Preparation, Mechanism, and Structural Study of Group 6 Transition Metal 2-Substituted η^3-Butadienyl Complexes: Crystal Structure of [WCl(CO)$_2${η^3-CH$_2$C(COSBu^n)C=CH$_2$}(1,10-phenanthroline)]

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Received June 22, 1998

The complexes [WCl(CO)$_2$(η^3-CH$_2$C(COX)C=CH$_2$)L$_2$] (X = Cl; L$_2$ = 2,2′-bipyridyl, 1,10-phenanthroline) (**1**) containing a 2-substituted butadienyl ligand were isolated from reactions of Ph$_4$P[WCl(CO)$_3$L$_2$] and excess 1,4-dichlorobut-2-yne in chlorinated solvents. Spectroscopic evidence supports analogous reactions for the chromium analogue. Addition of **1** to alcohol, amine, or thiol (HX) gave good yields of the related ester (X = OMe), amide (X = NEt$_2$), or thiolate (X = SBu^n) complexes, respectively. Mechanisms and supporting evidence for the formation of **1** and the ester complex are proposed and discussed. Some differences in reactivity of Ph$_4$P[MCl(CO)$_3$L$_2$] with 1,4-dichlorobut-2-yne in methanol are reported for M = Mo and M = W. The structure of [WCl(CO)$_2$(η^3-CH$_2$C(COSBu^n)C=CH$_2$)(1,10-phenanthroline)] was confirmed by single-crystal X-ray diffraction analysis.

Introduction

During the past decade several routes to η^3-bonded butadienyl transition metal complexes have been discovered, and the organic moiety containing a variety of substituents at C(2) has been characterized crystallographically. These complexes are important, because of their relationship to metal-coordinated η^2-alkenes and η^4-dienes, their relative ease of conversion to η^3-allyls, and their relevance to organic synthesis. In 1994 a review summarized the available synthetic routes to η^3-butadienyl derivatives of transition metals, highlighted their importance to the future development of C$_4$ organometallic chemistry, and identified areas that required further study.[1] Of particular relevance to this work was the lack of information concerning η^3-butadienyl complexes with sulfur substituents attached to the butadienyl moiety, and the rarity of mechanistic studies.

The author and others first prepared complexes of general formula [MoCl(CO)$_2$(η^3-CH$_2$C(COX)C=CH$_2$)bipy] (X = OMe, NRR′; bipy = 2,2′-bipyridyl) by reaction of Ph$_4$P[MoCl(CO)$_3$bipy] with 1,4-dichlorobut-2-yne in aqueous methanol or amine HNRR′.[2−4] In contrast, attempts to prepare related thiol complexes [MoCl(CO)$_2$(η^3-CH$_2$C(COSR)C=CH$_2$)bipy] from this anion and alkyne in the presence of thiol RSH were unsuccessful and gave highly insoluble products of variable elemental composition.[5] In addition, attempts to prepare the analogous tungsten complexes by direct reaction of anion and alkyne in aqueous methanol or amine were not successful and suggested differences in reactivity for the two different metal anions. More recently, the reactions of Ph$_4$P[MoCl(CO)$_3$L$_2$] (L$_2$ = bipy or 1,10-phenanthroline) with 1,4-dichlorobut-2-yne in chlorinated solvents have been shown to give butadienyl complexes containing a chlorocarbonyl 2-substitutent in high yield,[6] and this has provided access to both η^3-butadienyl thioester complexes and a variety of novel polymeric species containing several metal centers bridged by linked η^3-butadienyl units.[7] In this publication, reactions of the chromium, molybdenum, and tungsten complexes Ph$_4$P[MCl(CO)$_3$L$_2$] with 1,4-dichlorobut-2-yne in dichloromethane or methanol are compared, and mechanisms for the formation of the chlorocarbonyl and ester 2-substituted butadienyl complexes are presented with some supporting evidence. The related tungsten amide and thioester complexes are successfully prepared and characterized, and the first X-ray structure of an η^3-butadienyl complex containing a sulfur substituent is described.

