidene or neophylidene complexes that contain the Tp ligand have been prepared as shown in eq 76.[171] The 18-electron $WTp(CHR)(CH_2R)(NAr)$ species do not react with olefins. Upon treatment with $HBAr_F$ (where BAr_F^- is $B[3,5-(CF_3)_2C_6H_3]_4^-$) the cationic ether adducts are formed. (Addition of HCl produces WTp(CH−t-Bu)(NAr)Cl; $i-Pr_2O$ and acetonitrile adducts of the cation were also isolated.) The cationic species are obtained as a mixture of alkylidene isomers. The cationic species do not metathesize olefins in any sustained manner; apparently an olefin cannot compete with diethyl ether for the cationic d^0 metal center even though diethyl exchanges readily.



(76)

Addition of an amine or water to $WTp(CPh)Br_2$ led to formation of the imido- or oxoalkylidene complexes shown in eq 77.[172] Addition of bromine led to formation of HBr and insertion of what is presumed to be a benzylidyne ligand in an intermediate seven-coordinate complex into the tris(pyrazolyl)borate cage, as proven via an X-ray structure of the product (W=C = 2.067(8) Å). The alkylidyne ligand in an intermediate high oxidation state complex is expected to be especially reactive because an M≡C bond cannot coexist with an M≡X pseudo-triple-bond. This is believed to be the first example of expansion of the normally relatively inert tris(pyrazolyl)borate cage.

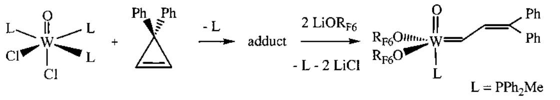


(77)

A crystal structure of the W=O complex was also reported in the full paper (W=C = 1.98(2) Å).[173]

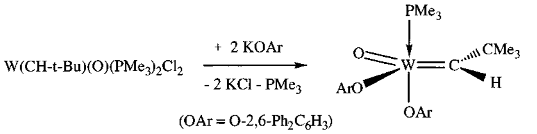
An alkylidene complex that contains the L_{OMe} ligand ($L_{OMe} = \{CpCo[P(OMe)_2(O)]_3]\}^-$), $L_{OMe}(Cl)W(CHTol)(O)$, can be prepared by treating $L_{OMe}Cl_2W\equiv CTol$ with a mixture of triethylamine and water or with hydroxylated alumina.[174] $L_{OMe}Cl(PrNH)W\equiv CTol$ was also found to be transformed into $L_{OMe}ClW(CHTol)(NPr)$ with time.

Examples of tungsten oxoalkylidene complexes could be prepared by treating a W(IV) species with 3,3-diphenylcyclopropene (eq 78).[175] (This type of reaction was first reported for titanium by Binger.[176]) The cyclopropene adduct is converted into the vinylalkylidene complex by an unknown mechanism upon addition of $LiOR_{F6}$ ($LiOC(CF_3)_2Me$). When L = $P(OMe)_3$, the adduct must be heated in order to convert it into the vinylalkylidene complex, but the trimethyl phosphite complex could not be isolated on account of the lability of the trimethyl phosphite. A THF adduct could be formed from the trimethyl phosphite complex, but it too could be observed only in solution. Preliminary investigations suggested that these species are active for some ROMP and ring-closing metathesis reactions, especially those that contain labile $P(OMe)_3$ or THF.



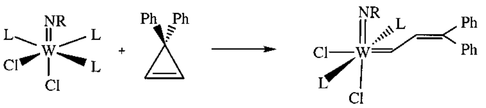
(78)

The reaction between $W(CH{-}t\text{-}Bu)(O)(PMe_3)_2Cl_2$ and 2 equiv of $KO{-}2,6\text{-}Ph_2C_6H_3$ yielded yellow crystalline *syn*-$W(CH{-}t\text{-}Bu)(O)(O{-}2,6\text{-}Ph_2C_6H_3)_2(PMe_3)$ (eq 79).[177] An X-ray study showed it to be a distorted trigonal bipyramid in which the oxo ligand, the neopentylidene ligand, and the oxygen of one phenoxide ligand all lie in the equatorial plane (W=O(1) = 1.689(6) Å; W=C(1) = 1.88(1) Å; W=C(1)−C(2) = 147.8 (9)°). In the analogous PPh_2Me complex the phosphine exchange rate is of the order of the NMR time scale at 22 °C. Both compounds react readily with 2,3-dicarbomethoxynorbornadiene and 2,3-bis(trifluoromethyl)norbornadiene in dichloromethane or toluene to give polymers that are >95% cis and >95% isotactic.



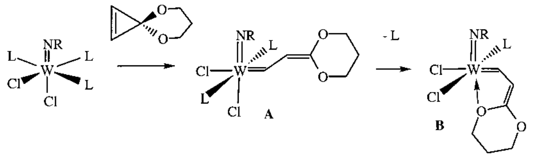
(79)

Several tungsten vinylalkylideneimido complexes could be prepared by analogous methods, namely, the addition of 3,3-diphenylcyclopropene to $W(NR)Cl_2L_3$ where R = $2,6\text{-}Me_2C_6H_3$ or $2,6\text{-}i\text{-}Pr_2C_6H_3$ and L = $P(OMe)_3$ or PEt_2Ph.[178] When L = PEt_2Ph, the cyclopropene in the initial adduct rearranges to the vinylalkylidene (eq 80) at room temperature. When

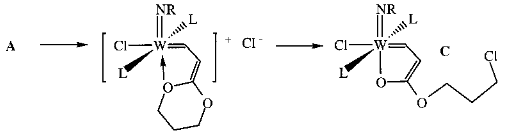


(80)

L = $P(OMe)_3$, the cyclopropene adduct can be observed and caused to rearrange to the vinylalkylidene thermally, photochemically, or chemically ($HgCl_2$). In some cases the chlorides could be replaced by OR_{F6} or OAr to give five-coordinate complexes of the type $W(CHCHCPh_2)(NR)(OR)_2L$. Reactions involving the ketalcyclopropene in eq 81 were complicated by loss of L and formation of the anti species **B** in which the oxygen is a donor to the metal and by rearrangement of **A** to **C** via the cationic species shown in eq 82 in which a ketal oxygen is coordinated to the metal.



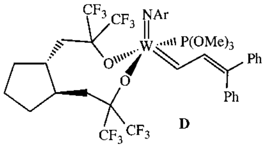
(81)



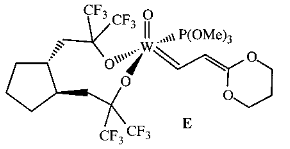
(82)

X-ray structures of $W(CHCHCPh_2)(NAr)(OR_{F6})_2$-$[P(OMe)_3]$ (W=C = 1.947(5) Å and W=C−C = 122.2(4)°) and a complex of type **C**, $W[CHCHC(O)(OC_3H_6Cl)](N{-}2,6{-}Me_2C_6H_3)(PEt_2Ph)_2Cl$ (W=C = 2.032(5)° and W=C−C = 120.0(4)°), confirmed the proposed structures.

The tungsten oxo- and imidovinylalkylidene complexes **D** and **E** could be prepared from the dichloride precursors.[136] Alkylidene isomers were observed, and



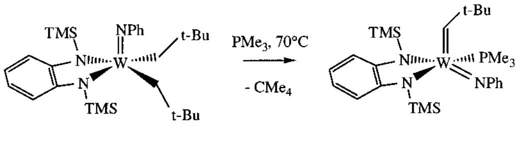
D



E

in the second case two different diastereomers were observed.

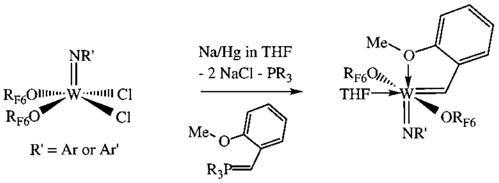
A square pyramidal tungsten neopentylidene complex has been prepared as shown in eq 83 (W=C = 1.884(13) Å and W=C−C = 148.4(9)°).[179] Although



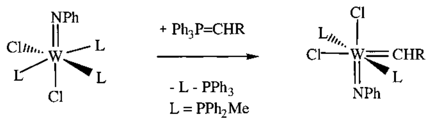
(83)

it is active for ROMP of norbornene, little initiator is consumed. In the absence of trimethylphosphine a methyl group in a trimethylsilyl group is activated to give a related neopentyl complex.[180] When the dineopentyl complex is treated with ethylene at 70 °C, it is converted into a tungstacyclopentane complex as a consequence of forming a neopentylidene complex, followed by a methylene complex, followed by bimolecular decomposition of the methylene complex in the presence of ethylene.[181]

It has been possible to prepare several tungsten imidoalkylidene complexes by transferring an alkylidene from phosphorus to a W(IV) species.[182] Two examples are shown in eqs 84 and 85. Electron-withdrawing alkoxides are necessary in order for the metal to be reduced and the alkylidene to transfer from P to W. THF is lost from the adduct shown in eq 84 upon heating a toluene solution of the THF adduct. An X-ray structure of $W[CH{-}2{-}(OMe)C_6H_4]$-$(N{-}2,6{-}Me_2C_6H_3)(OR_{F6})_2(THF)$ showed that W=C = 1.943(5) Å and W=C−C = 121.9(4)°. More extensive studies demonstrated that a variety of alkylidenes could be transferred to the reduced trisphosphine species to give isolable species (R = Ph, *p*-tolyl, 4-$(CF_3)C_6H_4$, 2-naphthyl, C_6F_5, $CH{=}CMe_2$), including a species in which the alkylidenes were linked through two linked *p*-C_6H_4 rings.[183] The reactions proceeded slowly at room temperature. Usually syn and anti alkylidene resonances were observed initially, although the syn form predominated with time. The alkylidene transfer was slow in THF and did not take place cleanly in dichloromethane. The larger ylides, $Ph_3P{=}CH{-}t{-}Bu$ and $Ph_3P{=}CHSiMe_3$, did not react readily with $W(NPh)Cl_2(PPh_2Me)_3$; reactions involving $W(NPh)Cl_2(PEt_2Ph)_3$ were generally unsuccessful, and use of $Ph_3P{=}CH_2$ and $Ph_3P{=}CHMe$ yielded complex mixtures. A variety of species could be observed in solution but could not be or were not isolated. Crystal structures of $W[CH{-}2{-}(OMe)C_6H_4]$-$(N{-}2,6{-}i{-}Pr_2C_6H_3)(OR_{F6})_2$ (W=C = 1.939(5) Å and W=C−C = 122.0(3)°) and $W[CH{-}4{-}MeC_6H_4](NC_6H_5)$-$Cl_2(PPh_2Me)_2$ (W=C = 1.975(3) Å and W=C−C = 138.1(3)°) were reported. The phosphine-free hexafluoro-*tert*-butoxide complexes were shown to be active for the metathesis of olefins and readily underwent Wittig-like reactions with carbonyl compounds. This method of making alkylidenes seems to be most successful when the product is a relatively unreactive 18-electron alkylidene complex, since in that case secondary reactions are minimized.

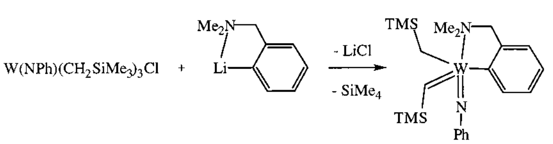


(84)



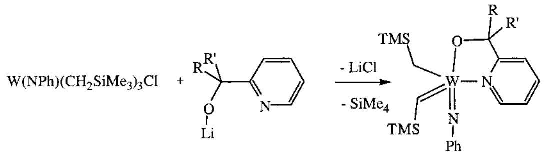
(85)

An aryldimethylamino derivative of a tungsten alkylidene was prepared by the α hydrogen abstraction reaction shown in eq 86.[184] $W(CHSiMe_3)(NPh)$-



(86)

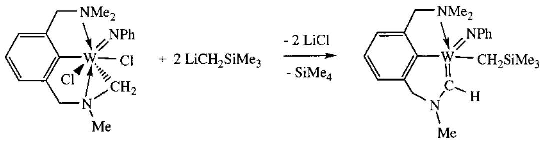
$(CH_2SiMe_3)_2$ could also be observed in the initial reaction mixture. The structure was confirmed in an X-ray study (W=C = 2.15(1) Å and W=C−C = 119.9(10)°). Addition of triphenylsilanol to the alkylidene complex led to formation of the analogous W[2-$(CH_2NMe_2)C_6H_3](CHSiMe_3)(NPh)(OSiPh_3)$ species.[185] Alkyl/alkylidene complexes also could be prepared by adding bidentate alkoxide derivatives of pyridine, as shown in eq 87.[186] Mixtures of syn and anti species were often observed, although the X-ray structure of the species in which R = R′ = Ph was shown to be the syn species, the major species in solution. An X-ray study of $W[2\text{-}(OCPh_2)C_5H_4N](CHSiMe_3)(NPh)(CH_2SiMe_3)$ showed W=C =1.876(5) Å and W=C−Si = 136.4(3)°.[187] None of the five-coordinate species was found to react readily with terminal olefins, although they did react in a Wittig-like manner with aldehydes and were active for the ROMP polymerization of norbornene.



R = R′ = Ph; R = H, R′ = t-Bu

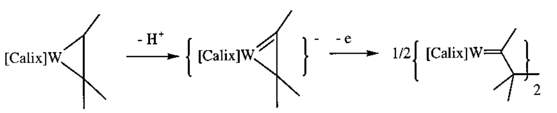
(87)

Addition of 2 equiv of trimethylsilylmethyllithium to the activated species shown in eq 88 produces an alkylidene derivative that contains nitrogen bound to the α carbon.[188] Therefore, α hydrogen abstraction in the methylene group bound to nitrogen appears to be more favorable than in a trimethylsilylmethyl ligand. (See eq 31 for a tantalum example.)

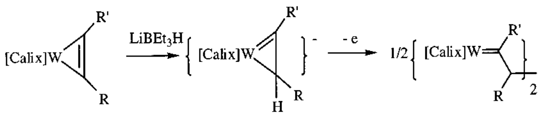


(88)

The chemistry of $(calix[4]arene)^{4-}$ complexes of tungsten has been developing rapidly. (A review of early transition metal calixarene chemistry has appeared.[189]) Anionic tungstacyclopropene complexes have been prepared either by deprotonation of olefin complexes (eq 89) or by attacking acetylene complexes with a borohydride reagent (eq 90). Oxidation by one electron then yields a bimetallic species as a result of coupling of the substituted carbon atoms in a radical intermediate.[190] In the case of an acenaphthalene complex, deprotonation yields a strained species that yields the reduced coupled product first (W=C = 1.918(12), 1.903(10) Å), which can then be oxidized by two electrons to the neutral alkylidene derivative (W=C = 1.921(5), 1.914(5) Å; eq 91).

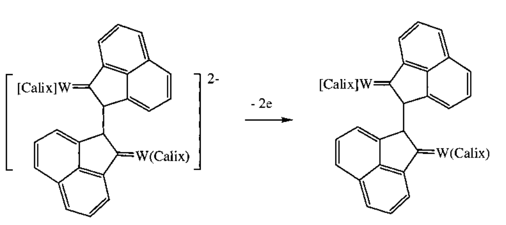


(89)



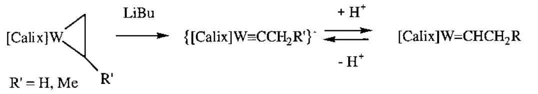
R = R′ = Ph; R = Ph, R′ = Me

(90)



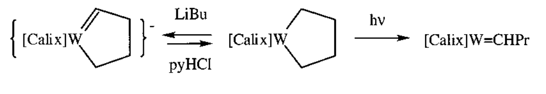
(91)

When the olefin in [calix]W(olefin) complexes is ethylene or propylene, then deprotonation leads to formation of an anionic alkylidyne complex (eq 92); the mechanism of this transformation is unclear.[191,192]



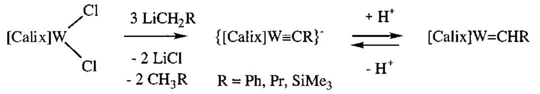
(92)

Protonation of the alkylidyne complex yields an alkylidene complex. This sequence constitutes the stepwise conversion of an olefin into an alkylidene. (It would seem that a base and its conjugate acid could be found that would allow the conversion to be catalytic.) The tungstacyclopentane complex shown in eq 93 rearranges to a butylidene complex upon photolysis and can be deprotonated to the anionic tungstacyclopentene complex shown. Related rearrangements are found to take place in tungsten complexes that contain a trianionic triamidoamine ligand (see elsewhere in this review). It is not known at this stage the degree to which the calixarene itself might be involved (e.g., as a site of electrophilic attack, etc.) in various reactions.