Results and Discussion

Reactions in Chlorinated Solvents. Addition of excess 1,4-dichlorobut-2-yne to a solution of Ph$_4$P[WCl-

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10.1021/om980521j CCC: $15.00
Publication on Web 11/06/1998

Table 1. Yields, Selected Infrared, and Analytical Data for $[WCl(CO)_2(\eta^3\text{-}CH_2C(COX)C{=}CH_2)L_2]$

	complex			infrared data[a]		analysis, found (calcd), %			
no.	X	L_2	yield, %	ν(C≡O)	ν(C=O)	C	H	N	S
1a	Cl	bipy	63	1899, 1963	1712	37.13(37.29)	2.45(2.19)	4.98(5.12)	
1b	Cl	phen	70	1907, 1972	1702	39.26(39.92)	2.33(2.10)	4.83(4.90)	
2a	OMe	bipy	59	1880, 1965	1688	39.01(39.81)	2.46(2.76)	5.42(5.16)	
2b	OMe	phen	64	1882, 1969	1684	42.25(42.36)	2.49(2.64)	4.87(4.94)	
3a	NEt_2	bipy	68	1885, 1969	1625	42.94(43.18)	3.70(3.77)	7.06(7.20)	
3b	NEt_2	phen	61	1880, 1961	1620	44.93(45.43)	4.00(3.62)	6.79(6.91)	
4a	SBu^n	bipy	57	1869, 1956	1629	42.07(41.96)	3.53(3.49)	4.13(4.66)	5.25(5.32)
4b	SBu^n	phen	62	1877, 1964	1636	44.17(44.19)	3.66(3.36)	4.45(4.48)	4.95(5.12)

[a] As Nujol mulls, cm^{-1}. All bands strong unless otherwise indicated.

Table 2. ^{1}H NMR Data for Tungsten Butadienyl Complexes 1−4[a]

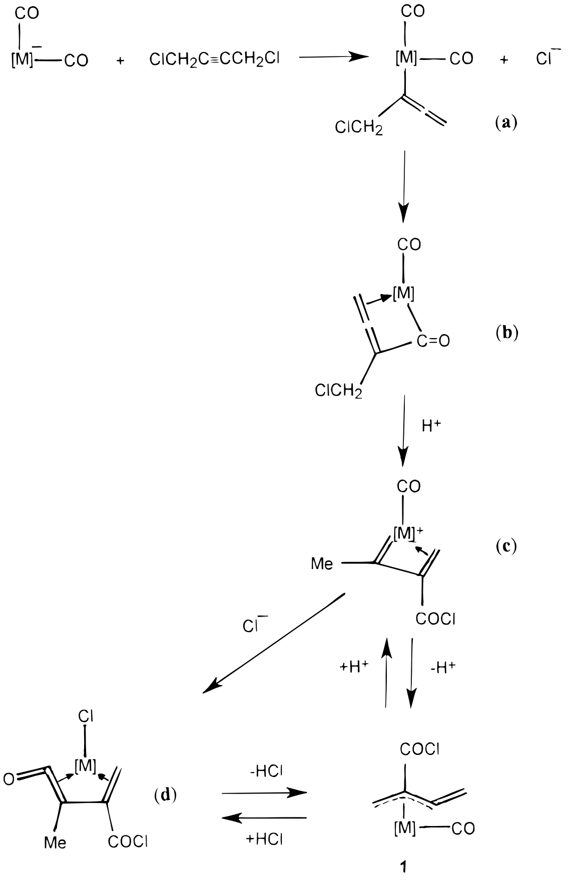
	H'_{anti} H'_{syn}	H''_{anti} H''_{syn}	aliphatic		
			CH_3	CH_2	aromatic
1b	3.09(d,1.46,H)	4.60(s,H)			8.28(m,H), 8.40(s,2H), 8.43(m,H)
	4.00(d,1.47,H)	5.83(s,H)			9.09(d,H), 9.18(d,H), 9.72(m,2H)
2b	2.12(d,1.31,H)	5.53(s,H)	2.05(s,3H)		8.13(m,2H), 8.25(s,2H), 8.93(m,2H)
	3.52(d,1.31,H)	6.33(s,H)			9.25(d,H), 9.46(d,H)
3b	2.29(d,1.27,H)	5.61(s,H)	0.64(m,3H)	2.31(m,2H), 2.69(m,H)	8.21(m,2H), 8.32(s,2H), 8.97(m,2H)
	3.74(d,1.27,H)	6.48(s,H)	0.97(m,3H)	3.63(m,H)	9.31(d,H), 9.50(d,H)
4b	2.10(d,1.28,H)	5.73(s,H)	0.64(t,3H)	0.27(m,2H), 0.75(m,2H)	8.23(m,2H), 8.33(s,2H), 9.02(m,2H)
	3.66(d,1.28,H)	6.55(s,H)		1.64(m,2H)	9.35(d,H), 9.56(d,H)

[a] Spectra recorded as solutions in dimethylformamide-d_7. Data reported in ppm, multiplicity, coupling constant (Hz), number of protons.

$(CO)_3L_2]$ in dichloromethane or chloroform at ambient temperature afforded orange microcrystalline complexes $[WCl(CO)_2(\eta^3\text{-}CH_2C(COCl)C{=}CH_2)L_2]$ (L_2 = bipy **1a** or phen **1b**), which were characterized by IR and ^{1}H NMR spectroscopy and by elemental analysis (Tables 1 and 2). Freshly prepared **1** was soluble in common organic solvents, but solid rapidly precipitated from solution on storage, and this is reflected in the slightly high %C value for **1b**. Analogous reactions carried out in the presence of acetonitrile gave low yields of **1** because of the known solvolysis of the anion to give $[W(MeCN)(CO)_3L_2]$.[8] Interestingly addition of pyridine to reactions of anion and alkyne completely inhibited the formation of **1** (vide infra). A mixture of $Ph_4P[CrCl(CO)_3L_2]$ and 1,4-dichlorobut-2-yne in the same solvent was stirred at −40 °C, followed by storage at low temperature for several days. The infrared spectrum of the resulting orange, filtered solution exhibited strong carbonyl absorptions at 1982 and 1908 cm^{-1} attributable to a *cis*-dicarbonyl species, and a broad peak of medium intensity at 1660 cm^{-1} could be assigned to the chlorocarbonyl moiety of an η^3-bonded butadienyl group. Attempts to isolate this compound were unsuccesssful, however, due the thermal instability of the complex in solution.

A mechanism for the formation of complexes $[MCl(CO)_2(\eta^3\text{-}CH_2C(COCl)C{=}CH_2)L_2]$ (M = Cr, Mo, W) can be postulated in which nucleophilic attack of the anion on 1,4-dichlorobut-2-yne by an S_N2 mechanism results in the production of a σ-allenyl (Scheme 1, **a**). Insertion of CO into the metal−allenyl bond results in an unsaturated 16-electron species and subsequent formation of the π-allenyl (Scheme 1, **b**). Although solvents were dried before use, the alkyne was handled in moist air, and under these conditions trace amounts of hydrogen ions will be present. Protonation of the coordinated allenyl and rearrangement give a cationic η^3-vinylcarbene containing a chlorocarbonyl substituent (Scheme 1, **c**). Deprotonation of this intermediate affords the η^3-butadienyl **1**. Only trace quantities of H^+ are required in the synthesis of **1** since the ion performs a catalytic role in the reaction pathway. In accord with this mechanism, the presence of pyridine in reactions of $Ph_4P[MCl(CO)_3L_2]$ and 1,4-dichlorobut-2-yne completely

Scheme 1



$[M] = MCl(CO)L_2$; M=Cr,Mo,W; L_2=bipy,phen.

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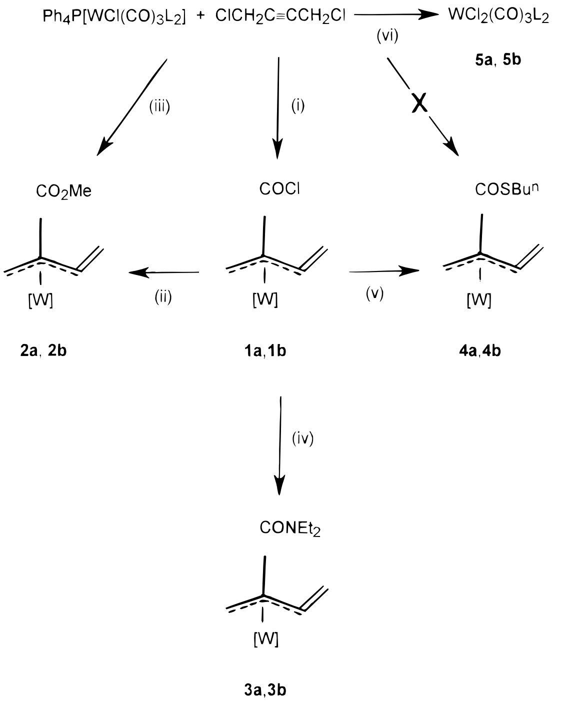
inhibits production of the butadienyl, because the amine acts as an acid-scavenger.