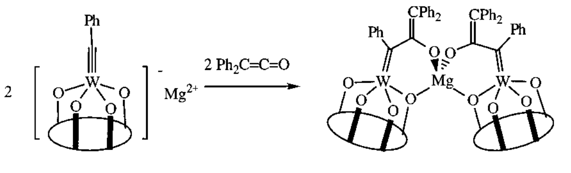
(93)

A variety of interconversions of alkylidene and alkylidyne ligands in the [calix]W system has been explored.[193,194] Addition of 3 equiv of lithium reagents to $[calix]WCl_2$ led to formation of anionic alkylidyne complexes (eq 94), although a benzylidene could be isolated when the less reducing dibenzylzinc was employed. Alkylidyne complexes in which R = Ph or $SiMe_3$ were characterized crystallographically (W≡C = 1.728(7) or 1.759(4) Å, respectively). The anionic alkylidene complexes could be protonated (e.g., with pyHCl) to give neutral alkylidene complexes, one of which (R = Ph) was characterized crystallographically (W=C = 1.913(4) Å). When pyridine was employed as an NMR solvent (and R = Pr), coupling of the alkylidene proton to carbon was lost as a consequence of rapid proton exchange. Addition of MeOTf to $\{[calix]W{\equiv}CR\}^-$ (R = Pr or $SiMe_3$) led to formation of disubstituted alkylidene species, [calix]W=C(Me)R; in the complex in which R = $SiMe_3$, W=C was found to be 1.914(10) Å. Some methylation at a calixarene oxygen also took place, although that butylidyne species could not be isolated and fully characterized. Addition of silver ion to $\{[calix]W{\equiv}CR\}^-$ yielded $\{[calix]W{=}CR(Ag)\}_2$ species, while addition of benz-



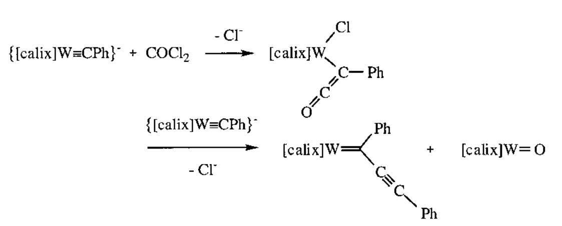
(94)

aldehyde or diphenylketene led to magnesium-containing alkylidenes, e.g., that shown in eq 95 in which W=C was shown to be 1.908(6) Å. Oxidation of the anionic alkylidyne complexes led either to alkylidene complexes (via hydrogen atom abstraction from the solvent) or to a dimeric coupled product. Oxidation of {[calix]W≡CPh}$^-$ with iodine yielded {[calix]W=CPh(I), which may be the only example of a halogen-substituted high oxidation state alkylidene.



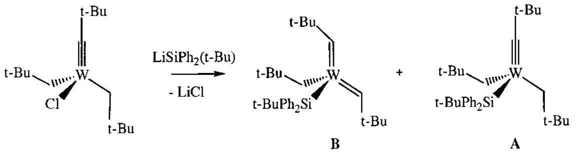
(95)

The reaction between various non-carbon electrophiles and {[calix]W≡CPh}$^-$ led to heteroatom-substituted (e.g., N or P) alkylidene complexes. When phosgene was employed, the ketenyl chloride complex was intercepted as an intermediate (eq 96). It was found to react with {[calix]W≡CPh}$^-$ to yield an alkylidene complex shown that contains a phenyl/phenylalkynyl-substituted alkylidene carbon atom plus the metal oxo species.[195] The W=C bond length in the disubstituted alkylidene complex was found to be 1.931(7) Å in an X-ray study.

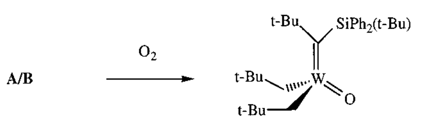


(96)

The reaction shown in eq 97 was found to yield a mixture of two interconverting species, a bisalkylidene (**B**) and an alkylidyne (**A**) complex.[196] The observation of only one alkylidene proton resonance (at 6.03 ppm) and one alkylidene carbon resonance (at 272.3 ppm) for **B** suggests that it adopts the anti,anti conformation, the syn,syn conformation being too hindered and the syn,anti conformation having two different alkylidene ligands. The two compounds were found to be in ready equilibrium. Solid-state NMR suggested that both were present in the solid state also. Upon oxidation of the mixture, the oxoalkylidene complex shown in eq 98 was obtained in low yield (32%; W=C = 1.920(7) Å). This process formally involves migration of the silyl ligand to the alkylidyne ligand in **A**.

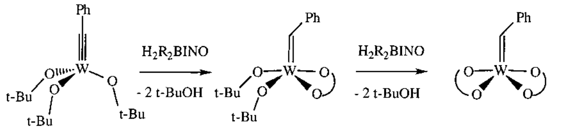


(97)



(98)

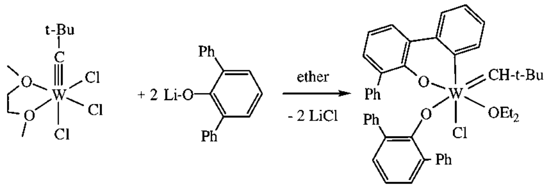
The reaction between (t-BuO)$_3$W≡CR (R = Ph, i-Pr, t-Bu) and rac-3,3′-disubstituted 1,1′-bi-2-naphthols (H$_2$R$_2$BINO; R = Br, Me, Ph) were found to produce five-coordinate alkylidene species that contain one or two [R$_2$BINO]$^{2-}$ ligands (e.g., eq 99).[197] Both types of species showed only a modest degree of reactivity toward norbornene unless GaBr$_3$ was added. The active catalysts formed in the presence of GaBr$_3$ are likely to be four-coordinate cationic species related to those prepared and studied by Osborn.[198] Little stereochemical control of ROMP reactions was observed.



(99)

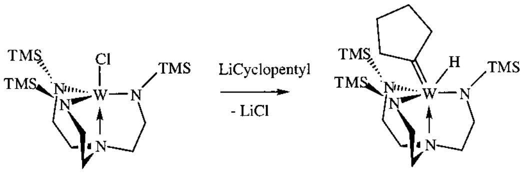
Addition of thiobenzophenone to W$_2$(OCH$_2$−t-Bu)$_8$ yielded an inseparable mixture of what were proposed to be W(CPh$_2$)(OCH$_2$−t-Bu)$_4$ (most likely a dimer) and W(S)(OCH$_2$−t-Bu)$_4$ (most likely a polymer).[199] Addition of ethanol to this mixture allowed [W(CPh$_2$)(OCH$_2$−t-Bu)(OEt)$_2$(μ-OEt)]$_2$ to be isolated and characterized crystallographically. The W=C bond length was found to be 1.967(6) Å.

The reaction between (dme)Cl$_3$W≡C−t-Bu and 2,6-diphenylphenoxide in diethyl ether leads to the alkylidene shown in eq 100 as a consequence of CH activation in one of the ortho phenyl groups in a 2,6-diphenylphenoxide ligand and transfer of that proton to the neopentylidyne α carbon atom.[200] The neopentylidene complex can also be prepared by treating W(O−2,6-Ph$_2$C$_6$H$_3$)$_2$Cl$_4$ with Mg(CH$_2$CMe$_3$)$_2$. This species is highly active for the metathesis of olefins,[201] although no new alkylidene complexes were observed. Therefore, it has not been proven that the integrity of this species is maintained in a catalytic reaction.



(100)

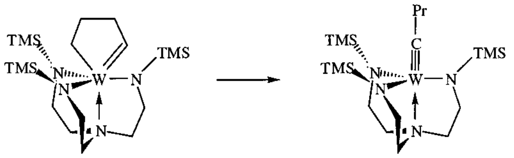
Attempted synthesis of a [N$_3$N]WR ([N$_3$N]$^{3-}$ = [(Me$_3$SiNCH$_2$CH$_2$)$_3$N]$^{3-}$) complex in which R = cyclopentyl led to formation of the cyclopentylidene hydride species shown in eq 101 (W=C = 1.97(1) Å).[202]



(101)

Cyclopentene is evolved upon heating the cyclopentylidene complex, and a paramagnetic monohydride, [N$_3$N]WH, is formed. A variety of studies suggested that the cyclopentylidene hydride complex is in rapid equilibrium with the [N$_3$N]W(cyclopentyl) species with $\Delta H° = 11.8(6)$ kcal mol^{-1} and $\Delta S° = 33(2)$ eu, or $K_{eq} \approx 0.1$ at 298 K. The attempted synthesis of

$[N_3N]W$(cyclobutyl) yielded the 1-tungstacyclopentene complex $[N_3N]W(CHCH_2CH_2CH_2)$ (eq 102), as confirmed in an X-ray study (W=C = 1.972(6) Å). The 1-tungstacyclopentene complex rearranged to a butylidyne complex when heated.



(102)

2.3.4. Theory of Group 6 Metals

Cundari and Gordon published three detailed papers in which ab initio methods were employed in order to study the principal resonance contributors to high oxidation state alkylidene complexes,[214] the effect of ligand and substituent modification,[215] and the nature of the olefin metathesis reaction with hypothetical Mo or W (XH = NH) or Re (XH = CH) complexes of the type $M(OH)_2(XH)(CH_2)$.[216] They discovered that high oxidation state M=C bonds are largely covalent with several major resonance contributors. They also found that the intrinsic nature of the M=C bond changes within relatively narrow limits as the ligands on M or the substituents on the alkylidene carbon are varied electronically. Finally, in hypothetical simplified metathesis catalysts they find (inter alia) that the HOMO is the Mo=C π bond, that both syn and anti isomers are low energy forms, and that the "90° rotated" alkylidene (in which the alkylidene substituents do not lie in the X−M−C plane) is relatively high in energy and stabilized by bending of the Mo=N−H bond in concert with electron pair donation from N to M.

An ab initio study of the reaction between $Cl_4Mo{=}CH_2$ and ethylene found that ethylene first bound weakly to Mo followed by exothermic formation of the metallacyclobutane ring.[217]

The addition of ethylene to $Mo(NH)(CHR)(OR')_2$ (R = H, Me; OR′ = CH_3, CF_3) has been studied using both ab initio molecular orbital and density functional theory.[218] Ethylene was found to favor attack on the CNO face of the pseudotetrahedral alkylidene complex. The calculated activation energy when R′ = CH_3 was significantly higher than when R′ = CF_3. The syn alkylidene was found to be more stable than the anti alkylidene, perhaps because of the presence of an agostic interaction, although the transition-state stabilities were similar. Therefore, the anti alkylidene is effectively more reactive, as has been proposed on the basis of experimental studies.[126]

The [2 + 2] cycloaddition of ethylene to multiple metal−ligand bonds in $Mo(E)OCl_2$ (E = S, Se, O, NH, PH, SiH_2, and CH_2) complexes has been studied using density functional methods.[219] The ethylene is found to approach the metal most easily on the E/O/Cl face, in accord with experimental findings when E is an alkylidene. The reaction is the most exothermic with the lowest barrier for E = SiH_2 followed by CH_2 and the other E's considered. The reactions are the least exothermic and have the highest barriers for E = O. These results rationalize why an olefin adds to an M=CHR bond, but not readily to M=O or M=NR, two other multiple bonds found commonly in alkylidene complexes.

Density functional methods were also used to study in detail how molybdacyclobutane complexes formed upon reaction of ethylene with complexes of the type $L_2Mo(X)(CH_2)$ (X = O, NH; L = Cl, OCH_3, OCF_3).[220] Several results of these calculations were consistent with others, namely, the nature of the HOMO and LUMO's, the relatively high energy of the rotated form of the alkylidene, and the effect of L upon the frontier orbitals. The authors also concluded that both trigonal bipyramidal or square pyramidal molybdacyclobutane species can form from the same basic transition state, with L = OCF_3 favoring the TBP molybdacycle and L = OCH_3 favoring the square pyramidal molybdacycle.

Molecular orbital calculations at the B3LYP level were performed to investigate the relative stabilities of $(CH_3)_2M(CH)X$ versus $(CH_3)M(CH_2)_2X$ where M = Mo or W.[221] The results indicate that the relative stabilities of the $(CH_3)M(CH_2)_2X$ forms increase with increasing π accepting ability of X, but when X is a silyl ligand, the two forms have approximately the same energy because of a π interaction between X and the electron density in the M=C or M≡C bonds.

SCF-Xα-SW calculations were carried out on Mo(VI) imidoalkylidene complexes, $Mo(NH)(CH_2)(OH)_2$, $Mo(NH)(CH_2)(OCH_3)_2$, and a complex in which the alkylidene ligand has been rotated 90°.[222] In $Mo(NH)(CH_2)(OH)_2$ the HOMO was identified as the Mo−C π bond and an agostic interaction involving the methylene proton pointing away from the imido ligand could be identified. The LUMO in $Mo(NH)(CH_2)(OH)_2$ is the M−N π antibonding orbital in the alkylidene plane, which is largely metal-centered on the COO face of the pseudotetrahedral complex. The electronic structure of $Mo(NH)(CH_2)(OCH_3)_2$ is roughly the same as that for $Mo(NH)(CH_2)(OH)_2$. Bending of the imido proton toward the alkylidene ligand is an important stabilizing feature in the "rotated" alkylidene complex, lowering the activation energy for rotation by approximately 50%.

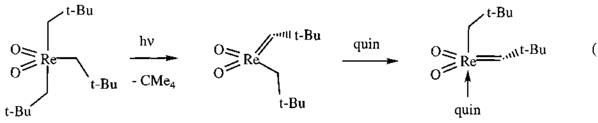
The structure and bonding in both low-valent and high-valent carbene complexes have been determined via quantum mechanical ab initio calculations at the MP2 level of theory for a variety of tungsten complexes such as $Cl_4W{=}CH_2$ and $\{F_5W{=}CH_2\}^-$.[223] In general the calculations support previous bonding models for both species, i.e., donor−acceptor interactions in low-valent species and normal covalent bonds between open-shell metal fragments and triplet carbenes in high-valent species. Negatively charged complexes such as $\{F_5W{=}CH_2\}^-$, however, were found to have donor−acceptor tungsten−carbon bonds.

Theoretical studies on alkyne addition to molybdenum alkylidenes have been carried out in order to assess the preference for α addition over β addition.[273] The barrier for acetylene addition was found to be higher than that for ethylene addition, even though the acetylene reaction is more exothermic. The most favorable addition of a terminal alkyne was found to be that which yields an α substituted metallacyclobutene complex, with the difference between α and β addition being 4 kcal/mol. These results could be explained in terms of a destabilizing interaction between the nonreacting π orbital in the alkyne and one of the lone pairs on the imido nitrogen.

2.4. Group 7 Metals

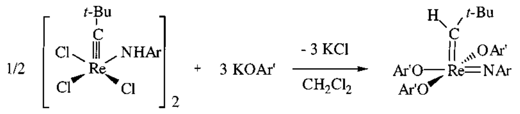
2.4.1. Rhenium

Photolysis of ReO$_2$(CH$_2$−t-Bu)$_3$ in pyridine or acetonitrile yields ReO$_2$(CH−t-Bu)(CH$_2$−t-Bu) in high yield (eq 103; Re═C = 1.869(9) Å, Re═C−C = 136.6(8)°).[203] An X-ray structure of a quinuclidine adduct showed the quinuclidine to be bound in the axial position of a TBP with the neopentylidene ligand lying in the equatorial plane (Re═C = 1.893(6) Å, Re═C−C = 136.8(4)°). The Re−N distance is relatively long (2.425(5) Å), consistent with a relatively weak binding of quinuclidine to the metal. In both compounds the neopentylmethylene protons are inequivalent in solution in proton NMR spectra, consistent with the lack of a mirror plane in each species, i.e., orientation of the alkylidene substituent perpendicular to the C═Re−C plane. Neither compound reacts readily with olefins or substituted acetylenes. Photolysis of ReO$_2$(CH$_2$−t-Bu)$_2$R, where R = Me or CH$_2$SiMe$_3$, also yields ReO$_2$(CH−t-Bu)(CH$_2$−t-Bu), but photolysis of ReO$_2$(CH$_2$−t-Bu)$_2$Ph yields ReO$_2$(CH$_2$−t-Bu)(py)$_3$.



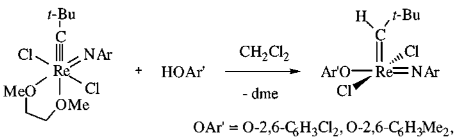
(103)

Five-coordinate alkylidene complexes of the general type Re(CH−t-Bu)(NAr)(OAr′)$_3$ can be prepared in high yield by treating [Re(C−t-Bu)(NHAr)Cl$_3$]$_2$ with 6 equiv of potassium phenoxide (eq 104).[204] Re(CH−t-Bu)(NAr)(O−2,6-C$_6$H$_3$Cl$_2$)$_3$ is essentially a square pyramid in which the alkylidene ligand occupies the apical position with Re═C = 1.87(2) Å and Re═C−C = 139(1)°. Re(CH−t-Bu)(NAr)(OC$_6$F$_5$)$_3$(THF) is prepared in high yield from Re(C−t-Bu)(NHAr)Cl$_3$(THF) and 3 equiv of KOC$_6$F$_5$. Re(CH−t-Bu)(NAr)(OC$_6$F$_5$)$_3$(THF) is pseudo-octahedral with THF bound at the coordination site trans to the alkylidene ligand (Re═C = 1.905(7) Å and Re═C−C = 140.3(6)°). Attempts to prepare pyridine adducts of Re(CH−t-Bu)(NAr)(OAr′)$_3$ complexes led to alkylidyne complexes of the type Re(C−t-Bu)(NAr)(OAr′)$_2$(py) (OAr′ = O−2,6-C$_6$H$_3$Cl$_2$, OC$_6$Cl$_5$). Alkylidene complexes of the type Re(CH−t-Bu)(NAr)(OAr′)Cl$_2$ (eq 105) can be prepared in high yield by treating Re(C−t-Bu)(NAr)Cl$_2$(dme) with 1 equiv of Ar′OH. None of these alkylidene complexes reacts readily with terminal, internal, or strained cyclic olefins. However, addition of GaBr$_3$ to Re(CH−t-Bu)(NAr)(OAr′)Cl$_2$ yields highly active catalysts for the metathesis of *trans*-3-heptene.



(104)

OAr' = OC$_6$F$_5$, O-2,6-C$_6$H$_3$Cl$_2$, OC$_6$Cl$_5$

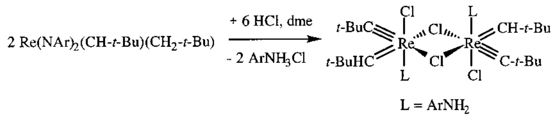


(105)

OAr' = O-2,6-C$_6$H$_3$Cl$_2$, O-2,6-C$_6$H$_3$Me$_2$, O-2,6-C$_6$H$_3$-*i*-Pr$_2$, O-2,6-C$_6$H$_3$(OMe)$_2$

$$\mathrm{Re(NR)_2(py)Cl_3} \xrightarrow[\mathrm{-\ 1.5\ ZnCl_2\ -\ py\ -\ CMe_3R'}]{\mathrm{1.5\ Zn(CH_2CMe_2R')_2}} \mathrm{Re(NR)_2(CHCMe_2R')(CH_2CMe_2R')} \qquad (106)$$

R = t-Bu or Ar; R' = Me or Ph



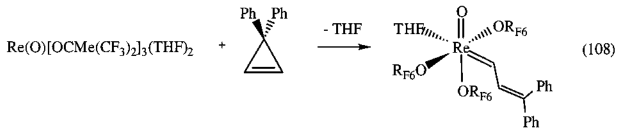
(107)

L = ArNH$_2$

Alkylation of Re(NAr′)$_2$(py)Cl$_3$ or Re(N−t-Bu)$_2$Cl$_3$ with dineopentyl or dineophyl zinc affords bisimidoalkyl alkylidene complexes (eq 106).[205,206] Treatment of Re(NR)$_2$(CHR′)(CH$_2$R′) complexes with an appropriate HCl source yields dimers of the general formula [Re(CR′)(CHR′)(RNH$_2$)Cl$_2$]$_2$ (eq 107). An X-ray study of [Re(C−t-Bu)(CH−t-Bu)(ArNH$_2$)Cl$_2$]$_2$ showed it to contain two bridging halides with mutually cis alkylidene and alkylidyne ligands trans to the bridging halides (Re═C = 1.89(1) Å, Re═C−C = 140(1)°; Re≡C = 1.76(1) Å, Re≡C−C = 167(1)°). Several monomeric derivatives having the general formula Re(C−t-Bu)(CH−t-Bu)L$_2$Cl$_2$ (L = t-BuNH$_2$, pyridine, $^1/_2$ TMEDA, $^1/_2$ phenylenediamine (pda)) were isolated. Treatment of Re(C−t-Bu)(CH−t-Bu)(pda)Cl$_2$ with HCl(g) in dimethoxyethane affords air- and water-stable [Re(C−t-Bu)(CH−t-Bu)Cl$_2$]$_x$ (x > 1). ReO$_2$(CH−t-Bu)(CH$_2$−t-Bu) is prepared by the acid-catalyzed hydrolysis of Re(NAr)$_2$(CH−t-Bu)(CH$_2$−t-Bu) via intermediate Re(NAr)(O)(CH−t-Bu)(CH$_2$−t-Bu). Treatment of Re(O)$_2$(CH−t-Bu)(CH$_2$−t-Bu) with HCl(g) in dimethoxyethane yields [Re(C−t-Bu)(CH−t-Bu)Cl$_2$]$_x$. [Re(C−t-Bu)(CH−t-Bu)Cl$_2$]$_x$ is a versatile precursor to a variety of bisalkoxide complexes of the general formula Re(C−t-Bu)(CH−t-Bu)(OR)$_2$ (OR = O−t-Bu, OCMe$_2$(CF$_3$), OCMe(CF$_3$)$_2$, O−2,6-C$_6$H$_3$-i-Pr$_2$, OSi(t-Bu)$_3$). Syn and anti forms of the Re(C−t-Bu)(CH−t-Bu)(OR)$_2$ complexes slowly interconvert thermally or photochemically. An X-ray study of *syn*-Re(C−t-Bu)(CH−t-Bu)[OCMe(CF$_3$)$_2$]$_2$(THF) (Re═C = 1.85(1) Å, Re═C−C = 151(1)°; Re≡C = 1.75(1) Å, Re≡C−C = 175(1)°) showed it to have a structure approximately half-way between a face-capped tetrahedron (THF trans to the neopentylidyne ligand) and a trigonal bipyramid. Interconversion of syn and anti isomers of Re(C−t-Bu)(CH−t-Bu)(OR)$_2$ complexes is a slow process, requiring several hours at temperatures of 100 °C or higher because the alkylidyne ligand, unlike an imido ligand in Mo or W complexes, strictly maintains an Re−C triple bond. Therefore, the orbital that is required to stabilize the alkylidene when it rotates by 90° is not readily available.

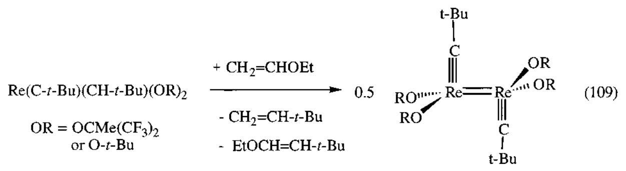
Compounds of the type Re(CCMe$_2$R)(CHCMe$_2$R)[OC(CF$_3$)$_2$Me]$_2$ react readily with olefins.[207,208] 1-Decene and methyl-9-decenoate react with Re(C−t-Bu)(CH−t-Bu)(OR$_{F6}$)$_2$ to give Re(C−t-Bu)[CH(CH$_2$)$_7$Me](OR$_{F6}$)$_2$ and Re(C−t-Bu)[CH(CH$_2$)$_7$CO$_2$Me](OR$_{F6}$)$_2$, respectively ($OR_{F6} = OCMe(CF_3)_2$). The new alkylidene complexes are unstable in the presence of excess terminal olefin and decompose upon attempted isolation. However, vinylferrocene reacts relatively smoothly with $Re(C-t\text{-}Bu)(CH-t\text{-}Bu)(OR_{F6})_2$ in a noncoordinating solvent to yield *tert*-butylethylene and primarily *anti*-$Re(C-t\text{-}Bu)(CHFc)(OR_{F6})_2$ (Fc = ferrocenyl). *anti*-$Re(C-t\text{-}Bu)(CHFc)(OR_{F6})_2$ was shown to be a pseudotetrahedral species with an unusually acute $Re{=}C_\alpha{-}C_\beta$ angle (114.8 (7)°; Re=C = 1.88(1) Å) and short Re≡C bond (1.70 (1) Å; Re≡C−C = 174.0(8)°). In the presence of THF or dimethoxyethane, complexes of the type $Re(C-t\text{-}Bu)(CHR)(OR_{F6})_2S_2$ (R = Me, Et, Ph; S = THF or 0.5 dme) could be prepared in high yield from $Re(C-t\text{-}Bu)(CH-t\text{-}Bu)(OR_{F6})_2$ and $CH_2{=}CHR$. Heteroatom-substituted (O, S, or N) terminal olefins react more rapidly than ordinary olefins with $Re(C-t\text{-}Bu)(CH-t\text{-}Bu)(OR_{F6})_2$ in the presence of THF to yield complexes of the type *syn*- or *anti*-$Re(C-t\text{-}Bu)(CHX)(OR_{F6})_2(THF)_2$ (X = OR, SR, NR_2, or paradimethylaminophenyl). The X-ray structure of *syn*-$Re(C-t\text{-}Bu)(CHOEt)(OR_{F6})_2(THF)_2$ showed it to be a pseudo-octahedral complex containing cis alkylidyne and alkylidene ligands and a THF ligand trans to each (Re=C = 1.883(9) Å; $Re{=}C_\alpha{-}O$ = (129.9(6)°; Re≡C = 1.713(8) Å; Re≡C−C = 177.7(8)°). 2-Pentene or methyl oleate are metathesized in the presence of $Re(C-t\text{-}Bu)(CH-t\text{-}Bu)(OR_{F6})_2$, and intermediate alkylidene complexes can be observed in each case. Addition of 3-hexene to $Re(C-t\text{-}Bu)(CH-t\text{-}Bu)(OR_{F6})_2$ followed by TMEDA yields $Re(C-t\text{-}Bu)(CHEt)(OR_{F6})_2(TMEDA)$. Internal olefins are metathesized only very slowly by $Re(C-t\text{-}Bu)(CH-t\text{-}Bu)(OR_{F6})_2$ in the presence of several equivalents of THF or dme, or especially in neat THF or dme. These findings were the first that confirmed through observation of new alkylidene complexes that Re(VII) is active for the metathesis of olefins.

The reaction shown in eq 108 led to a Re(VII) oxoalkylidene species.[209] Two isomers were observed that have alkylidene H_α resonances at 12.66 and 12.31 ppm; the former was converted into the latter in solution over a period of 20 h. An X-ray study showed the complex to have the "syn,mer" arrangement in which the Re=C bond was found to be 1.917 Å. No Wittig-type reactions with acetone or benzaldehyde were observed. Olefin metathesis activity was observed upon addition of $GaBr_3$, $AlCl_3$, etc., although the nature of the active species was not established. No intermediate alkylidene complexes could be observed.

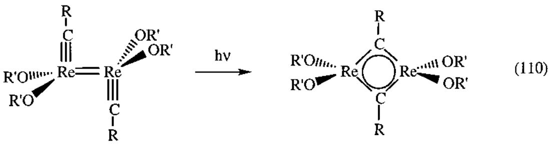


(108)

Base-free rhenium alkylidene complexes in which an oxygen is directly attached to the alkylidene carbon are not stable. For example, $Re(C-t\text{-}Bu)(CH-t\text{-}Bu)(OR)_2$ (OR = O−t-Bu or $OCMe(CF_3)_2$) reacts with ethyl vinyl ether to give dark-red $[Re(C-t\text{-}Bu)(OR)_2]_2$ (eq 109).[210] X-ray studies show that these compounds are structurally analogous dimers that possess an inversion center, a staggered, ethane-like geometry, an *unbridged* metal−metal double bond, and normal Re≡C bond lengths (1.721(7) and 1.728(8) Å, respectively). It is proposed that the $Re(C-t\text{-}Bu)(CH-t\text{-}Bu)(OR)_2$ complexes form via coupling of alkylidene ligands in $Re(C-t\text{-}Bu)(CHOEt)(OR)_2$ species. They are the only examples of M=M species that do not contain any bridging or semibridging ligands between the two metals. These dimers do not form stable adducts with pyridine or dimethylphenylphosphine and do not react readily with olefins or acetylenes. However, $[Re(C-t\text{-}Bu)(O-t\text{-}Bu)_2]_2$ does react rapidly at −40 °C in ether with 1 equiv of I_2 to afford pentane-soluble, vermillion crystals consistent with the formulation $Re(CCMe_2Ph)(O-t\text{-}Bu)_2I_2$. It is not known whether this species is a monomer or a dimer. Other examples of complexes of the type $Re(CR')(CH-t\text{-}Bu)(OR)_2$ in which R′ = CMe_2Ph or OR = $OCMe_2(CF_3)$ are also known.[211] Interestingly, photolysis of compounds of the type $[Re(CCMe_2R)(OR')_2]_2$ (R = Me or Ph; OR′ = O−t-Bu, $OCMe_2(CF_3)$, or $OCMe(CF_3)_2$) in benzene with a medium-pressure mercury lamp yields compounds of the type $[Re(OR')_2]_2(\mu\text{-}CCMe_2R)_2$ (eq 110) in an intramolecular and irreversible manner.[211] The fact that compounds can be formed that contain two bridging alkylidyne ligands, which is not an unusual circumstance, makes it even more surprising that the Re=Re compounds exist.

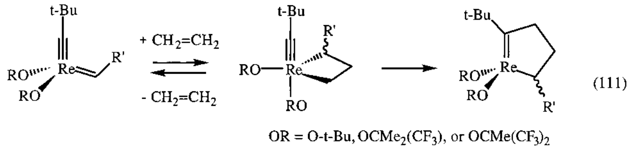


(109)



(110)

Ethylene reacts with $Re(C-t\text{-}Bu)(CH-t\text{-}Bu)(O-t\text{-}Bu)_2$ and $Re(C-t\text{-}Bu)(CH-t\text{-}Bu)[OCMe_2(CF_3)]_2$ to give trigonal bipyramidal rhenacyclobutane complexes at low temperatures and Re(V) rhenacyclopentene complexes formed by addition of ethylene to the C=Re≡C unit at higher temperatures (eq 111).[212]



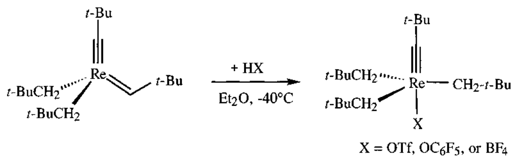
(111)

OR = O-t-Bu, $OCMe_2(CF_3)$, or $OCMe(CF_3)_2$

R′ = t-Bu or SPh

It is not known whether the Re(V) species are formed directly from the rhenacyclobutane complex or via some other species. An analogous reaction involving $Re(C-t\text{-}Bu)(CH-t\text{-}Bu)[OCMe(CF_3)_2]_2$ yields only a TBP rhenacyclobutane complex, while one involving $Re(C-t\text{-}Bu)(CHSPh)[OCMe(CF_3)_2]_2$ yielded a stable rhenacyclopentene complex at 25 °C. The structure of $Re[CH(SPh)CH_2CH_2C(t\text{-}Bu)][OCMe(CF_3)_2]_2(PMe_2Ph)$ was found to be roughly a trigonal bipyramid that contains an axial alkoxide, an axial phosphine ligand, and the expected rhenacyclopentene ring (Re=C = 1.90(1) Å). This finding suggests that decomposition in the presence of ethylene in metathesis reactions with a variety of compounds of this sort may involve reduction to Re(V) via irreversible "3 + 2 cycloaddition" across the C=Re≡C unit.

The reaction of Re(C−t-Bu)(CH−t-Bu)(CH$_2$−t-Bu)$_2$ with triflic acid, pentafluorophenol, HBF$_4$·OEt$_2$, or [H(OEt$_2$)$_2$][BAr$_F$] (BAr$_F^-$ = {B[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$}$^-$) yields complexes of the general formula Re(C−t-Bu)(CH$_2$−t-Bu)$_3$X (eq 112) in 60−80% yield.[213] Cationic ether or water adducts, {Re(C−t-Bu)(CH$_2$−t-Bu)$_3$(S)}X, are obtained when X is a weakly coordinating anion (eq 113). Re(C−t-Bu)(CH$_2$−t-Bu)$_3$X reacts with coordinating ligands L (L = py, CH$_3$CN, CD$_3$OD, THF) to form neopentane and Re(C−t-Bu)(CH−t-Bu)(CH$_2$−t-Bu)(L)$_n$X (n = 1−3) species (e.g., eq 114).



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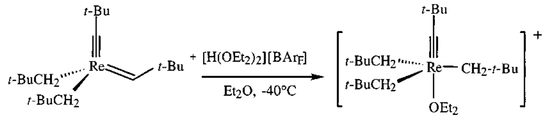
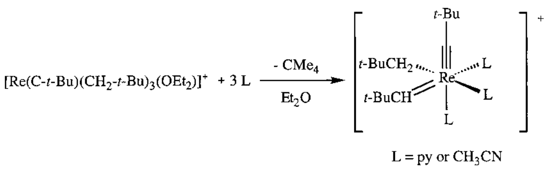


(113)



(114)

The reaction of Re(C−t-Bu)(CH−t-Bu)(CH$_2$−t-Bu)(py)$_2$(OTf) with NaC$_5$H$_5$, NaL$_{OEt}$ (L$_{OEt}$ = [CpCo(PO(OEt)$_2$)$_3$)], or NaHBpz$_3$ in THF yields Re(C−t-Bu)(CH−t-Bu)(CH$_2$−t-Bu)(η^5-C$_5$H$_5$), Re(C−t-Bu)(CH−t-Bu)(CH$_2$−t-Bu)(L$_{OEt}$), or Re(C−t-Bu)(CH−t-Bu)(CH$_2$−t-Bu)(HBpz$_3$), respectively, while the reaction between Re(C−t-Bu)(CH−t-Bu)(CH$_2$−t-Bu)(py)$_2$(OTf) and 1,4,7-trithiacyclononane produces colorless [Re(C−t-Bu)(CH−t-Bu)(CH$_2$−t-Bu)(η^3−S$_3$C$_6$H$_{12}$)]$^+$[OTf]$^-$ in 96% yield. Re(C−t-Bu)(CH−t-Bu)(CH$_2$−t-Bu)(L) (L = Cp, L$_{OEt}$) and [Re(C−t-Bu)(CH−t-Bu)(CH$_2$−t-Bu)(η^3−S$_3$C$_6$H$_{12}$)]$^+$[OTf]$^-$ react with triflic acid to form Re(C−t-Bu)(CH−t-Bu)(L)(OTf) and [Re(C−t-Bu)(CH−t-Bu)(OTf)(η^3−S$_3$C$_6$H$_{12}$)]$^+$[OTf]$^-$, respectively. A similar reaction between Re(C−t-Bu)(CH−t-Bu)(CH$_2$−t-Bu)(L$_{OEt}$) and [H(OEt$_2$)$_2$]$^+$[BAr$_F$]$^-$ in ether produces [Re(C−t-Bu)(CH−t-Bu)(OEt$_2$)(L$_{OEt}$)]$^+$[BAr$_F$]$^-$. Re(C−t-Bu)(CH−t-Bu)(CH$_2$−t-Bu)(py)$_2$(OTf) reacts with H$_2$C=CHR (R = OCH$_2$CH$_3$, C$_6$H$_5$) to yield neohexene and Re(C−t-Bu)(CHR)(CH$_2$−t-Bu)(py)$_2$(OTf) complexes. Re(C−t-Bu)(CH−t-Bu)(CH$_2$−t-Bu)(py)$_2$(OTf) reacts with ethylene to form the unstable methylidene complex Re(C−t-Bu)(CH$_2$)(CH$_2$−t-Bu)(py)$_2$(OTf), which can be trapped upon addition of bipyridine to yield red Re(C−t-Bu)(CH$_2$)(CH$_2$−t-Bu)(bpy)(OTf). Re(C−t-Bu)(CH−t-Bu)(CH$_2$−t-Bu)(py)$_2$(OTf) reacts with excess ethylene to form colorless Re(C−t-Bu)[(CH$_2$)$_3$−t-Bu](C$_2$H$_4$)(py)$_2$(OTf) in 85% yield. Re(C−t-Bu)(CH−t-Bu)(CH$_2$−t-Bu)(CH$_3$CN)(OTf) metathesizes 100 equiv of *cis*-2-pentene in less than 5 min, but the catalyst is not long-lived. The compounds reported here suggest that cationic rhenium alkylidene complexes are viable metathesis catalysts. However, the optimum combination of ligands has yet to be found.