Support for this mechanism was obtained on isolation of a minor byproduct from the reaction mixture during the synthesis of the molybdenum form of **1b**. The IR and ^{1}H NMR spectra of this yellow crystalline product supported the formation of an η^4-vinylketene[9] (Scheme 1, **d**) and hence the presence of HCl and a vinyl carbene in the proposed mechanism. The chemistry of η^4-vinylketene complexes of a variety of transition metals, including those of group 6, has been explored and reviewed in some detail,[10−12] in part because of their relationship to the Dötz annulation reaction.[13] Work by Klimes and Weiss demonstrated that treatment of $Fe_2(CO)_9$ with a cyclopropene afforded an η^3-vinylcarbene, which underwent facile carbonylation with CO at room temperature to give the η^4-vinylketene, this process being reversible at 60 °C.[14] Conversion between η^3-butadienyl and η^4-vinylketene has been observed before in the reversible protonation of $[(Me_5cp)Mo(CO)_2(\eta^3\text{-}CH_2CHC{=}CH_2)]$ (cp = cyclopentadienyl) by triflic acid to give $[(Me_5cp)Mo(CO)(OSO_2CF_3)(\eta^4\text{-}CH_2{=}CHC(Me){=}C{=}O)]$, and the structure of the iodo analogue of this vinylketene has been confirmed by X-ray analysis.[15] Extended Hückel molecular orbital calculations based on the crystallographic coordinates of this cyclopentadienyl complex predicted protonation should occur at the terminal carbon of the C=C unit in the organic fragment to form a cationic η^3-vinylcarbene intermediate. By analogy, protonation at C(4) of the butadienyl ligand C(1)C(2)C(3)=C(4) in **1** would produce an η^3-vinylcarbene (Scheme 1, **c**), and subsequent ligand-induced migration of CO in the presence of chloride ion would lead to the formation of an η^4-vinylketene complex $[MoCl_2(CO)(\eta^4\text{-}CH_2C(COCl)C(Me){=}C{=}O)L_2]$ (Scheme 1, **d**). Attempts to isolate the proposed η^3-vinylcarbene have been unsuccessful to date.

Reactions of 1 with Alcohols, Amines, and Thiols. Addition of methanol and triethylamine to a solution of **1** in dichloromethane gave ester-substituted complexes of general formula $[WCl(CO)_2(\eta^3\text{-}CH_2C(CO_2Me)C{=}CH_2)L_2]$ (L_2 = bipy **2a**, phen **2b**) (Scheme 2). Unlike its molybdenum counterpart, $Ph_4P[WCl(CO)_3L_2]$ reacted with 1,4-dichlorobut-2-yne in the presence of aqueous methanol to give $WCl_2(CO)_3L_2$, but replacement of water by triethylamine gave the ester complex **2**. Attempts to prepare these complexes from longer chain (n-PrOH, n-BuOH) or bulky (i-PrOH, i-BuOH, sec-BuOH) alcohols gave non-carbonyl-containing products only. Substitution of methanol by excess diethylamine or *n*-butanethiol and triethylamine in these reactions afforded the complexes $[WCl(CO)_2(\eta^3\text{-}CH_2C(CONEt_2)C{=}CH_2)L_2]$ (**3a**, **3b**) and $[WCl(CO)_2(\eta^3\text{-}CH_2C(COSBu^n)C{=}CH_2)L_2]$ (**4a**, **4b**), respectively. Yields, analytical data, and selected infrared data for complexes **1**−**4** are given in Table 1, and ^{1}H NMR data in Table 2. The tungsten complexes were of lower solubility than their molybdenum analogues, and attempts to improve their elemental analyses by recrystallization were not wholly successful. The bipyridyl complexes were of limited solubility, and consequently ^{1}H NMR spectra were obtained for the phenanthroline complexes only.

Scheme 2



Conditions: CH_2Cl_2, 20°C; (i) excess 1,4-dichlorobut-2-yne; (ii) MeOH; (iii) MeOH and NEt_3; (iv) excess $HNEt_2$; (v) $HSBu^n$ and NEt_3; (vi) MeOH and H_2O. [W] = $WCl(CO)_2L_2$

Despite the formation of ester complex **2** on addition of chlorocarbonyl complex **1** to methanol, it cannot be assumed that reaction of the anion and alkyne in methanol yields **2** through the intermediacy of **1**, since pyridine completely inhibits formation of the latter in dichloromethane, but supports production of the former in the presence of methanol. It is likely therefore that the anion and alkyne react in alcohol and dichloromethane by different or divergent reaction pathways. A study of reaction rates for formation of the molybdenum analogue of **2b** from $Ph_4P[MoCl(CO)_3L_2]$ and 1,4-dichlorobut-2-yne in methanol with different additional reagents has proved informative. Reactions involving pyridine (pK_a conjugate acid 5.23) gave the ester complex within several hours; however, replacement by triethylamine (pK_a 10.75) or the sterically hindered base 2,4,6-trimethylpyridine (pK_a 7.43) increased the rate of reaction to give the product within minutes. If the amine coordinates to the metal center of an intermediate, it seems unlikely that the bulk of the latter reagent would accelerate the reaction. In addition, use of $Me_2N(CH_2)_2NMe_2$ might result in coordination to two

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[9] For $[MoCl_2(CO)(phen)(\eta^4\text{-}CH_2{=}C(COCl)C(Me){=}C{=}O)]$, ^{1}H NMR in CD_2Cl_2 ppm [number of protons, multiplicity, coupling constants]: 8.00−9.66 [8H], 4.16 [1H, d, 0.92 Hz], 2.99 [1H, d, 0.92 Hz], 0.77 [3H, s]. IR spectrum Nujol mull, cm^{-1}: 1923 (carbonyl), 1757 (C=O), 1657 (COCl). Elemental analysis for $MoC_{19}H_{13}N_2O_3Cl_3$. Calcd,%: 43.89C, 2.50H, 5.39N. Found%: 43.78C, 2.44H, 5.27N.