3. Alkylidyne Complexes

Alkylidyne complexes that have appeared in the alkylidene section, usually those in which alkylidene ligands are also present, will not be repeated in this section.

3.1. Chromium

What are believed to be the only known d^0 chromium alkylidyne complexes have been prepared as shown in eq 115.[224,225] These species contain a dialkylamino group directly attached to the alkylidyne α carbon atom. These particular species are not stable above −50 °C as a consequence of ready loss of CO. However, isocyanide complexes (eq 116) or trimethyl phosphite complexes are more stable. Dicationic isocyanide complexes, [(η^5-C$_5$R$_5$)(t-BuNC)$_3$Cr≡CNEt$_2$](PF$_6$)$_2$ (R = H, Me) and a mixed isocyanide phosphite complex, [Cp(Br)(t-BuNC)[P(OMe)$_3$]Cr≡CNEt$_2$]PF$_6$, have also been prepared. The strong IR absorption in the range 1560−1637 cm^{-1} suggests that the amino group is strongly conjugated with the chromium−carbon triple bond. X-ray studies of [(η^5-C$_5$H$_5$)(t-BuNC)$_2$(Br)Cr≡CNEt$_2$]PF$_6$ and [(η^5-C$_5$Me$_5$)(t-BuNC)$_3$Cr≡CNEt$_2$](PF$_6$)$_2$ nevertheless reveal short Cr≡C bond lengths of 1.745 and 1.735 Å, respectively.

$$(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Cr}{\equiv}\text{CN}{-}\text{i-Pr}_2 \xrightarrow[\text{CH}_2\text{CL}_2,\ -78\ °\text{C}]{\text{Br}_2} \\ \text{R} = \text{H or Me} \\ [(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2(\text{Br})\text{Cr}{\equiv}\text{CN}{-}\text{i-Pr}_2]\text{Br} \quad (115)$$

$$[\text{Cp}(\text{CO})_2(\text{Br})\text{Cr}{\equiv}\text{CN}{-}\text{i-Pr}_2]\text{Br} \xrightarrow[-2\text{CO}\ -\ \text{TlBr}]{\text{TlPF}_6,\ 2\ \text{t-BuNC}} \\ [\text{Cp}(\text{t-BuNC})_2(\text{Br})\text{Cr}{\equiv}\text{CN}{-}\text{i-Pr}_2]\text{PF}_6 \quad (116)$$

3.2. Molybdenum and Tungsten

High oxidation state amino carbyne complexes of molybdenum and tungsten have been prepared. Oxidation with iodine produced the compounds shown in eqs 117 and 118,[224] while oxidation of Cp(CO)$_2$W≡CNEt$_2$ with bromine produced CpBr$_2$(CO)W≡CNEt$_2$.[226]

$$\text{I(CO)}_2\text{L}_2\text{W}{\equiv}\text{CNEt}_2 + \text{I}_2 \rightarrow \text{I}_3\text{(CO)L}_2\text{W}{\equiv}\text{CNEt}_2 \\ \text{L} = \text{P(OMe)}_3 \quad (117)$$

$$\text{I(CO)(RNC)}_3\text{W}{\equiv}\text{CNEt}_2 \xrightarrow{\text{I}_2} \\ \text{R} = \text{Me, t-Bu} \\ \text{I}_3\text{(RNC)}_3\text{W}{\equiv}\text{CNEt}_2 \xrightarrow{\text{RNC}} [\text{I}_2\text{(RNC)}_4\text{W}{\equiv}\text{CNEt}_2]\text{I} \quad (118)$$

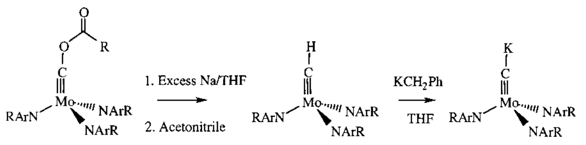
Table 2. Tabulation of Isolated Alkylidyne Complexes[a]

$[(\eta^5\text{-}C_5R_5)Br(L)_2Cr{\equiv}CN{-}i\text{-}Pr_2]X$	L = CO, t-BuNC; X = Br, PF_6	225
$[(\eta^5\text{-}C_5R_5)(t\text{-}BuNC)_3Cr{\equiv}CNEt_2](PF_6)_2$	R = H, Me	225
$[Cp(Br)(t\text{-}BuNC)[P(OMe)_3]Cr{\equiv}CNEt_2]PF_6$		225
$Mo(C{-}t\text{-}Bu)[OCMe_2(CF_3)]_2[N(Ar)P{=}CHCMe_2Ph]$		156
$Mo(CCMe_2Ph)(NHAr)(Tp)X$	X = NMe_2, *o*-tol, OPh, OMe	157
$[aryl(R)N]_3Mo{\equiv}C{-}X$	R = t-Bu; X = $CO_2{-}t\text{-}Bu$, H, K; aryl = 3,5-$Me_2C_6H_3$	230
$(AdO)_3Mo{\equiv}CCH_2SiMe_3$		231
$M(CR)(TIPT)_3$	M = Mo, W; R = t-Bu, Pr, Me; TIPT = 2,4,6-i-$Pr_3C_6H_2S^-$	255
$[M(C{-}t\text{-}Bu)(TMT)_3]_2$	M = Mo, W; TMT = 2,4,6-$Me_3C_6H_2S^-$	255
$[Et_3NH][M(C{-}t\text{-}Bu)(TMT)_3Cl]$	M = Mo, W	255
$[(C_6F_5NCH_2CH_2)_3N]Mo{\equiv}C{-}t\text{-}Bu$		261
$[(Me_3SiNCH_2CH_2)_3N]Mo{\equiv}CR$	R = H, Pr, t-Bu	262
$\{[(R_3SiNCH_2CH_2)_3N]Mo{\equiv}CCH{=}\}_2$	$SiR_3 = SiMe_3, SiMe_2Ph$	263
$[(Me_3SiNCH_2CH_2)_3N]Mo{\equiv}COSiMe_3$		264
$W(C{-}t\text{-}Bu)(CH_2{-}t\text{-}Bu)_3[Si(SiMe_3)_3]$		93
$W(CR)Tp^*X_2$	R = t-Bu, X = Cl; R = Ph, X = Br	164, 166
$L_{OMe}ClW(CTol)(NHPr)$		174
$L_{OR}X_2W{\equiv}CTol$	OR = OMe, OEt, O−i-Pr; X = Cl, Br, F, OEt	174, 253, 254
$L_{OR}XX'W{\equiv}CTol$	X = F, X′ = NMe_2; X = Cl, X′ = OR; X = Cl, X′ = NHPr	174
$\{[calix]W{\equiv}CR\}^-$	R = Ph, Pr, $SiMe_3$	191,194
$I_3(CO)[P(OMe)_3]W(CNEt_2)$		224
$[I_2(RNC)_4W(CNEt_2)]I$		224
$CpBr_2(CO)W{\equiv}CNEt_2$		226
$Tp^*X_2W{\equiv}CNEt(R)$	X = Br, I	229
$[(py)_n(Me_3CCH_2)(i\text{-}PrO)_2W{\equiv}CEt]_2$	n = 0 or 1	235
$(t\text{-}BuO)_3W{\equiv}CR$	R = 4-pyridyl, 3,5-dimethyl-4-pyridyl, 4-$C_6H_4NMe_2$, 4-C_6H_4SMe	236, 237
$W(CAd)(O{-}t\text{-}Bu)_3$		238
$W(CAd)(O{-}t\text{-}Bu)_2(OTf)(dme)$		238
$CpW(CAd)R_2$	R = Cl, O−t-Bu, CH_2−t-Bu, CH_2Ph, Me	238
$CpW(CAd)RCl$	R = CH_2−t-Bu, NMe_2, NH−t-Bu	238
$CpW(CAd)(NMe_2)(CH_2{-}t\text{-}Bu)$		238
$(t\text{-}BuO)_3W{\equiv}Cmesityl$		240
$(RCH_2)_3W{\equiv}C{-}t\text{-}Bu$	R = Ph, $SiMe_3$	241
$(t\text{-}BuCH_2)_3W{\equiv}CSiMe_3$		241
$py_n(t\text{-}BuCH_2)_3W{\equiv}C{-}C{\equiv}W(CH_2{-}t\text{-}Bu)_3py_n$	n = 0 or 1	241
$(Me_3SiCH_2)_3W{\equiv}C{-}C{\equiv}W(CH_2SiMe_3)_3$		241
$py_n(RCH_2)_3W{\equiv}CPh$	R = t-Bu, $SiMe_3$, n = 0 or 1	241
trans-$[(Me_3CO)_3W{\equiv}CCH{=}CHC{\equiv}W(O{-}t\text{-}Bu)_3]$		244
cis,cis-$[(Me_3CO)_3W{\equiv}CCH{=}CHC{\equiv}]_2$		244
trans-$[(Et_2O)(CF_3Me_2CO)_3W{\equiv}CCH{=}]_2$		244
cis-$W(CCH{=}CHC{\equiv}CEt)(OCMe_2CF_3)_3(bipy)$		244
$[(Me_3CO)_3W{\equiv}C(1,2\text{-}C_6H_4)C{\equiv}]_2$		244
$(RO)_3W{\equiv}C{-}C{\equiv}W(OR)_3$	OR = O−t-Bu, $OCMe_2Et$, $OC(CF_3)Me_2$	245−247
$(t\text{-}BuO)_3W{\equiv}C(CH_2)_nC{\equiv}W(O{-}t\text{-}Bu)_3$	n = 0 or 1	248
$(t\text{-}BuO)_3W{\equiv}C(CH_2)_nC{\equiv}W(O{-}t\text{-}Bu)_3$	n = 3, 4, 5	248
$Cp^*(NO)(PPh_3)Re{-}C{\equiv}C{-}C{\equiv}W(O{-}t\text{-}Bu)_3$		249
$(dme)X_3W{\equiv}CR$	X = Cl, Br; R = t-Bu, Pr, Ph	252
$[Et_3NH][W(CR)(TIPT)_3Cl]$	R = Me, t-Bu	255
$W(CMe)(TMT)_3(py)$		255
$(t\text{-}BuCH_2)_3W{\equiv}CSiMe_3$		256
$[(Me_3SiNCH_2CH_2)_3N]W{\equiv}CR$	R = Me, Et, $OSiMe_3$	258
$[(Me_3SiNCH_2CH_2)_3N]W{\equiv}CR$	R = H, Me, Pr, Ph, $SiMe_3$, t-Bu	260
$[(C_6F_5NCH_2CH_2)_3N]W{\equiv}CR$	R = H, Me, n-Pr, $SiMe_3$, CMe_3, or Ph	261
$[(C_6F_5NCH_2CH_2)_3N]W{\equiv}CR$	R = H, Me, n-Pr, $SiMe_3$, t-Bu, Ph	261
$[(C_6F_5NCH_2CH_2)_3N]W{\equiv}COV(Mes)_3$		264
$Re(C{-}t\text{-}Bu)(NAr)(OAr'')_2(py)$	OAr″ = O−2,6-$Cl_2C_6H_3$, OC_6Cl_5	204
$[Re(CR)(OR')_2]_2$	R = t-Bu, CMe_2Ph; R′ = t-Bu, CMe_2CF_3, $CMe(CF_3)_2$	211
$Re(C{-}t\text{-}Bu)(CH_2{-}t\text{-}Bu)_3X$	X = OTf, OC_6F_5, BF_4	213
$\{Re(C{-}t\text{-}Bu)(CH_2{-}t\text{-}Bu)_3(Et_2O)\}[BAr_F]$		213
$[NEt_4][Re(C{-}t\text{-}Bu)(NHAr)Cl_4]$		266
$Re(C{-}t\text{-}Bu)(NHAr)Cl_3L$	L = py, THF	266
$Re(C{-}t\text{-}Bu)(NAr)Cl_2L_2$	$L_2 = py_2$, dme	266
$Re(C{-}t\text{-}Bu)(NAr)(OR)_2(THF)_x$	x = 0, R = O−t-Bu, $OC(CF_3)Me_2$, $OC(CF_3)_2Me$, OAr; x = 1, R = $OC(CF_3)_2H$	266
$ReCp^*(C{-}t\text{-}Bu)X_3$	X = Cl, Br, I	267, 268
$[H_2(mq)(PPh_3)_2Re(CCH_2R)]PF_6$	R = Pr, Ph, tolyl; mq = 2-mercaptoquinolate	269

[a] Complexes that also contain an alkylidene ligand may be found in Table 1.

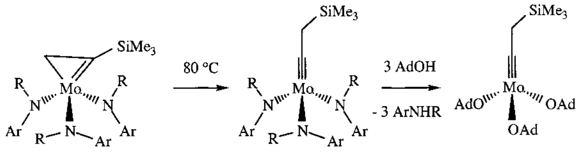
Similar reactions were employed in order to prepare $CpX_2(CO)Mo{\equiv}CNEt_2$ (X = Br or I),[227] $CpI_2(CO)W{\equiv}CNEt_2$ and its Cp* analogue,[228] and $\{CpI(EtNC)I(CO)W{\equiv}CNEt_2\}^+$ and its Cp* analogue.[228] Oxidation of compounds of the type $Tp^*(CO)_2W{\equiv}CNEt(R)$ (R = Me, Et) with bromine or iodine has also been shown to yield complexes of the type Tp*$X_2W{\equiv}CNEt(R)$ (X = Br, I).[229]

Treatment of $\{(ArRN)_3Mo{\equiv}CO\}^-$ (R = t-Bu; Ar = 3,5-dimethylphenyl) with pivalolyl chloride yields the derivative shown in eq 119.[230] The methylidyne species is formed ($\delta H_\alpha = 5.66$ ppm, $J_{CH} = 157$ Hz) upon treatment of this compound with excess sodium followed by acetonitrile. This species can be deprotonated to yield a potassium salt of $\{(ArRN)_3Mo{\equiv}C\}^-$, which exists as a dimer in the absence of some ligand to bind to potassium. The chemical shift of the "carbide" carbon in this species is 494 ppm. Upon addition of benzo-15-crown-5, $K(crown)_2\{(ArRN)_3Mo{\equiv}C\}$ is formed, which was shown in an X-ray study to contain discrete separated ions. In $\{(ArRN)_3Mo{\equiv}C\}^-$, the Mo≡C bond length was found to be 1.713(9) Å.



(119)

The η^2-vinyl species shown in eq 120 was found to rearrange to the alkylidyne complex via a 1,2 migration of the trimethylsilyl group (Ar = 3,5-dimethylphenyl, R = isopropyl).[231] Upon addition of 3 equiv of 1-adamantyl alcohol the triadamantyloxy alkylidyne complex could be isolated as a crystalline solid that retained 1 equiv of ArNHR. A crystal structure showed the Mo≡C bond length to be 1.754(6) Å. The $(AdO)_3Mo(CCH_2SiMe_3)$ complex reacts readily with 3-hexyne or 2-butyne to yield $(AdO)_3Mo(CR)$ (R = Et or Me) and was shown to metathesize $MeC{\equiv}CCH_2CH_2OTs$ to yield $TsOCH_2CH_2C{\equiv}CCH_2CH_2OTs$ and 2-butyne. The Mo≡C bond length in $(AdO)_3Mo(CEt)$ was found to be 1.743(4) Å in an X-ray study. This route to adamantyloxymolybdenum alkylidyne complexes is more convenient than the route to previous trialkoxyalkylidyne complexes,[232,233] which was relatively tedious and not amenable to production of more than ~1 g. However, so far only adamantoxy derivatives have been insoluble enough to isolate in pure form.



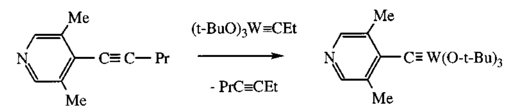
(120)

A wide variety of $(t\text{-}BuO)_3W{\equiv}CR$ species can be prepared in a reaction between $W_2(t\text{-}BuO)_6$ and $RC{\equiv}CR$.[234] This reaction is sensitive to the nature of the alkoxide, which cannot be varied widely. A rare related reaction that does not involve a hexaalkoxide has been reported (eq 121).[235] In the solid state the

$$(Me_3CCH_2)(i\text{-}PrO)_2W{\equiv}W(O{-}i\text{-}Pr)_2(CH_2CMe_3) \xrightarrow{EtC{\equiv}CEt} [(Me_3CCH_2)(i\text{-}PrO)_2W{\equiv}CEt]_2 \quad (121)$$

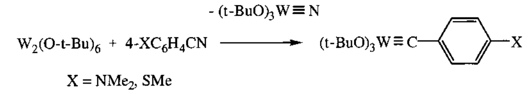
product exists as a weakly associated dimer through two bridging isopropoxide groups, as shown in an X-ray study; the propylidyne and an isopropoxy ligand occupy approximate axial positions in a trigonal bipyramid (W≡C = 1.765(7) Å). A pyridine adduct, $(py)(Me_3CCH_2)(i\text{-}PrO)_2W{\equiv}CEt$, is also proposed to be a dimer in the solid state. Steric factors are extremely important in the successful reaction of W≡W species with alkynes, alkyne adducts and a variety of other species often being the preferred products.

Pyridyl-substituted methylidyne complexes could be prepared as shown in reaction 122. The 3,5-dimethyl derivative shown was found to be a polymeric species with a square pyramidal core geometry around tungsten.[236] An analogous species containing the parent pyridyl group was found to be a polymeric species with a trigonal bipyramidal core geometry around tungsten. Both are luminescent at room temperature as solids or in solution. In contrast, species such as $(t\text{-}BuO)_3W{\equiv}CPh$ fail to luminesce at room temperature.