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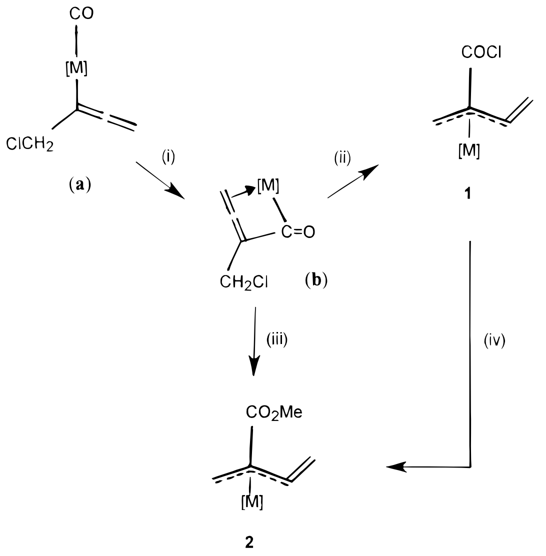
Scheme 3



Conditions: (i) with or without tertiary amine; (ii) no tertiary amine, ±H+ as scheme 1; (iii) tertiary amine, MeOH, -HCl; (iv) MeOH, -HCl.

[M] = $MCl(CO)_2L_2$; M=Mo,W; L_2=bipy,phen.

metal centers to form a dimeric intermediate that would impose steric or kinetic restrictions on the reaction pathway. No such difference in reaction rate was observed for triethylamine and the bifunctional amine, and thus it is likely that the amine serves simply to control the pH of the reaction. The effect of a tertiary amine in the proposed mechanistic pathway to formation of chlorocarbonyl complex **1** (Scheme 1) would therefore be to prevent the final two steps. However reaction of $Ph_4P[MoCl(CO)_3L_2]$ and 1,4-dichlorobut-2-yne in basic methanol would not prevent the first two steps of this mechanism from being common to the production of both **1** and **2**. Scheme 3 illustrates how the presence or absence of the tertiary amine could control the reaction pathway to these two complexes, with pyridine acting as an acid scavenger to inhibit formation of **1** and assisting removal of HCl from an intermediate to yield **2**.

Spectroscopic Data. The IR spectra of all the complexes were dominated by a pair of strong absorption bands between 1970 and 1860 cm^{-1}, attributed to the stretching modes of *cis*-dicarbonyl species. Absorptions due to the carbonyl group of the butadienyl moiety decreased through the range 1712−1634 cm^{-1} in an order reflecting the differing electronegativities of X in the family of complexes $[WCl(CO)_2(\eta^3\text{-}CH_2C(COX)C{=}CH_2)L_2]$. A weak band near 1670 cm^{-1} could be assigned to the uncoordinated double bond of the butadienyl group.

The poor solubilities of the complexes in common organic solvents precluded measurement of ^{13}C NMR spectra; however proton NMR spectra of complexes in dimethylformamide-d_7 were recorded where possible, and pertinent data are presented in Table 2. The spectra of representative complexes were found to be invariant over the temperature range −70 to +25 °C, and there was no evidence of dynamic behavior observed for some other complexes of the type $[MCl(CO)_2(\eta^3\text{-allyl})L_2]$.[20] All spectra were consistent with the presence of *trans*-butadienyl ligands, with the terminal methylene protons of the η^3-bonded species giving rise to doublets (coupling constants of ca. 1.2 Hz) near 2.2 ppm (H_{anti}) and 3.6 ppm (H_{syn}) and those of the double bond occurring as singlets near 5.6 ppm (H_{anti}) and 6.5 ppm (H_{syn}). This differs from the spectra of the molybdenum analogues, where the equivalent pair of high-field signals appear as singlets and the lower field pair are doublets with coupling constants of ca. 2.2 Hz.[4,7a] Peaks assigned to the methyl groups of the ester and amide complexes were shifted upfield due to the anisotropic effect of the bipyridyl or phenanthroline ring systems, and each CH_2 unit in the thiolate complexes produced a complex overlapping multiplet due to the slightly differing magnetic environments of the two protons. The triplet resonance assigned to the methyl group in the *n*-alkyl thiol complex **4b** was significantly upfield, occurring at 0.64 ppm.

Table 3. Crystal Data for 4b

formula	$C_{23}H_{21}ClN_2O_3SW$
fw	624.78
space group	$P2_1/n$
cryst syst	monoclinic
a, Å	9.5195(13)
b, Å	12.4665(9)
c, Å	19.039(2)
α, deg	
β, deg	91.948(11)
γ, deg	
cryst size, mm	0.50 × 0.35 × 0.03
V, Å^3	2258.1(4)
μ (Mo Kα), mm^{-1}	5.354
λ (Mo Ka), Å	0.710 73
ρ(calcd), g cm^{-3}	1.838
Z	4
no. of reflns collcd	5222
no. of independent reflns	3976
limiting indices	$-1 \le h \le 11, -1 \le k \le 14, -22 \le l \le 22$
2θ, deg	1.95−25.00
F(000)	1216
T, K	293(2)
R	0.0667
R_w	0.1217
refinement method	full-matrix least-squares on F^2
largest diff peak and hole, e Å^{-3}	1.667, −1.433

Crystal Structure Determination. A solid-state crystal structure determination was carried out on $[WCl(CO)_2(\eta^3\text{-}CH_2C(COSBu^n)C{=}CH_2)(1,10\text{-phenanthroline})]$ (**4b**) to determine the stereochemistry of the unusual η^3-butadienyl fragment. Table 3 contains crystal data for **4b**, and important interatomic parameters are given in Table 4. Figure 1 shows a view of the molecule and the atomic labeling scheme used. The central tungsten atom can be described as heptacoordinate, being bonded to two carbonyl groups [W−C(11) 1.993(18) Å; W−C(12) 1.964(17) Å], two nitrogens of 1,10-phenanthroline [W−N(1) 2.213(11) Å; W−N(2) 2.211(11) Å], a chlorine atom [W−Cl 2.468(4) Å], and a

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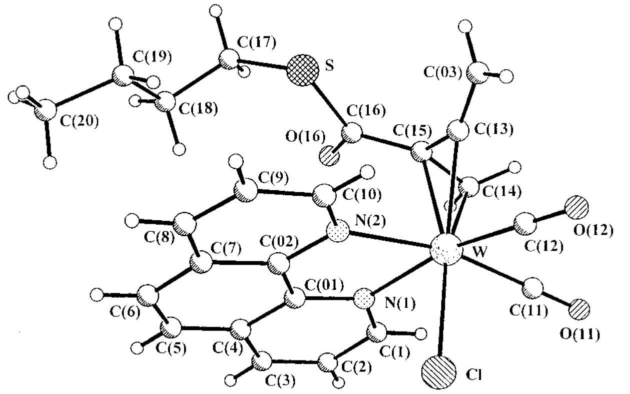


Figure 1. Structure of [WCl(CO)$_2${η^3-CH$_2$C(COSBu^n)C=CH$_2$}(1,10-phenanthroline)] (**4b**) with atom-labeling scheme.

Table 4. Interatomic Distances (Å) and Angles (deg) with Standard Deviations in Parentheses for WCl(CO)$_2$(η^3-CH$_2$C(COSBu^n)C=CH$_2$)(phen)

W−C(11)	1.993(18)	W−C(14)	2.318(18)
W−C(12)	1.964(17)	W−C(15)	2.197(19)
W−N(1)	2.213(11)	W−C(13)	2.181(17)
W−N(2)	2.211(11)	C(14)−C(15)	1.38(2)
W−Cl	2.468(4)	C(13)−C(15)	1.43(2)
C(15)−C(16)	1.47(2)	C(03)−C(13)	1.29(2)
C(16)−O(16)	1.17(2)	C(11)−O(11)	1.15(2)
C(16)−S	1.79(2)	C(12)−O(12)	1.16(2)

C(11)−W−C(12)	82.1(6)	C(14)−C(15)−C(13)	108(2)
N(1)−W−N(2)	74.7(4)	C(15)−C(13)−C(03)	142(2)
O(11)−C(11)−W	180(2)	O(12)−C(012)−W	78.9(14)
C(15)−C(16)−O(16)	123(2)	O(16)−C(16)−S	122(2)
C(16)−S−C(17)	100.9(9)		

bidentate, 2-substituted butadienyl unit C$_9$H$_{13}$OS. The C(11)−W−C(12) bond angle of 82.1(6)° is typical of a pair of mutually *cis*-carbonyl groups and is in accord with the value of 82.5° calculated from infrared ν(CO) solution intensity measurements. The metal−carbon and C−O carbonyl bond lengths [C(11)−O(11) 1.15(2) Å; C(12)−O(12) 1.16(2) Å] are unexceptional, and both carbonyl groups are essentially linear [W−C(11)−O(11) 180(2)°; W−C(12)−O(12) 179(2)°]. The rings of the phenanthroline unit are approximately planar within experimental error, and the bond lengths and angles are similar to values found for other tungsten phenanthroline complexes.[16a]