(122)

An alternative method of preparing tri-t-butoxytungsten alkylidyne complexes is to treat $W_2(OCMe_3)_6$ with a nitrile. For example, para-substituted benzylidyne complexes of tungsten were prepared as shown in eq 123.[237] They were shown to have "zigzag" structures in which the X group is donated to a neighboring metal (W≡C = 1.754(7) and 1.757(6) Å, respectively for X = NMe_2 and SMe). The basic geometry around tungsten was found to be trigonal bipyramidal with the donor (N or S) bound trans to the alkylidyne ligand.



(123)

1-Adamantylmethylidyne complexes, $W(CAd)(OCMe_3)_3$, can be prepared by treating $W_2(OCMe_3)_6$ with 1-adamantanecarbonitrile. It was converted into $W(CAd)(triflate)(OCMe_3)_2(dme)$ by addition of $Me_3Si(triflate)$ (dme = 1,2-dimethoxyethane).[238] $W(CAd)(triflate)(OCMe_3)_2(dme)$ reacts with NaCp to yield $CpW(CAd)(OCMe_3)_2$. $CpW(CAd)(OCMe_3)_2$ can be converted into $CpW(CAd)Cl_2$ in dichloromethane by treating it with Me_3SiCl. Alkylation of $CpW(CAd)Cl_2$ yields $CpW(CAd)(CH_2CMe_3)Cl$ or $CpW(CAd)R_2$ complexes (R = CH_2CMe_3, CH_2Ph, or CH_3). Both $CpW(CAd)(CH_2CMe_3)Cl$ and $CpW(CAd)(CH_2CMe_3)_2$ tautomerize to give mixtures containing $CpW(CCMe_3)(CH_2Ad)Cl$ and $CpW(CCMe_3)(CH_2CMe_3)(CH_2Ad)$, respectively. An X-ray study of $CpW(CAd)(CH_2CMe_3)_2$ is consistent with some α agostic interaction of a neopentyl proton in each neopentyl ligand with the metal (W≡C =1.746(9) Å, W≡C−C = 166.2(6)°). In contrast, $CpW(CAd)(NMe_2)(CH_2CMe_3)$ shows no evidence of tautomerizing to $CpW(CCMe_3)(NMe_2)(CH_2Ad)$ at room temperature over the course of 2 weeks, while $CpW(CAd)(NHCMe_3)Cl$ tautomerizes to two rotameric forms of $CpW(NCMe_3)(CHAd)Cl$.

The reaction between $W_2(OCMe_2CF_3)_6$ and acetonitrile proceeded very slowly at room temperature (weeks) to yield 2-butyne and 2 equiv of $(CF_3Me_2CO)_3W{\equiv}N$; the second equivalent presumably was formed via the rapid reaction of intermediate $(CF_3Me_2CO)_3W{\equiv}CMe$ with acetonitrile.[239] A similar reaction involving benzonitrile proceeded at a much more rapid rate, but again, only diphenylacetylene and $(CF_3Me_2CO)_3W{\equiv}N$ were observed.

The reaction between $W_2(OCMe_3)_6$ and $RC{\equiv}P$ was found to proceed as shown in eq 124 (R = t-Bu or mesityl).[240] The reaction was most clean when R was

$$W_2(O{-}t\text{-}Bu)_6 \xrightarrow[-THF\,-\,(O-t\text{-}Bu)_3W\equiv CR]{+RC\equiv P\,+\,W(CO)_5(THF)} [(O{-}t\text{-}Bu)_3W{\equiv}P]W(CO)_5 \quad (124)$$

mesityl. Alkyl groups that are smaller than *tert*-butyl or mesityl led to formation of many other unidentified products. The terminal phosphido complex, $(OCMe_3)_3W{\equiv}P$, was too reactive to be isolated in free form.

Treatment of a variety of tri-*tert*-butoxyalkylidyne complexes with Grignard or lithium reagents produces a variety of trialkyl alkylidyne species such as $(PhCH_2)_3W{\equiv}C{-}t\text{-}Bu$ and $(t\text{-}BuCH_2)_3W{\equiv}C{-}C{\equiv}W(CH_2{-}t\text{-}Bu)_3$ (see Table 2).[241] The stabilities and physical properties of the various $(RCH_2)_3W{\equiv}CR'$ compounds depend markedly on the nature of R and R′, and no species that contain alkyls with one or more β hydrogens could be prepared. The structure of $(py)(t\text{-}BuCH_2)_3W{\equiv}CPh$ was shown to be a trigonal bipyramid with the benzylidyne and pyridine donor in apical positions (W≡C = 1.74(3) Å). The main motive for preparing a variety of trialkyl alkylidyne complexes was to explore their utility for chemical vapor deposition.

Tungsten alkylidyne complexes, $W(C{-}t\text{-}Bu)(CH_2{-}t\text{-}Bu)_3$ and $W(C{-}t\text{-}Bu)Cl_3(dme)$, have been used as a source of supported alkylidene complexes.[242,243] Upon addition of these alkylidyne species to niobia or silica, a proton is transferred to the alkylidyne in the process of the metal being attached to the surface through alkoxide linkages. Wittig-like reactions were used to quantitate the available alkylidene. The supported complexes were catalysts for the metathesis of a variety of olefins.

Reaction of 0.5 equiv of *trans*-5-decene-3,7-diyne with $W(CEt)(OCMe_3)_3$ yields *trans*-$(Me_3CO)_3W{\equiv}CCH{=}CHC{\equiv}W(OCMe_3)_3$ via intermediate *trans*-$(Me_3CO)_3W{\equiv}CCH{=}CHC{\equiv}CEt$, while reaction of 1 equiv of *cis*-5-decene-3,7-diyne with $W(CEt)(OCMe_3)_3$ yields *cis*,*cis*-$(Me_3CO)_3W{\equiv}CCH{=}CHC{\equiv}CCH{=}CHC{\equiv}W(OCMe_3)_3$ via *cis*-$(Me_3CO)_3W{\equiv}CCH{=}CHC{\equiv}CEt$.[244] Reaction of additional *cis*- or *trans*-5-decene-3,7-diyne with either bimetallic species results in decomposition. Bipyridyl adducts of related metal-capped oligomers have been prepared and are more stable but relatively insoluble. Reaction of 0.5 equiv of 1,4-dibutynylbenzene with $W(CEt)(OCMe_3)_3$ yields $(Me_3CO)_3W{\equiv}C(1,4\text{-}C_6H_4)C{\equiv}W(OCMe_3)_3$, while reaction of 1 equiv of 1,2-dipentynylbenzene with $W(CEt)(OCMe_3)_3$ yields $(Me_3CO)_3W{\equiv}C(1,2\text{-}C_6H_4)C{\equiv}C(1,2\text{-}C_6H_4)C{\equiv}W(OCMe_3)_3$. Addition of ≥4 equiv of 1,4-dibutynyl or 1,2-dipentynylbenzene to $W(CEt)(OCMe_3)_3$ results in formation of a yellow intractable product in less than 50% yield. Either instability or insolubility appears to limit the utility of compounds in this general class as catalysts for the synthesis of polymers via a step-growth alkyne metathesis reaction.

The dimeric species, $(t\text{-}BuO)_3W{\equiv}C{-}C{\equiv}W(O{-}t\text{-}Bu)_3$,[234] was shown to have a structure in which the two ends of the molecule are staggered and W≡C = 1.819(16) Å.[245] In a second structural study of this compound, in this case *not* a toluene solvate, the W≡C bond length was found to be 1.79(1) Å.[246] Although in each structure the C−C bond was relatively short (1.38 Å), there was no compelling structural argument for any significant delocalization throughout the W≡C−C≡W core. $(RO)_3W{\equiv}C{-}C{\equiv}W(OR)_3$ compounds in which OR = $COMe_2Et$ or $OC(CF_3)Me_2$ were prepared by similar methods.[247] On the basis of a spectroscopic analysis, the authors argue for some communication between the two W≡C bonds. Similar compounds that contain three to five methylene groups between the two alkylidyne carbon atoms were prepared as shown in eq 125.[248] (The nitrile

$$2(t\text{-}BuO)_3W{\equiv}W(O{-}t\text{-}Bu)_3 \xrightarrow[-2(t\text{-}BuO)_3W\equiv N]{+NC(CH_2)_nCN} (t\text{-}BuO)_3W{\equiv}C(CH_2)_nC{\equiv}W(O\text{-}t\text{-}Bu)_3 \quad (125)$$

complex, $(t\text{-}BuO)_3W{\equiv}N$, is insoluble and can be filtered off quantitatively.[234]) When n = 4 or 5, addition of CO to the bimetallic alkylidyne yields complexes that contain the cyclic alkynes bound in the form of a dimetalatetrahedrane complex, $(t\text{-}BuO)_3W[\mu\text{-}C_2(CH_2)_n][\mu\text{-}O{-}t\text{-}Bu]W(O{-}t\text{-}Bu)_2(CO)$.

The reaction between $Cp^*(NO)(PPh_3)Re{-}C{\equiv}C{-}C{\equiv}CMe$ and ditungstenhexa-*tert*-butoxide proceeds as shown in eq 126.[249] The Re/W product was found

$$\begin{gathered}Cp^*(NO)(L)Re{-}C{\equiv}C{-}C{\equiv}CMe + (t\text{-}BuO)_3W{\equiv}W(O{-}t\text{-}Bu)_3 \rightarrow \\ Cp^*(NO)(L)Re{-}C{\equiv}C{-}C{\equiv}W(O{-}t\text{-}Bu)_3 + (t\text{-}BuO)_3W{\equiv}CMe \quad (126)\end{gathered}$$

to be a dimer containing two bridging *tert*-butoxides and in which the W≡C bond length was found to be 1.769(8) Å. There is no evidence for anything other than the strict single/triple bond alteration shown between Re and W. A similar reaction had been shown to yield $Cp(CO)_2Ru{-}C{\equiv}W(O{-}t\text{-}BuO)_3$.[250]

The original method of preparing $W(C{-}t\text{-}Bu)Cl_3(dme)$ was via the addition of 3 equiv of HCl to $W(C{-}t\text{-}Bu)(CH_2{-}t\text{-}Bu)_3$ in pentane in the presence of dimethoxyethane.[251] An appealing new method of synthesizing compounds of the type $W(CR)X_3(dme)$ in good to excellent yields is shown in eq 127.[252] The

$$\begin{gathered}(t\text{-}BuO)_3W{\equiv}CR \xrightarrow[+3BX_3\,-\,3BX_2(O-t\text{-}Bu)]{pentane/dme} (dme)X_3W{\equiv}CR \quad (127)\\ R = t\text{-}Bu,\ Pr,\ Ph;\ X = Cl,\ Br\end{gathered}$$

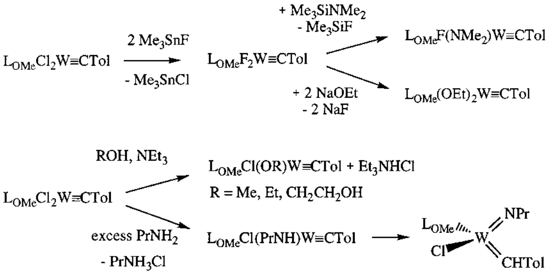
starting $(t\text{-}BuO)_3W{\equiv}CR$ complexes are readily available from the reaction between $(t\text{-}BuO)_3W{\equiv}W(O{-}t\text{-}Bu)_3$ and $RC{\equiv}N$ (to give $(t\text{-}BuO)_3W{\equiv}CR$ plus insoluble $(t\text{-}BuO)_3W{\equiv}N$) or excess $RC{\equiv}CMe$ (to give $(t\text{-}BuO)_3W{\equiv}CR$ and $MeC{\equiv}CMe$).[234]

Several alkylidene and alkylidyne derivatives have been prepared that contain the "Kläui ligand", $\{CpCo[P(OR)_2(O)]_3]\}^-$ (L_{OR} where OR = OMe, OEt, or O−i-Pr). The first alkylidyne complexes are shown in eqs 128 and 129.[253] The second of these is prepared

$$Br_3(dme)W{\equiv}CTol + NaL_{OR} \xrightarrow{-NaBr} L_{OR}Br_2W{\equiv}CTol + NaL_{OR} \quad (128)$$
$$R = Me, Et, i\text{-}Pr$$

$$L_{OR}(CO)_2W{\equiv}CTol \xrightarrow[-2CO]{Cl_3CCCl_3} L_{OR}Cl_2W{\equiv}CTol \quad (129)$$

by oxidation (essentially chlorination) of a Fisher-type carbene complex. Iodobenzene dichloride was later found to be a more convenient oxidizing agent.[254] Attempted oxidation of $L_{OR}(CO)_2Mo{\equiv}CTol$ with $PhICl_2$, however, led to loss of the alkylidyne ligand. Various fluoride, methoxide, and dimethylamido derivatives could be prepared as shown in eq 130, as could chloroalkoxo or -imido species (eq 131).[174] The amidoalkylidyne complex is slowly tranformed into two imidoalkylidene species via migration of a proton from the amido group to the alkylidyne group (eq 131b). A related $L_{OMe}Cl(O)W{=}CHTol$ species could be prepared as one isomer by treating $L_{OMe}Cl_2W{\equiv}CTol$ with a mixture of triethylamine and water or with hydroxylated alumina. The alkylidene complexes were active for ROMP in the presence of aluminum trichloride. As in any reactions involving aluminum trichloride as an activator, the true catalyst may not be of the same type as the starting complex.



(130)

(131a)

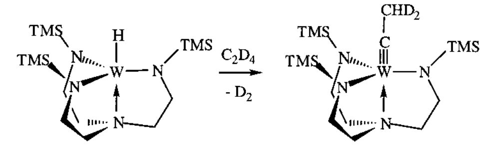
(131b)

Complexes of the type $Mo(C{-}t\text{-}Bu)(TMT)_3$ and $Mo(C{-}t\text{-}Bu)(TIPT)_3$ (TMT = 2,4,6-trimethylbenzenethiolate; TIPT = 2,4,6-triisopropylbenzenethiolate) can be prepared by adding 3 equiv of LiSAr (SAr = TMT or TIPT) to $Mo(C{-}t\text{-}Bu)Cl_3(dme)$.[255] The TMT derivative is believed to be dimeric. Reactions between $M(C{-}t\text{-}Bu)Cl_3(dme)$ (M≡Mo or W), ArSH, and NEt_3 gave complexes of the type $[Et_3NH][M(C{-}t\text{-}Bu)(SAr)_3Cl]$. $W(C{-}t\text{-}Bu)(SAr)_3$ complexes can be prepared by removing chloride ion from the $[Et_3NH][W(C{-}t\text{-}Bu)(SAr)_3Cl]$ species with zinc chloride. $M(C{-}t\text{-}Bu)(SAr)_3$ complexes do not react with 3-hexyne, 2-butyne, or phenylacetylene, and only minute traces of 3-heptyne metathesis products are observed after 3 days at 25 °C. Both $Mo(CPr)(TIPT)_3$ and $W(CMe)(TIPT)_3$ are stable and isolable. These studies suggest that $M(CR)(SAr)_3$ complexes react too slowly with ordinary acetylenes to be active catalysts either because coordination of sulfur (in a dimer) competes effectively with coordination of the acetylene or because the metal is simply not electrophilic enough, or both.

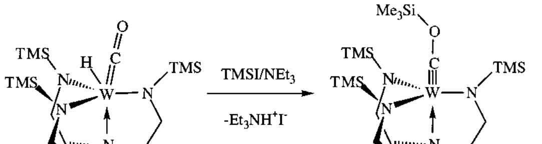
A scrambling reaction that interconverts an alkyl and an alkylidyne ligand is normally not readily observable. However, it can be observed in $(t\text{-}BuCH_2)_3W{=}CSiMe_3$.[256] The approach to the equilibrium shown in eq 132 follows first-order kinetics with $\Delta H^‡ = 27.5$ kcal/mol and $\Delta S^‡ = -2.0$ eu for the forward reaction and $\Delta H^‡ = 25.4$ kcal/mol and $\Delta S^‡ = -9.5$ eu for the reverse reaction. Crossover experiments indicated that the reaction was unimolecular. The intermediate in the exchange reaction is proposed to be a bisalkylidene complex, which is formed via transfer of an α hydrogen from an alkyl α carbon to the alkylidyne α carbon atom. A ^{13}C label is also scrambled among the carbon positions in $(Me_3CCH_2)_3W{\equiv}^{13}CCMe_3$ over a period of 24 h at 60 °C, presumably by movement of the α hydrogen atoms in a similar, strictly degenerate process.[257]

$$(Me_3CCH_2)_3W{\equiv}CSiMe_3 \rightleftarrows (Me_3CCH_2)_2(MeSiCH_2)W{\equiv}CCMe_3 \quad (132)$$

The two π and one σ orbitals emerging in the "pocket" of the $[(Me_3SiNCH_2CH_2)_3N]M$ framework ($[(Me_3SiNCH_2CH_2)_3N]^{2-} = [N_3N]^{2-}$) are conducive to formation of alkylidyne complexes. For example, $[N_3N]WH$ in C_6D_6 reacts with ethylene to produce $[N_3N]W{\equiv}CMe$ quantitatively.[258] The reaction is proposed to proceed via insertion of ethylene into the WH bond followed by α,α-dehydrogenation, according to the labeling study shown in eq 133. The reaction between $[N_3N]WH$ and propylene at 45 °C for 24 h produces a mixture of $[N_3N]W{\equiv}CCH_2CH_3$ and $[N_3N]WH_3$, which is formed by addition of dihydrogen to $[N_3N]WH$. Upon addition of trimethylamine to a mixture of $[N_3N]W(H)(CO)$ and Me_3SiI, colorless $[N_3N]W{\equiv}COTMS$ is formed (eq 134). It was proposed that Me_3SiI is attacked by the terminal oxygen in the carbonyl ligand reversibly to give $\{[N_3N]W(H)(COSiMe_3)\}^+I^-$ and that the resulting cationic complex is deprotonated by triethylamine to yield the observed product.