Within the metal−butadienyl unit, the W−C(14) and W−C(15) distances of 2.318(18) and 2.197(19) Å, respectively, and the C(14)−C(15)−C(13) separations of 1.38(2) and 1.43(2) Å plus a C(14)−C(15)−C(13) angle of 108(2)° are typical of parameters found in 2-substituted η^3-allyl complexes of tungsten[16b] and the related η^3-butadienyl ligand in [W(η^5-C$_5$H$_5$)(CO)$_2$(η^3-C(CN)$_2$C(Ph)C=C(CN)$_2$)].[17] However the W−C(13) distance of 2.181(17) Å is noticeably shorter than that normally observed between tungsten and the terminus of an allyl system, and this may reflect a contribution from a canonical form such as **A**, in which W−C(03) has a bond order between 1 and 2. The fourth carbon atom C(03) of the butadienyl system is bent away from the metal and at a distance of 3.264 Å is considered to be nonbonded to the metal center. The carbonyl and alkyl chain of the COSBu^n substitutent are orientated away from the terminal C=CH$_2$ moiety, and the butyl group is located well above the phen plane [closest approach C(8) to C(20) 2.116 Å]. The carbon−carbon bond length C(13)−C(03) at the terminus of the butadienyl was at 1.29(2) Å, considerably shorter than the C−C(terminal) separation of 1.344 ± 0.001 Å in free butadiene[18] and found in related structures, but is within the range found for the uncoordinated C=CH$_2$ of a ligated allene.[19]

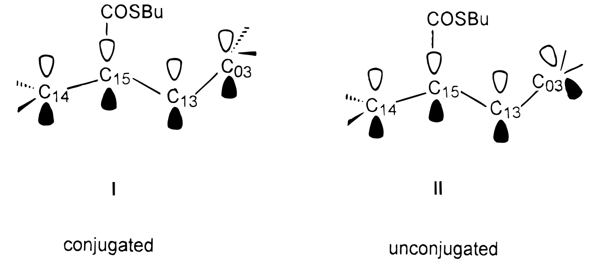
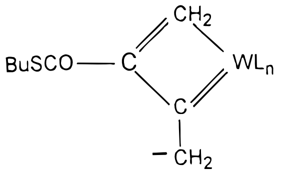


Figure 2. Extreme orientations of the C(03) and C(14) pπ orbitals in the η^3-butadienyl ligand.



A

The C$_9$H$_{13}$OS ligand can be related to a 2-substituted η^3-allyl system, with a double bond substituted on one terminus. For **4b**, the torsion angle between the C(03)=C(13) vector and the three metal-bonded atoms of the butadienyl was found to be 103.89°. The angle between the two planes defined by C(03) and its hydrogen atoms and by C(03), C(13), and C(14) was 179.98°, while at the opposite end of the ligand, the torsion angle between the C(15)−C(14) vector and the plane containing C(14) and its hydrogen atoms was found to be 148.98°. The uncoordinated double bond can be considered as being between the limits of being unconjugated or conjugated with the allyl unit, depending upon the positions of the hydrogen atoms on the terminal carbon atoms C(03) and C(14). With the C(14) hydrogen atoms and the allyl unit nonplanar, the double bond is conjugated if the H atoms on C(03) are orthogonal to the plane of the allyl system (Figure 2, I) and unconjugated with these H atoms coplanar with the allyl system (Figure 2, II). The orthogonality of the terminal CH$_2$ units was shown by an improper torsion angle between the plane C(03), H(H3A), H(3B) and the plane C(14), H(14A), H(14B) of 86.27°, and thus the double bond is not conjugated to the allyl system.

Experimental Section

Solvents and liquid reactants were dried over molecular sieves 4A and thoroughly degassed by dinitrogen prior to use. All reactions were carried out under an atmosphere of dinitrogen. The complexes Ph$_4$P[MCl(CO)$_3$L$_2$] (M = Cr, Mo, or W) were prepared according to the literature procedures.[21] All other chemicals were purchased from Aldrich and used without further purification. Infrared spectra were recorded on a Perkin-Elmer 781 spectrometer as paraffin mulls, and NMR spectra were obtained using a JEOL GX 270 MHz FT instrument, with samples dissolved in dimethylformamide-d_7 and tetramethylsilane used as an internal standard.