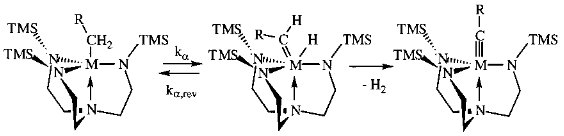


(133)



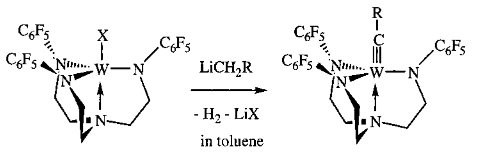
(134)

Attempted syntheses of $[(Me_3SiNCH_2CH_2)_3N]WCH_2R$ complexes led to formation of complexes of the type $[N_3N]W{\equiv}CR$ (R = H, Me, Pr, Ph, $SiMe_3$, t-Bu) and molecular hydrogen via an α elimination/α abstraction sequence (or α,α-dehydrogenation) shown in eq 135.[259,260] The attempted synthesis of a cyclopentyl derivative produced the cyclopentylidene hydride species shown earlier in eq 101 ($W{=}C = 1.97(1)$ Å).[202] When the cyclopentylidene complex is heated, cyclopentene is evolved and a paramagnetic monohydride, $[N_3N]WH$, is formed. All evidence supports the proposal that alkylidene hydrides form much more readily than olefin hydrides, even in the presence of β protons, and in at least one case (cyclopentyl) the two rates differ by a factor of approximately 6 orders of magnitude. Steric factors in $[N_3N]WR$ complexes may play a significant role in preventing more rapid formation of an olefin hydride. The attempted synthesis of $[N_3N]W$(cyclopropyl) yielded ethylene and $[N_3N]W{\equiv}CH$, while $[N_3N]W$(cyclobutyl) was converted into a 1-tungstacyclopentene complex. When heated, the 1-tungstacyclopentene complex rearranged to a butylidyne complex (eq 102). These studies emphasize the great preference for α elimination over β elimination in complexes of this general type for tungsten.



(135)

Alkylation of $[N_3N_F]WCl$ with $LiCH_2R$ (R = Me, n-Pr, $SiMe_3$, CMe_3) reagents in toluene at room temperature led to evolution of molecular hydrogen and formation of the corresponding tungsten(VI) alkylidyne complexes $[N_3N_F]W{\equiv}CR$ (R = Me, n-Pr, $SiMe_3$, CMe_3, or Ph; eq 136).[261] The reaction between $LiCH_2SiMe_3$ and $[N_3N_F]WCl$ at −10 °C allowed intermediate $[N_3N_F]W(CH_2SiMe_3)$ to be isolated; it was found to decompose in a first-order manner to give $[N_3N_F]W{\equiv}CSiMe_3$ ($\Delta H^\ddagger$ of 20.3 ± 0.2 kcal/mol and a $\Delta S^\ddagger$ of −7 ± 1 eu). An X-ray study of $[N_3N_F]W{\equiv}CSiMe_3$ showed it to have the expected, relatively undistorted structure in which the $W{\equiv}C$ distance is 1.768(6) Å. Although attempts to prepare $[N_3N_F]WCH_3$ were not successful, $[N_3N_F]W{\equiv}CH$ could be prepared by reacting $[N_3N_F]WCl$ with cyclopropyllithium in toluene. $[N_3N_F]MoCl$ reacts with $LiCH_2SiMe_3$ or $LiCH_2CMe_3$ in toluene to yield $[N_3N_F]Mo(CH_2CMe_3)$ or $[N_3N_F]Mo(CH_2SiMe_3)$, respectively. Thermolysis of $[N_3N_F]Mo(CH_2CMe_3)$ produced $[N_3N_F]Mo{\equiv}CCMe_3$ in a first-order reaction at 121 °C ($k = 7.9(5) \times 10^{-5}\ s^{-1}$). Several labeling experiments were consistent with the proposal that β elimination competes with α elimination and loss of molecular hydrogen in the $[N_3N_F]^{3-}$ system, in contrast to the $[N_3N]^{3-}$.

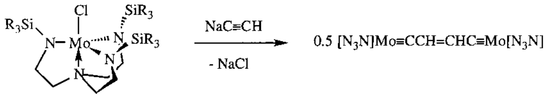


(136)

R = Me, n-Pr, $SiMe_3$, CMe_3, or Ph; X = Cl, I

In contrast, many analogous alkyl complexes of molybdenum, $[N_3N]MoR$ (R = Me, Et, Bu, CH_2Ph, CH_2SiMe_3, CH_2CMe_3, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclopentenyl, phenyl), are relatively stable.[262] It could be shown that $[N_3N]Mo$(cyclopentyl) was in equilibrium with $[N_3N]Mo$(cyclopentylidene)(H), although the equilibrium lay far toward $[N_3N]Mo$(cyclopentyl). Interestingly, the rate of formation of $[N_3N]Mo$(cyclopentylidene)(H) (~1000 s^{-1} at room temperature) is approximately the same rate at which $[N_3N]W$(cyclopentylidene)(H) is formed from $[N_3N]W$(cyclopentyl). $[N_3N]Mo$(cyclopentyl) also decomposed at high temperatures to give paramagnetic $[N_3N]MoH$ in good yield. Of the complexes that contain linear alkyls, only $[N_3N]Mo(CH_2CMe_3)$ decomposed cleanly (but slowly at high temperatures) by α,α-dehydrogenation to give $[N_3N]Mo{\equiv}CCMe_3$; no $[N_3N]Mo{\equiv}CH$ could be detected upon attempted thermolysis of $[N_3N]MoMe$ at 120 °C. The rate of formation of $[N_3N]Mo{\equiv}CCMe_3$ from $[N_3N]Mo(CH_2CMe_3)$ was estimated to be at least several orders of magnitude slower than the rate of formation of $[N_3N]W{\equiv}CCMe_3$ from $[N_3N]W(CH_2CMe_3)$. $[N_3N]Mo$(cyclopropyl) evolved ethylene in a first-order process upon being heated to give $[N_3N]Mo{\equiv}CH$, while $[N_3N]Mo$(cyclobutyl) was converted into $[N_3N]Mo{\equiv}CCH_2CH_2CH_3$.

$Mo[(R_3SiNCH_2CH_2)_3N]Cl$ derivatives react with $LiC{\equiv}CR'$ (R′ = Me or Ph) to give paramagnetic $Mo[(R_3SiNCH_2CH_2)_3N](C{\equiv}CR')$ complexes in high yields.[263] However, attempts to prepare $Mo[(R_3SiNCH_2CH_2)_3N](C{\equiv}CH)$ complexes led to diamagnetic dimers that contain a linkage of the type $Mo{\equiv}C{-}CH{=}CH{-}C{\equiv}Mo$ formed by coupling of acetylide β carbon atoms (eq 137). Electrochemical studies suggest that all Mo(IV) complexes are readily oxidized by one electron.



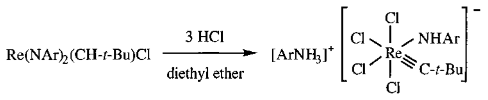
(137)

$R_3Si = SiMe_3, SiPhMe_2$

$[N_3N]Mo(CO)$ was reduced by magnesium powder in the presence of Me_3SiCl to yield the diamagnetic oxycarbyne complex $[N_3N]Mo{\equiv}COSiMe_3$.[264] Reaction of $[N_3N_F]WCO$ with $V(Mes)_3(THF)$ yielded $[N_3N_F]W(CO)V(Mes)_3$, the structure of which was determined in an X-ray study. A description of this complex as a “vanadoxyalkylidyne” complex, $[N_3N_F]W{\equiv}COV(Mes)_3$, appeared to be justified on the basis of the W−C(1) bond length of 1.88(2) Å and chemical shifts for the ligand protons in the proton NMR spectrum and C_6F_5 fluorines in the ^{19}F NMR spectra that are characteristic of diamagnetic compounds, as noted above.

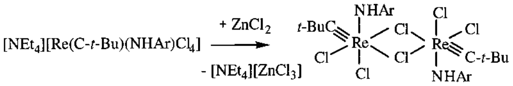
3.3. Rhenium

Rhenium imidoalkylidyne complexes were prepared and examined as alkyne metathesis catalysts.[265,266] $Re(NAr)_2(CH{-}t\text{-}Bu)Cl$ (Ar = 2,6-C_6H_3−i-Pr_2) reacts with 3 equiv of HCl in diethyl ether to give $[ArNH_3][Re(C{-}t\text{-}Bu)(NHAr)Cl_4]$ as an insoluble orange powder (eq 138), from which $[NEt_4][Re(C{-}t\text{-}Bu)(NHAr)Cl_4]$ can be prepared by cation exchange. Addition of $ZnCl_2$ to $[NEt_4][Re(C{-}t\text{-}Bu)(NHAr)Cl_4]$ yields $[Re(C{-}t\text{-}Bu)(NHAr)Cl_3]_2$, an X-ray study of



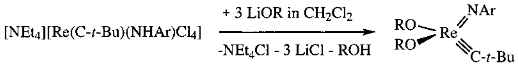
(138)

which shows it to be a dimer in which each Re is a square pyramid with the neopentylidyne α carbon atom in the apical position and a weakly bound bridging chloride ligand trans to it (eq 139; $Re\equiv C = 1.75(1)$ Å, $Re\equiv C-C = 165(1)°$). Complexes of the type



(139)

$Re(C-t\text{-}Bu)(NAr)(OR)_2$ can be prepared from $[NEt_4][Re(C-t\text{-}Bu)(NHAr)Cl_4]$, as shown in eq 140. The Re(C−t-Bu)(NAr)(OR)$_2$ species react with alkynes to yield two types of rhenacyclobutadiene complexes, one of which readily loses alkyne and is active for the metathesis of alkynes. The labile rhenacyclobutadiene complex is formed when an acetylene attacks a C/O/O face in Re(CR′)(NAr)(OR)$_2$. Nonlabile, metathesis-inactive rhenacycles are formed when an acetylene attacks a C/N/O face. Only acetylenes containing bulky groups are metathesized for some period of time, and only complexes that contain OC(CF$_3$)$_2$Me ligands are active at room temperature. The steric bulk of the acetylene groups and the alkoxides is believed to direct formation of the labile rhenacyclobutadiene intermediates and to allow alkyne metathesis to proceed until stable rhenacycles or Re(V) decomposition products are formed.



(140)

OR = O-t-Bu, OC(CF$_3$)Me$_2$, O-2,6-C$_6$H$_3$-i-Pr$_2$, OC(CF$_3$)$_2$Me

The unusual d^1 complex, ReCp*(C−t-Bu)X$_2$ (X = Cl or Br) was formed in the reaction between ReCp*O(CH$_2$−t-Bu)$_2$ and Cp*TiX$_3$.[267,268] An analogous iodo compound can be prepared in the reaction between ReCp*O(CH$_2$−t-Bu)$_2$ and iodotrimethylsilane. Similar reactions are not successful for complexes that contain alkyls such as ethyl or benzyl. The mechanism is not known. Oxidation of the ReCp*(C−t-Bu)X$_2$ species with chlorine, bromine, or iodine yields the ReCp*(C−t-Bu)X$_3$ species (X = Cl, Br, I) as analytically pure materials. The neopentylidyne carbon resonances were found at 374 ppm (X = Cl) and 372 ppm (X = Br).

An unusual rhenium(VII) alkylidyne complex is formed from ReH$_4$(mq)L$_2$ (mq is the monoanion of 2-mercaptoquinoline and L = PPh$_3$), as shown in eq 141.[269] The reaction is also successful when the

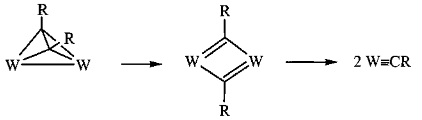
$$ReH_4(mq)L_2 \xrightarrow[CH_2Cl_2]{+HC\equiv CR\ +\ HPF_6\ -\ H_2} [H_2(mq)L_2Re\equiv CCH_2R]PF_6 \quad (141)$$
$$R = Pr, Ph, tol$$

alkyne is an internal alkyne, as long as one of the groups is an alkyl (R = CH$_2$Ph, Bu). Accordingly, a reaction involving 1-pentyne yields the same product (R = Pr) as one involving 2-pentyne. The product is a classical dihydride complex rather than a dihydrogen complex of Re(V), according to observation of ReH stretching modes between 2000 and 1900 cm^{-1}. Since [Ph$_3$C]PF$_6$ also can be employed, it is proposed that a hydride is first removed from ReH$_4$(mq)L$_2$ to yield "[ReH$_3$(mq)L$_2$]$^+$". Vinylidene complexes, $[H_3(mq)L_2Re=C=CHR]^+$, are proposed intermediates, although none was observed. Deprotonation of $[H_2(mq)L_2Re\equiv CCH_2R]^+$ yields purple $H(mq)L_2Re\equiv CCH_2R$.

3.4. Theory of Alkylidyne Complexes

Density functional theory was employed in order to study alkyne metathesis by high oxidation state molybdenum alkylidyne complexes.[270] By use of $Cl_3Mo\equiv CH$ as the model, calculations showed that the alkyne approaches the $Mo\equiv C$ unit parallel to it. Nonzero overlap between π and π* orbitals then allows for donation of electron density from the π orbital of the acetylene to the empty π* orbital of the carbyne and for back-donation from the π orbital of the carbyne to the empty π* orbital of the acetylene. It is primarily this synergistic interaction that allows the trigonal bipyramidal metallacycle to form, while the organic equivalent formation of cyclobutadiene is symmetry-forbidden. Formation of the alternative metallatetrahedrane complex was found to be a formally symmetry-forbidden process with a much higher barrier (40 kJ/mol). A significant bonding interaction was found between Mo and the β carbon atom in the metallacyclobutadiene complex.

The reaction of W$_2$(OR)$_6$ with disubstituted alkynes to give 2 equiv of $(RO)_3W\equiv CR$ has been studied theoretically using DFT calculations.[271] The lowest energy pathway was found to be a "flattening" of the ditungstatetrahedrane to give a 1,3-ditungstacyclobutadiene complex, which dissociates into 2 equiv of the trialkoxytungsten alkylidyne complex (eq 142).



(142)

Ditungstacyclobutadiene complexes in which the metal is in the 6+ state are not known, but they are known when the metal is in a reduced state (e.g., W(V), W(V)). Inclusion of relativistic effects was found to yield the best results.

The structure and bonding in low-valent and high-valent tungsten carbyne complexes have been determined with the aid of quantum mechanical ab initio calculations.[272] The $W\equiv C$ bond strength in $W\equiv CR$ compounds is strongly influenced by the nature of R, with R groups with lone-pair electrons yielding lower bond dissociation energies. This can be explained using the $^1\Sigma^+$ ground state of CR$^+$ as the reference state for the ligand in low oxidation state species and the $^4\Sigma^-$ excited state of CR as the reference state in high oxidation state species.

References

(1) Schrock, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 6577.
(2) Schrock, R. R. *J. Am. Chem. Soc.* **1974**, *96*, 6796.
(3) Herndon, J. W. *Coord. Chem. Rev.* **1999**, *181*, 177.
(4) Herndon, J. W. *Coord. Chem. Rev.* **2000**, *209*, 387.
(5) Herndon, J. W. *Coord. Chem. Rev.* **2001**, *214*, 215.

(6) Schrock, R. R. In *Reactions of Coordinated Ligands*; Braterman, P. R., Ed.; Plenum: New York, 1986.
(7) Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991**, *39*, 1.
(8) Schrock, R. R. *Pure Appl. Chem.* **1994**, *66*, 1447.
(9) Murdzek, J. S.; Schrock, R. R. In *Carbyne Complexes*; VCH: New York, 1988.
(10) Mayr, A.; Hoffmeister, H. *Adv. Organomet. Chem.* **1991**, *32*, 227.
(11) Engel, P. F.; Pfeffer, M. *Chem. Rev.* **1995**, *95*, 2281.
(12) Schrock, R. R. *Tetrahedron* **1999**, *55*, 8141.
(13) Schrock, R. R. In *Topics in Organometallic Chemistry. Alkene Metathesis in Organic Synthesis*; Fürstner, A., Ed.; Springer: Berlin, 1998; Vol. 1, p 1.
(14) Schrock, R. R. *Polyhedron* **1995**, *14*, 3177.
(15) Bunz, U. H. F.; Kloppenburg, L. *Angew. Chem., Int. Ed.* **1999**, *38*, 478.
(16) Fürstner, A.; Guth, O.; Rumbo, A.; Seidel, G. *J. Am. Chem. Soc.* **1999**, *121*, 11108.
(17) Fürstner, A.; Mathes, C. *Org. Lett.* **2001**, *3*, 221.
(18) Fürstner, A.; Rumbo, A. *J. Org. Chem.* **2000**, *65*, 2608.
(19) Hoveyda, A. H.; Schrock, R. R. *Chem.*—*Eur. J.* **2001**, *7*, 945.
(20) Fujiwara, T.; Takeda, T. *Chem. Lett.* **1998**, 741.
(21) Rahim, M. A.; Taguchi, H.; Watanabe, M.; Fujiwara, T.; Takeda, T. *Tetrahedron Lett.* **1998**, *39*, 2153.
(22) Takeda, T.; Nozaki, N.; Aseki, N.; Fujiwara, T. *Tetrahedron Lett.* **1999**, *40*, 5353.
(23) Beckhaus, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 686.
(24) Beckhaus, R.; Santamaría, C. *J. Organomet. Chem.* **2001**, *617–618*, 81.
(25) Petasis, N. A.; Lu, S. P.; Bzowej, E. I.; Fu, D. K.; Staszewski, J. P.; Akritopoulouzanze, I.; Patane, M. A.; Hu, Y. H. *Pure Appl. Chem.* **1996**, *68*, 667.
(26) Petasis, N. A. In *Transition Metals for Organic Synthesis*; Beller, M., Bolm, C., Ed.; Wiley-VCH: Weinheim, 1998; Vol. 1, p 361.
(27) Cheon, J.; Rogers, D. M.; Girolami, G. S. *J. Am. Chem. Soc.* **1997**, *119*, 6804.
(28) Cheon, J.; DuBois, L. H.; Girolami, G. S. *J. Am. Chem. Soc.* **1997**, *119*, 6814.
(29) Riley, P. N.; Fanwick, P. E.; Rothwell, I. P. *J. Chem. Soc., Chem. Commun.* **1997**, 1109.
(30) Polse, J. L.; Kaplan, A. W.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 6316.
(31) Kaplan, A. W.; Polse, J. L.; Ball, G. E.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 11649.
(32) van der Heijden, H.; Hessen, B. *J. Chem. Soc., Chem. Commun.* **1995**, 145.
(33) Adams, C. S.; Legzdins, P.; Tran, E. *J. Am. Chem. Soc.* **2001**, *123*, 612.
(34) Binger, P.; Müller, P.; Philipps, P.; Gabor, B.; Mynott, R.; Herrmann, A. T.; Langhauser, F.; Krüger, C. *Chem. Ber.* **1992**, *125*, 2209.
(35) van Doorn, J. A.; van der Heijden, H.; Orpen, A. G. *Organometallics* **1994**, *13*, 4271.
(36) van Doorn, J. A.; van der Heijden, H.; Orpen, A. G. *Organometallics* **1995**, *14*, 1278.
(37) Sinnema, P.-J.; van der Veen, L.; Spek, A. L.; Veldman, N.; Teuben, J. H. *Organometallics* **1997**, *16*, 4245.
(38) Kahlert, S.; Görls, H.; Scholz, J. *Angew. Chem., Int. Ed.* **1998**, *37*, 1857.
(39) Krüger, C.; Mynott, R.; Siedenbiedel, C.; Stehling, L.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1668.
(40) Baumann, R.; Stumpf, R.; Davis, W. M.; Liang, L.-C.; Schrock, R. *J. Am. Chem. Soc.* **1999**, *121*, 7822.
(41) DeAngelis, S.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1092.
(42) Fryzuk, M. D.; Mao, S. S. H.; Zaworotko, M. J.; MacGillivray, L. R. *J. Am. Chem. Soc.* **1993**, *115*, 5336.
(43) Fryzuk, M. D.; Duval, P. B.; Mao, S. S. S. H.; Zaworotko, M. J.; MacGillivray, L. R. *J. Am. Chem. Soc.* **1999**, *121*, 2478.
(44) Fryzuk, M. D.; Duval, P. B.; Mao, S. S. S. H.; Rettig, S. J.; Zaworotko, M. J.; MacGillivray, L. R. *J. Am. Chem. Soc.* **1999**, *121*, 1707.
(45) Fryzuk, M. D.; Duval, P. B.; Patrick, B. O.; Rettig, S. J. *Organometallics* **2001**, *20*, 1608.
(46) Babu, R. P. K.; McDonald, R.; Cavell, R. G. *Chem. Commun.* **2000**, 481.
(47) Babu, R. P. K.; McDonald, R.; Cavell, R. G. *Organometallics* **2000**, *19*, 3462.
(48) Cavell, R. G.; Babu, R. P. K.; Aparna, K. *J. Organomet. Chem.* **2000**, *617*, 158.
(49) Wu, Y. D.; Peng, Z. H.; Xue, Z. L. *J. Am. Chem. Soc.* **1996**, *118*, 9772.
(50) Wu, Y.-D.; Peng, Z.-H.; Chan, K. W. K.; Liu, X.; Tuinman, A. A.; Xue, Z. *Organometallics* **1999**, *18*, 2081.
(51) Axe, F. U.; Andzelm, J. W. *J. Am. Chem. Soc.* **1999**, *121*, 5396.
(52) Buijink, J. K.; Teuben, J. H.; Kooijman, H.; Spek, A. L. *Organometallics* **1994**, *13*, 2922.
(53) Hessen, B.; Buijink, J. K. F.; Meetsma, A.; Teuben, J. H.; Helgesson, G.; Hakansson, M.; Jagner, S.; Spek, A. L. *Organometallics* **1993**, *12*, 2268.
(54) Moore, M.; Gambarotta, S.; Yap, G.; Liable-Sands, L. M.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1997**, 643.
(55) Duncalf, P. J.; Harrison, R. J.; McCamley, A.; Royan, B. W. *J. Chem. Soc., Chem. Commun.* **1995**, 2421.
(56) Antiñolo, A.; Otero, A.; Fajardo, M.; García-Yebra, C.; Gil-Sanz, R.; López-Mardomingo, C.; Martín, A.; Gómez-Sal, P. *Organometallics* **1994**, *13*, 4679.
(57) Cockcroft, J. K.; Gibson, V. C.; Howard, J. A. K.; Poole, A. D.; Siemeling, U.; Wilson, C. *J. Chem. Soc., Chem. Commun.* **1992**, 1668.
(58) Chan, M. C. W.; Cole, J. M.; Gibson, V. C.; Howard, J. A. K.; Lehmann, C.; Poole, A. D.; Siemeling, U. *J. Chem. Soc., Dalton Trans.* **1998**, 103.
(59) Siemeling, U.; Gibson, V. C. *J. Organomet. Chem.* **1992**, *426*, 25.
(60) De Castro, I.; De La Mata, J.; Gómez, M.; Gómez-Sal, P.; Royo, P.; Selas, J. M. *Polyhedron* **1992**, *11*, 1023.
(61) Mashima, K.; Kaidza, M.; Nakayama, Y.; Nakamura, A. *Organometallics* **1997**, *16*, 1345.
(62) Biasotto, F.; Etienne, M.; Dahan, F. *Organometallics* **1995**, *14*, 1870.
(63) Etienne, M.; White, P. S.; Templeton, J. L. *Organometallics* **1993**, *12*, 4010.
(64) Antiñolo, A.; del Hierro, I.; Fajardo, M.; Garcia-Yuste, S.; Otero, A.; Blacque, O.; Kubicki, M. M.; Amandrut, J. *Organometallics* **1996**, *15*, 1966.
(65) Caselli, A.; Solari, E.; Scopelliti, R.; Floriani, C. *J. Am. Chem. Soc.* **1999**, *121*, 8296.
(66) Kleckley, T. S.; Bennett, J. L.; Wolczanski, P. T.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **1997**, *119*, 247.
(67) Veige, A. S.; Wolczanski, P. T.; Lobkovsky, E. B. *Angew. Chem. Int. Ed.* **2001**, *40*, 19.
(68) Li, L.; Hung, M.; Xue, Z. *J. Am. Chem. Soc.* **1995**, *117*, 12746.
(69) Luo, L. B.; Li, L. T.; Marks, T. J. *J. Am. Chem. Soc.* **1997**, *119*, 8574.
(70) Hughes, R. P.; Maddock, S. M.; Rheingold, A. L.; Guzei, I. A. *Polyhedron* **1998**, *17*, 1037.
(71) Miller, G. A.; Cooper, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 709.
(72) Berry, D. H.; Koloski, T. S.; Carroll, P. J. *Organometallics* **1990**, *9*, 2952.
(73) Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389.
(74) Antonelli, D. M.; Schaefer, W. P.; Parkin, G.; Bercaw, J. E. *J. Organomet. Chem.* **1993**, *462*, 213.
(75) van Asselt, A.; Bercaw, J. E.; Burger, B. J.; Gibson, V. C. *J. Am. Chem. Soc.* **1986**, *108*, 5347.
(76) Gibson, V. C.; Parkin, G.; Bercaw, J. E. *Organometallics* **1991**, *10*, 220.
(77) Briggs, M. P.; Young, V. G.; Wigley, D. E. *Chem. Commun.* **1997**, 791.
(78) De Castro, I.; Galakhov, M. V.; Gómez, M.; Gómez-Sal, P.; Martin, A.; Royo, P. *J. Organomet. Chem.* **1996**, *514*, 51.
(79) Jolly, M.; Mitchell, J. P.; Gibson, V. C. *J. Chem. Soc., Dalton Trans.* **1992**, 1331.
(80) Wengrovius, J. H.; Schrock, R. R.; Churchill, M. R.; Missert, J. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 4515.
(81) Mashima, K.; Kaidzu, M.; Tanaka, Y.; Nakayama, Y.; Nakamura, A.; Hamilton, J. G.; Rooney, J. J. *Organometallics* **1998**, *17*, 4183.
(82) Mashima, K.; Tanaka, Y.; Kaidzu, M.; Nakamura, A. *Organometallics* **1996**, *15*, 2431.
(83) Hirpo, W.; Curtis, M. D. *Organometallics* **1994**, *13*, 2706.
(84) De Castro, I.; Galakhov, M. V.; Gómez, M.; Gómez-Sal, P.; Royo, P. *Organometallics* **1996**, *15*, 1362.
(85) Courtenay, S.; Stephan, D. W. *Organometallics* **2001**, 1442.
(86) Boncella, J. M.; Cajigal, M. L.; Abboud, K. A. *Organometallics* **1996**, *15*, 1905.
(87) Braunschweig, H.; Paetzold, P.; Spaniol, T. P. *Chem. Ber.* **1993**, *126*, 1565.
(88) Braunschweig, H.; Paetzold, P.; Boese, R. *Chem. Ber.* **1993**, *126*, 1571.
(89) Diminnie, J. B.; Xue, Z. *J. Am. Chem. Soc.* **1997**, *119*, 12657.
(90) Diminnie, J. B.; Blanton, J. R.; Cai, H.; Quisenberry, K. T.; Xue, Z. *Organometallics* **2001**, *20*, 1504.
(91) Diminnie, J. B.; Hall, H. D.; Xue, Z. *Chem. Commun.* **1996**, 2383.
(92) Fellmann, J. D.; Rupprecht, G. A.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 5964.
(93) Xue, Z.; Li, L.; Hoyt, L. K.; Diminnie, J. B.; Pollitte, J. L. *J. Am. Chem. Soc.* **1994**, *116*, 2169.
(94) Li, L.; Diminnie, J. B.; Liu, X.; Pollitte, J. L.; Xue, Z. *Organometallics* **1996**, *15*, 3520.
(95) Lockwood, M. A.; Clark, J. R.; Parkin, B. C.; Rothwell, I. P. *Chem. Commun.* **1996**, 1973.
(96) Vilardo, J. S.; Lockwood, M. A.; Hanson, L. G.; Clark, J. R.; Parkin, B. C.; Fanwick, P. E.; Rothwell, I. P. *J. Chem. Soc., Dalton Trans.* **1997**, 3353.
(97) Liu, X. X.; Li, L.; Diminnie, J. B.; Yap, G. P. A.; Rheingold, A. L.; Xue, Z. *Organometallics* **1998**, *17*, 4597.
(98) Freundlich, J.; Schrock, R. R.; Cummins, C. C.; Davis, W. M. *J. Am. Chem. Soc.* **1994**, *116*, 6476.

(99) Freundlich, J. S.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1996**, *118*, 3643.

(100) Freundlich, J. S.; Schrock, R. R.; Davis, W. M. *Organometallics* **1996**, *15*, 2777.

(101) Abbenhuis, H. C. L.; Feiken, N.; Grove, D. M.; Jastrzebski, J. T. B. H.; Kooijman, H.; van der Sluis, P.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1992**, *114*, 9773.

(102) Abbenhuis, H. C. L.; Grove, D. M.; van der Sluis, P.; Spek, A. L.; van Koten, G. *Recl. Trav. Chim. Pays-Bas* **1990**, *109*, 446.

(103) Abbenhuis, H. C. L.; Rietveld, M. H. P.; Haarman, H. F.; Hogerheide, M. P.; Spek, A. L.; van Koten, G. *Organometallics* **1994**, *13*, 3259.

(104) Abbenhuis, H. C. L.; Feiken, N.; Haarman, H. F.; Grove, D. M.; Horn, E.; Kooijman, H.; Spek, A. L.; van Koten, G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 996.

(105) Abbenhuis, H. C. L.; Feiken, N.; Haarman, H. F.; Grove, D. M.; Horn, E.; Spek, A. L.; Pfeffer, M.; van Koten, G. *Organometallics* **1993**, *12*, 2227.

(106) Rietveld, M. H. P.; Lohner, P.; Nijkamp, M. G.; Grove, D. M.; Veldman, N.; Spek, A. L.; Pfeffer, M.; van Koten, G. *Chem.—Eur. J.* **1997**, *3*, 817.

(107) Rietveld, M. H. P.; Klumpers, E. G.; Jastrzebski, J. T. B. H.; Grove, D. M.; Veldman, N.; Spek, A. L.; van Koten, G. *Organometallics* **1997**, *16*, 4260.

(108) Rietveld, M. H. P.; Teunissen, W.; Hagen, H.; van de Water, L.; Grove, D. M.; van der Schaaf, P. A.; Mühlebach, A.; Kooijman, H.; Smeets, W. J. J.; Veldman, N.; Spek, A. L.; van Koten, G. *Organometallics* **1997**, *16*, 1674.

(109) Fryzuk, M. D.; Johnson, S. A.; Rettig, S. J. *Organometallics* **1999**, *18*, 4059.

(110) Fryzuk, M. D.; Johnson, S. A.; Rettig, S. J. *J. Am. Chem. Soc.* **2001**, *123*, 1602.

(111) Dawson, D. Y.; Arnold, J. *Organometallics* **1997**, *16*, 1111.

(112) Schmidt, J. A. R.; Chmura, S. A.; Arnold, J. *Organometallics* **2001**, *20*, 1062.

(113) Schmidt, J. A. R.; Arnold, J. *J. Am. Chem. Soc.* **2001**, *123*, 8424.

(114) Dufaud, V.; Niccolai, G. P.; Thivolle-Cazzat, J.; Basset, J.-M. *J. Am. Chem. Soc.* **1995**, *117*, 4288.

(115) Fryzuk, M. D.; Haddad, T. S.; Mylvaganam, M.; McConville, D. H.; Rettig, S. J. *J. Am. Chem. Soc.* **1993**, *115*, 2782.

(116) Turner, H. W.; Fellmann, J. D.; Rocklage, S. M.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1980**, *102*, 7809.

(117) Rocklage, S. M.; Turner, H. W.; Fellmann, J. D.; Schrock, R. R. *Organometallics* **1982**, *1*, 703.

(118) Wu, Y. D.; Chan, K. W. K.; Xue, Z. *J. Am. Chem. Soc.* **1995**, *117*, 9259.

(119) Coles, M. P.; Gibson, V. C.; Clegg, W.; Elsegood, M. R. J.; Porrelli, P. A. *Chem. Commun.* **1996**, 1963.

(120) Sundermeyer, J.; Weber, K.; Pritzkow, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 731.

(121) Sundermeyer, J.; Weber, K.; Nürnberg, O. *J. Chem. Soc., Chem. Commun.* **1992**, 1631.

(122) Oskam, J. H.; Fox, H. H.; Yap, K. B.; McConville, D. H.; O'Dell, R.; Lichtenstein, B. J.; Schrock, R. R. *J. Organomet. Chem.* **1993**, *459*, 185.

(123) Fox, H. H.; Schrock, R. R. In *Synthetic Methods of Organometallic and Inorganic Chemistry*; Herrmann, W. A., Ed.; Georg Thieme Verlag: Stuttgart, 1997; Vol. 7, p 149.

(124) Schrock, R. R.; Crowe, W. E.; Bazan, G. C.; DiMare, M.; O'Regan, M. B.; Schofield, M. H. *Organometallics* **1991**, *10*, 1832.

(125) Oskam, J. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1992**, *114*, 7588.

(126) Oskam, J. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 11831.

(127) Feast, W. J.; Gibson, V. C.; Marshal, E. L. *J. Chem. Soc., Chem. Commun.* **1992**, 1157.

(128) Bazan, G. C.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C.; O'Regan, M. B.; Thomas, J. K.; Davis, W. B. *J. Am. Chem. Soc.* **1990**, *112*, 8378.

(129) Feast, W. J.; Gibson, V. C.; Ivin, K. J.; Kenwright, A. M.; Khosravi, E. *J. Chem. Soc., Chem. Commun.* **1994**, 1399, 2737.

(130) Fox, H. H.; Lee, J.-K.; Park, L. Y.; Schrock, R. R. *Organometallics* **1993**, *12*, 759.

(131) Totland, K. M.; Boyd, T. J.; Lavoie, G. G.; Davis, W. M.; Schrock, R. R. *Macromolecules* **1996**, *29*, 6114.

(132) McConville, D. H.; Wolf, J. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 4413.

(133) Schrock, R. R.; Lee, J.-K.; O'Dell, R.; Oskam, J. H. *Macromolecules* **1995**, *28*, 5933.

(134) O'Dell, R.; McConville, D. H.; Hofmeister, G. E.; Schrock, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 3414.

(135) Fujimura, O.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 2499.

(136) Fujimura, O.; de la Mata, F. J.; Grubbs, R. H. *Organometallics* **1996**, *15*, 1865.

(137) Fujimura, O.; Grubbs, R. H. *J. Org. Chem.* **1998**, *63*, 824.

(138) Alexander, J. B.; La, D. S.; Cefalo, D. R.; Hoveyda, A.; Schrock, R. R. *J. Am. Chem. Soc.* **1998**, *120*, 4041.

(139) Alexander, J. B.; Schrock, R. R.; Davis, W. M.; Hultzsch, K. C.; Hoveyda, A. H.; Houser, J. H. *Organometallics* **2000**, *19*, 3700.

(140) La, D. S.; Alexander, J. B.; Cefalo, D. R.; Graf, D. D.; Hoveyda, A. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1998**, *120*, 9720.

(141) Weatherhead, G. S.; Houser, J. H.; Ford, J. G.; Jamieson, J. Y.; Schrock, R. R.; Hoveyda, A. H. *Tetrahedron Lett.* **2000**, *49*, 9553.

(142) Weatherhead, G. S.; Ford, J. G.; Alexanian, E. J.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2000**, *122*, 1828.

(143) La, D. S.; Ford, J. G.; Sattely, E. S.; Bonitatebus, P. J.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1999**, *121*, 11603.