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Preparation of 1a. A stirred solution of $Ph_4P[WCl(CO)_3\text{-}bipy]$ (0.79 g, 1.0 mmol) in dichloromethane (50 cm^3) was cooled to −5 °C, and 1,4-dichlorobut-2-yne (0.15 cm^3, 1.53 mmol) was added dropwise. After 0.5 h at this temperature the mixture was allowed to warm to room temperature and then stirred for a further 2.5 h. Addition of petroleum ether (40−60 °C, 50 cm^3) and cooling precipitated the crude, orange-red product, which was filtered from solution, washed with petroleum ether, and dried in vacuo.

Preparation of 1b. A mixture of 1,4-dichlorobut-2-yne (0.5 cm^3, 5.11 mmol) and $Ph_4P[WCl(CO)_3phen]$ (2.64 g, 3.21 mmol) in dichloromethane (5 cm^3) was stirred at room temperature for 2 h. The orange-brown product was isolated from the liquor by filtration, washed with a little *n*-hexane, and dried in vacuo.

Attempted Preparation of 2a and 2b. Freshly prepared $Ph_4P[WCl(CO)_3L_2]$ (1.0 mmol) was added to aqueous methanol (50 cm^3, 1% v/v) at room temperature, and 1,4-dichlorobut-2-yne (0.15 cm^3, 1.53 mmol) was added dropwise. After 3 h the dark yellow liquid was filtered, petroleum ether (25 cm^3) was added, and storage at −5 °C over several days precipitated crystals of $WCl_2(CO)_3L_2$, which were identified by their IR spectra.

Preparation of 2a and 2b. Methanolic triethylamine (10 cm^3, 5% v/v NEt_3 in MeOH) was stirred with freshly prepared $Ph_4P[WCl(CO)_3L_2]$ (1.0 mmol). To this mixture 1,4-dichlorobut-2-yne (0.5 cm^3, 5.11 mmol) was added dropwise. After 4 h the solution was cooled to −5 °C, and storage precipitated the dark red product.

Preparation of 3a and 3b. A solution of a freshly prepared sample of **1** (1.0 mmol) in dichloromethane (180 cm^3) was stirred with a mixture of excess diethylamine (0.5 cm^3) in dichloromethane (50 cm^3) at room temperature. After 3 h the dark red solution was filtered, petroleum ether was added, and storage afforded the products as orange-red rectangular crystals.

Preparation of 4a and 4b. A freshly prepared sample of **1** (1.0 mmol) was prepared and stirred in dichloromethane (150 cm^3) at room temperature for 18 h with triethylamine (0.5 cm^3, 3.59 mmol) and *n*-butanethiol (0.5 cm^3, 4.67 mmol). The mixture was filtered, petroleum ether was added (40−60 °C), and the product precipitated as dark red microcrystals on storage at ambient temperature.

Structure Determination. A single crystal of **4b** (0.50 × 0.35 × 0.03 mm) was grown from a CH_2Cl_2-petroleum ether mixture and mounted on a Siemans automatic four-circle diffractometer. Using graphite-monochromated molybdenum radiation ($\lambda = 0.710\,73$ Å), a total of 5222 reflections were collected at room temperature in the range $1.95 \leq \theta \leq 25$, of which 3976 were unique with $I \leq 3\sigma(I)$. The structure was solved by full-matrix least-squares on F^2 using the SHELX suite of programs.[23] In the final stages of refinement, all atoms except hydrogen were allowed to vibrate anisotropically.

Conclusion

The η^3-$CH_2C(COCl)C{=}CH_2$ moiety has proved a versatile ligand, giving access to a variety of 2-substituted complexes of molybdenum and tungsten(II). On the basis of the structural evidence described above, we consider these complexes to be derivatives of buta-2,3-dienyl systems, in which the uncoordinated carbon−carbon double bond is unconjugated with respect to the π-delocalization within the η^3-allyl fragment. Differences in reactivity of the anion $[MCl(CO)_3L_2]^-$ with 1,4-dichloro-2-butyne in dichloromethane and methanol may be explained by a common initial mechanism, which diverges in the presence or absence of donor reagents such as water or tertiary amine. Some experimental evidence has been found to support this proposition, and further mechanistic studies on these and related η^3-butadienyl systems would prove interesting.

Acknowledgment. We thank Kevin Sudlow (U.W.E.) and Christopher Davey (U.N.L.) for assistance with some of the structural studies. Elemental analyses were carried out by the Analytical Services, University of Bristol, and NMR spectra recorded by the University of Portsmouth.

Supporting Information Available: Tables of atomic coordinates and isotropic displacement parameters for the hydrogen atoms, anisotropic thermal parameters, and bond lengths and angles (4 pages). Ordering information is given on any current masthead page.

OM980521J

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