(144) Aeilts, S. L.; Cefalo, D. R.; Bonitatebus, P. J.; Houser, J. H.; Hoveyda, A. H.; Schrock, R. R. *Angew. Chem., Int. Ed.* **2001**, *40*, 1452.

(145) Zhu, S. S.; Cefalo, D. R.; La, D. S.; Jamieson, J. Y.; Davis, W. M.; Hoveyda, A. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1999**, *121*, 8251.

(146) Robbins, J.; Bazan, G. C.; Murdzek, J. S.; O'Regan, M. B.; Schrock, R. R. *Organometallics* **1991**, *10*, 2902.

(147) Schrock, R. R.; Luo, S.; Zanetti, N.; Fox, H. H. *Organometallics* **1994**, *13*, 3396.

(148) Schrock, R. R.; Luo, S.; Lee, J. C. J.; Zanetti, N. C.; Davis, W. M. *J. Am. Chem. Soc.* **1996**, *118*, 3883.

(149) Bell, A.; Clegg, W.; Dyer, P. W.; Elsegood, M. R. J.; Gibson, V. C.; Marshall, E. L. *J. Chem. Soc., Chem. Commun.* **1994**, 2547.

(150) Gibson, V. C.; Marshall, E. L.; Redshaw, C.; Clegg, W.; Elsegood, M. R. J. *J. Chem. Soc., Dalton Trans.* **1996**, 4197.

(151) Feher, F. J.; Tajima, T. L. *J. Am. Chem. Soc.* **1994**, *116*, 2145.

(152) Feher, F. J.; Hwang, T.-L.; Schwab, J. J.; Shaka, A. J.; Ziller, J. W. *Magn. Reson. Chem.* **1997**, *35*, 730.

(153) Schattenmann, F. J.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1996**, *118*, 3295.

(154) Jamieson, J. Y.; Schrock, R. R.; Davis, W. M.; Bonitatebus, P. J.; Zhu, S. S.; Hoveyda, A. H. *Organometallics* **2000**, *19*, 925.

(155) Jamison, G. M.; Saunders, R. S.; Wheeler, D. R.; McClain, M. D.; Loy, D. A.; Ziller, H. W. *Organometallics* **1996**, *15*, 16.

(156) Jamison, G. M.; Saunders, R. S.; Wheeler, D. R.; Alam, T. M.; McClain, M. D.; Loy, D. A. *Organometallics* **1996**, *15*, 3244.

(157) Vaughan, W. M.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1995**, *14*, 1567.

(158) Fairhurst, S. A.; Hughes, D. L.; Marjani, K.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1998**, 1899.

(159) Hughes, D. L.; Marjani, K.; Richards, R. L. *J. Organomet. Chem.* **1995**, *505*, 127.

(160) Ortiz, C. G.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1999**, *18*, 4253.

(161) de la Mata, F. J.; Gómez, J.; Royo, P. *J. Organomet. Chem.* **1998**, *564*, 277.

(162) Acebrón, S.; Galakhov, M. V.; Gómez-Sal, P.; Martín, A.; Royo, P.; Vázquez de Miguel, A. *J. Organomet. Chem.* **1999**, *580*, 110.

(163) Ivin, K. J.; Mol, J. C. *Olefin Metathesis and Metathesis Polymerization*; Academic Press: San Diego, 1997.

(164) Blosch, L. L.; Abboud, K.; Boncella, J. M. *J. Am. Chem. Soc.* **1991**, *113*, 7066.

(165) Blosch, L. L.; Gamble, A. S.; Boncella, J. M. *J. Mol. Catal.* **1992**, *76*, 229.

(166) Jeffrey, J. C.; McCleverty, J. A.; Mortimer, M. D.; Ward, M. D. *Polyhedron* **1994**, *13*, 353.

(167) Blosch, L. L.; Gamble, A. S.; Abboud, K.; Boncella, J. M. *Organometallics* **1992**, *11*, 2342.

(168) Vaughan, W. M.; Abboud, K. A.; Boncella, J. M. *J. Organomet. Chem.* **1995**, *485*, 37.

(169) Vaughan, W. M.; Bonella, J. M.; Abboud, K. A. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1995**, *51*, 1075.

(170) Crane, T. W.; White, P. S.; Templeton, J. L. *Organometallics* **1999**, *18*, 1897.

(171) Gamble, A. S.; Boncella, J. M. *Organometallics* **1993**, *12*, 2814.

(172) Ahn, S.; Mayr, A. *J. Am. Chem. Soc.* **1996**, *118*, 7408.

(173) Mayr, A.; Ahn, S. *Inorg. Chem. Acta* **2000**, *300*−*302*, 406.

(174) Kläui, W.; Hardt, T. *J. Organomet. Chem.* **1998**, *553*, 241.

(175) de la Mata, F. J.; Grubbs, R. H. *Organometallics* **1996**, *15*, 577.

(176) Binger, P.; Müller, P.; Benn, R.; Mynott, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 610.

(177) O'Donoghue, M. B.; Schrock, R. R.; LaPointe, A. M.; Davis, W. M. *Organometallics* **1996**, *15*, 1334.

(178) Johnson, L. K.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 8130.

(179) Vanderlende, D. D.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1994**, *13*, 3378.

(180) Vaughan, W. M.; Abboud, K. A.; Boncella, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 11015.

(181) Wang, S.-Y. S.; VanderLende, D. D.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1998**, *17*, 2628.

(182) Johnson, L. K.; Virgil, S. C.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 5384.

(183) Johnson, L. K.; Frey, M.; Ulibarri, T. A.; Virgil, S. C.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 8167.

(184) van der Schaaf, P. A.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Chem. Soc., Chem. Commun.* **1992**, 717.

(185) van der Schaaf, P. A.; Grove, D. M.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1993**, *12*, 3955.

(186) van der Schaaf, P. A.; Abbenhuis, R. A. T. M.; van der Noort, W. P. A.; de Graaf, R.; Grove, D. M.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1994**, *13*, 1433.

(187) van der Schaaf, P. A.; Abbenhuis, R. A. T. M.; Grove, D. M.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Chem. Soc., Chem. Commun.* **1993**, 504.

(188) Brandts, J. A. M.; Kruiswijk, E.; Boersma, J.; Spek, A. L.; van Koten, G. *J. Organomet. Chem.* **1999**, *585*, 93.

(189) Floriani, C. *Chem.—Eur. J.* **1999**, *5*, 19.

(190) Guillemot, G.; Solari, E.; Floriani, C. *Organometallics* **2000**, *19*, 5218.

(191) Giannini, L.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1998**, *120*, 823.

(192) Giannini, L.; Guillemot, G.; Solari, E.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1999**, *121*, 2797.

(193) Giannini, L.; Solari, E.; Zanotti-Gerosa, A.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2825.

(194) Giannini, L.; Solari, E.; Dovesi, S.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1999**, *121*, 2784.

(195) Dovesi, S.; Solari, E.; Scopelliti, R.; Floriani, C. *Angew. Chem., Int. Ed.* **1999**, *38*, 2388.

(196) Chen, T.; Wu, Z.; Li, L.; Sorasaenee, K. R.; Diminnie, J. B.; Pan, H.; Guzei, I. A.; Rheingold, A. L.; Xue, Z. *J. Am. Chem. Soc.* **1998**, *120*, 13519.

(197) Heppert, J. A.; Dietz, S. D.; Eilerts, N. W.; Henning, R. W.; Morton, M. D.; Takusagawa, F. *Organometallics* **1993**, *12*, 2565.

(198) Youinou, M. T.; Kress, J.; Fischer, J.; Aguero, A.; Osborn, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 1488.

(199) Chisholm, M. H.; Streib, W. E.; Tiedtke, D. B.; Wu, D. *Chem.—Eur. J.* **1998**, *4*, 1470.

(200) Couturier, J. L.; Paillet, C.; Leconte, M.; Basset, J.-M.; Weiss, K. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 628.

(201) Lefebvre, F.; Leconte, M.; Pagano, S.; Mutch, A.; Basset, J.-M. *Polyhedron* **1995**, *14*, 3209.

(202) Schrock, R. R.; Shih, K.-Y.; Dobbs, D.; Davis, W. M. *J. Am. Chem. Soc.* **1995**, *117*, 6609.

(203) Cai, S.; Hoffman, D. M.; Wierda, D. A. *Organometallics* **1996**, *15*, 1023.

(204) Schofield, M. H.; Schrock, R. R.; Park, L. Y. *Organometallics* **1991**, *10*, 1844.

(205) Toreki, R.; Schrock, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 2448.

(206) Toreki, R.; Schrock, R. R. *J. Am. Chem. Soc.* **1992**, *114*, 3367.

(207) Toreki, R.; Vaughan, G. A.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1993**, *115*, 127.

(208) Schrock, R. R.; Toreki, R.; Vaughan, G. A.; Farooq, A. In *Transition-Metal Carbyne Complexes*; Kreissl, F. R., Ed.; Kluwer Academic: Dordrecht, The Netherlands, 1992.

(209) Flatt, B. T.; Grubbs, R. H.; Blanski, R. L.; Calabrese, J. C.; Feldman, J. *Organometallics* **1994**, *13*, 2728.

(210) Toreki, R.; Schrock, R. R.; Vale, M. G. *J. Am. Chem. Soc.* **1991**, *113*, 3610.

(211) Toreki, R.; Schrock, R. R.; Davis, W. M. *J. Organomet. Chem.* **1996**, *520*, 69.

(212) Vaughan, G. A.; Toreki, R.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1993**, *115*, 2980.

(213) LaPointe, A. M.; Schrock, R. R. *Organometallics* **1995**, *14*, 1875.

(214) Cundari, T. R.; Gordon, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 5231.

(215) Cundari, T. R.; Gordon, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 539.

(216) Cundari, T. R.; Gordon, M. S. *Organometallics* **1992**, *11*, 55−63.

(217) Sodupe, M.; Lluch, J. M.; Oliva, A.; Bertran, J. *New J. Chem.* **1991**, *15*, 321.

(218) Wu, Y.-D.; Peng, Z.-H. *J. Am. Chem. Soc.* **1997**, *119*, 8043.

(219) Monteyne, K.; Ziegler, T. *Organometallics* **1998**, *17*, 5901.

(220) Folga, E.; Ziegler, T. *Organometallics* **1993**, *12*, 325.

(221) Choi, S.-H.; Lin, Z.; Xue, Z. *Organometallics* **1999**, *18*, 5488.

(222) Fox, H. H.; Schofield, M. H.; Schrock, R. R. *Organometallics* **1994**, *13*, 2804.

(223) Vyboishchikov, S. F.; Frenking, G. *Chem.—Eur. J.* **1998**, *4*, 1428.

(224) Filippou, A. C.; Fischer, E. O. *J. Organomet. Chem.* **1990**, *382*, 143.

(225) Filippou, A. C.; Lungwitz, B.; Wanninger, K. M. A.; Herdtweck, E. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 924.

(226) Filippou, A. C.; Grünleitner, W.; Fischer, E. O. *J. Organomet. Chem.* **1991**, *401*, C37.

(227) Filippou, A. C.; Fischer, E. O.; Grünleiter, W. *J. Organomet. Chem.* **1990**, *386*, 333.

(228) Filippou, A. C.; Grünleiter, W. *Z. Naturforsch., B* **1989**, *44*, 1572.

(229) Filippou, A. C.; Hofmann, P.; Kiprof, P.; Schmidt, H. R.; Wagner, C. *J. Organomet. Chem.* **1993**, *459*, 233.

(230) Peters, J. C.; Odom, A. L.; Cummins, C. C. *Chem. Commun.* **1997**, 1995.

(231) Tsai, Y. C.; Diaconescu, P. L.; Cummins, C. C. *Organometallics* **2000**, *19*, 5260.

(232) McCullough, L. G.; Schrock, R. R.; Dewan, J. C.; Murdzek, J. S. *J. Am. Chem. Soc.* **1985**, *107*, 5987.

(233) Murdzek, J. S.; Schrock, R. R. *Organometallics* **1987**, *6*, 1373.

(234) Listemann, M. L.; Schrock, R. R. *Organometallics* **1985**, *4*, 74.

(235) Chisholm, M. H.; Eichhorn, B. W.; Folting, K.; Huffman, J. C. *Organometallics* **1989**, *8*, 49.

(236) Pollagi, T. P.; Geib, S. J.; Hopkins, M. D. *J. Am. Chem. Soc.* **1994**, *116*, 6051.

(237) Brison, H. A.; Pollagi, T. P.; Stoner, T. C.; Geib, S. J.; Hopkins, M. D. *Chem. Commun.* **1997**, 1263.

(238) Warren, T. H.; Schrock, R. R.; Davis, W. M. *J. Organomet. Chem.* **1998**, *569*, 125.

(239) Chisholm, M. H.; Folting, K.; Lynn, M. L.; Tiedtke, D. B.; Lemoigno, F.; Eisenstein, O. *Chem.—Eur. J.* **1999**, *5*, 2318.

(240) Scheer, M.; Kramkowski, P.; Schuster, K. *Organometallics* **1999**, *18*, 2874.

(241) Chisholm, M. H.; Huffman, J. C.; Klang, J. A. *Polyhedron* **1990**, *9*, 1271.

(242) Buffon, R.; Leconte, M.; Choplin, A.; Basset, J.-M. *J. Chem. Soc., Chem. Commun.* **1993**, 361.

(243) Buffon, R.; Leconte, M.; Choplin, A.; Basset, J.-M. *J. Chem. Soc., Dalton Trans.* **1994**, 1823.

(244) Krouse, S. A.; Schrock, R. R. *J. Organomet. Chem.* **1988**, *355*, 257.

(245) Caulton, K. G.; Cayton, R. H.; Chisholm, M. H.; Huffman, J. C.; Lobkovsky, E. B.; Xue, Z. *Organometallics* **1992**, *11*, 321.

(246) Gilbert, T. M.; Rogers, R. D. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1993**, *49*, 677.

(247) Gilbert, T. M.; Rogers, R. D. *J. Organomet. Chem.* **1991**, *421*, C1.

(248) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Lucas, E. A. *Organometallics* **1991**, *10*, 535.

(249) Dembinski, R.; Szafert, S.; Haquette, P.; Lis, T.; Gladysz, J. A. *Organometallics* **1999**, *18*, 5438.

(250) Kontsantonis, G. A.; Seleague, J. P. *J. Am. Chem. Soc.* **1991**, *113*, 2316.

(251) Schrock, R. R.; Sancho, J.; Pedersen, S. F. *Inorg. Synth.* **1989**, *26*, 44.

(252) Stevenson, M. A.; Hopkins, M. D. *Organometallics* **1997**, *16*, 3572.

(253) Kläui, W.; Hardt, T.; Schulte, H.-J.; Hamers, H. *J. Organomet. Chem.* **1995**, *498*, 63.

(254) Kläui, W.; Hardt, T. *J. Organomet. Chem.* **1996**, *526*, 313.

(255) Murdzek, J. S.; Blum, L.; Schrock, R. R. *Organometallics* **1988**, *7*, 436.

(256) Caulton, K. G.; Chisholm, M. H.; Streib, W. E.; Xue, Z. L. *J. Am. Chem. Soc.* **1991**, *113*, 6082.

(257) Xue, Z. L.; Chuang, S. H.; Caulton, K. G.; Chisholm, M. H. *Chem. Mater.* **1998**, *10*, 2365.

(258) Dobbs, D. A.; Schrock, R. R.; Davis, W. M. *Inorg. Chem.* **1997**, *36*, 171.

(259) Shih, K.-Y.; Totland, K.; Seidel, S. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 12103.

(260) Schrock, R. R.; Seidel, S. W.; Mösch-Zanetti, N. C.; Dobbs, D. A.; Shih, K.-Y.; Davis, W. M. *Organometallics* **1997**, *16*, 5195.

(261) Seidel, S. W.; Schrock, R. R.; Davis, W. M. *Organometallics* **1998**, *17*, 1058.

(262) Schrock, R. R.; Seidel, S. W.; Mösch-Zanetti, N. C.; Shih, K.-Y.; O'Donoghue, M. B.; Davis, W. M.; Reiff, W. M. *J. Am. Chem. Soc.* **1997**, *119*, 11876.

(263) Shih, K.-Y.; Schrock, R. R.; Kempe, R. *J. Am. Chem. Soc.* **1994**, *116*, 8804.

(264) Greco, G. E.; O'Donoghue, M. B.; Seidel, S. W.; Davis, W. M.; Schrock, R. R. *Organometallics* **2000**, *19*, 1132.

(265) Schrock, R. R.; Weinstock, I. A.; Horton, A. D.; Liu, A. H.; Schofield, M. H. *J. Am. Chem. Soc.* **1988**, *110*, 2686.

(266) Weinstock, I. A.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1991**, *112*, 135.

(267) Herrmann, W. A.; Felixberger, J. K.; Anwander, R.; Herdtweck, E.; Kiprof, P.; Riede, J. *Organometallics* **1990**, *9*, 1434.

(268) Felixberger, J. K.; Kiprof, P.; Herdtweck, E.; Herrmann, W. A.; Jakobi, R.; Gütlich, P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 334.

(269) Leeaphon, M.; Fanwick, P. E.; Walton, R. A. *J. Am. Chem. Soc.* **1992**, *114*, 1890.

(270) Woo, T.; Folga, E.; Ziegler, T. *Organometallics* **1993**, *12*, 1289.

(271) Fantacci, S.; Re, N.; Rosi, M.; Sgamellotti, A.; Guest, M. F.; Sherwood, P.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1997**, 3845.

(272) Vyboishchikov, S. F.; Frenking, G. *Chem.—Eur. J.* **1998**, *4*, 1439.

(273) Sheng, Y.-H.; Wu, Y.-D. *J. Am. Chem. Soc.* **2001**, *123*, 6662.

(274) Cefalo, D. R.; Kiely, A. F.; Wuchrer, M.; Jamieson, J. Y.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2001**, *123*, 3139.

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