ELSEVIER

Coordination Chemistry Reviews 143 (1995)
501–533

COORDINATION CHEMISTRY REVIEWS

Hydrocarbyl ligand derivatives of group 6–group 9 heterometallic clusters

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Received 11 November 1994; revised 12 January 1995

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Abstract

The synthesis and reactivity of group 6–group 9 heterometallic clusters containing hydrocarbon ligands is reviewed. A variety of methods has been employed in the synthesis of this class of clusters. These methods are organized into several general reaction types: metal exchange reactions, the reactions between dinuclear compounds, reactions utilizing mononuclear metal alkylidynes, and condensation reactions with other mononuclear reagents. The reactions of the resulting heterometallic clusters with alkynes, protons and carbon electrophiles, and miscellaneous substitution reactions are discussed. Applications in catalysis are briefly summarized.

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SSDI 0010-8545(95)01140-4

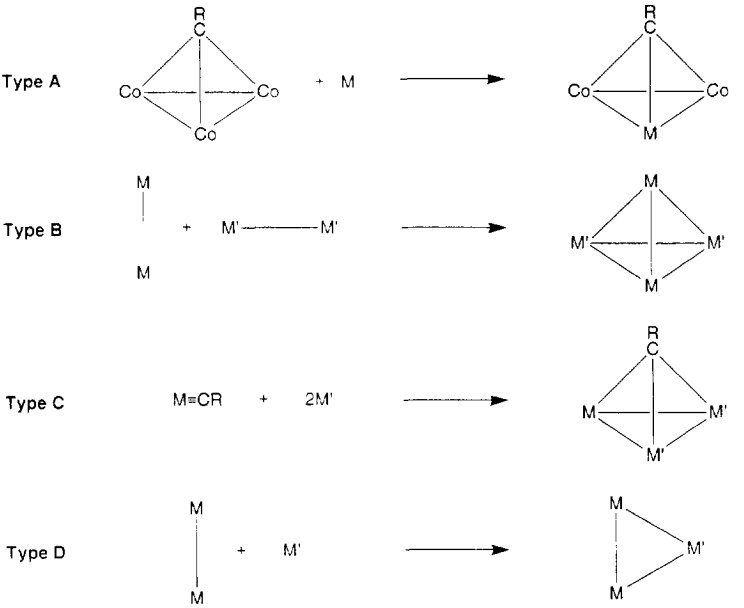
Keywords: Group 6–group 9 heterometallic clusters; Hydrocarbon ligands; Synthesis; Reactivity.

1. Introduction

The study of mixed-metal clusters has developed into an active field, in part due to observations that combinations of diverse metals in a cluster core can lead to site selective reactions and unique transformations of various substrates [1]. Furthermore, heterometallic clusters have an important role in the design and compositional control of supported bimetallic catalysts [2]. The goal of this review is to discuss the synthesis and reactivity of group 6–group 9 heterometallic clusters containing hydrocarbon ligands. In order to maintain a reasonable scope, clusters containing sulphido or phosphido ligands are excluded, in part because sulfur and phosphorus are frequently poisons for heterogeneous catalysts. The majority of the clusters discussed are either trinuclear μ_3-alkylidyne clusters or tetranuclear heterometallic clusters. Although a large number of group 6–group 9 mixed-metal cluster have been synthesized, several general routes have been employed and will be discussed below. The reactions of heterometallic clusters with various reagents lead to the observation of site-selectivity. The reactions of μ_3-alkylidyne and tetranuclear heterometallic clusters with alkynes, protons and carbon electrophiles, and miscellaneous substitution reactions are discussed. Several clusters have also been involved in catalytic studies and some mention is made of the general results.

2. General synthetic methods

Heterometallic trinuclear and tetranuclear clusters have been synthesized by utilizing a variety of methods. However several general schemes can be discerned, and for the purposes of this review they have been divided into the following four categories. Reactions of Type A involve metal exchange, that is, replacing one or more vertices on a preexisting cluster with a heterometal fragment. Type B reactions include the formation of mixed-metal clusters from the condensation of dinuclear reagents. The well developed use of mononuclear metal alkylidynes, and derivatives thereof, in reactions with mono- and dinuclear reagents is separated into its own category, Type C. Finally, the reactions of dinuclear species with mononuclear reagents are included under Type D reactions. Scheme I illustrates these reaction types in very general terms. While the focus of this review is the synthesis and reactivity of heterometallic clusters, it is useful to note that the majority of the compounds discussed are composed of fragments which are isolobal with CH or CH_2. Table 1 includes a representative list of some of these fragments and their isolobal relationships [3]. Table 2 contains a comprehensive compilation of information related to the syntheses of these mixed-metal clusters.



Scheme I.

Table 1
Isolobal relationships

CH	CH_2
$Co(CO)_3$	$Co(CO)(\eta^5\text{-Cp})$
$Ir(CO)_3$	$Rh(CO)(\eta^5\text{-Cp})$
$Cr(CO)_2(\eta^5\text{-Cp})$	$Cr(CO)_5$
$Mo(CO)_2(\eta^5\text{-Cp})$	$Mo(CO)_5$
$W(CO)_2(\eta^5\text{-Cp})$	$W(CO)_5$

2.1. *Type A: metal exchange reactions*

The reactions of trinuclear and tetranuclear clusters with various organometallic reagents lead to metal exchange and the formation of mixed-metal clusters that preserve the original nuclearity of the precursors. These typically involve the reactions of tri- or tetranuclear cobalt clusters with $M(CO)_3(\eta^5\text{-Cp})$ ($M \equiv Cr$, Mo, W) fragments, although heterometallic cluster precursors containing cobalt have also been employed. The metal exchange reagents have included organometallic dimethylarsenides, $M(CO)_3(AsMe_2)(\eta^5\text{-Cp})$, metal salts $[X][M(CO)_3(\eta^5\text{-Cp})]$ ($X \equiv$ Na, K, PPN), metal hydrides, $M(CO)_3H(\eta^5\text{-Cp})$, metal chlorides, $M(CO)_3Cl(\eta^5\text{-Cp})$, and dinuclear compounds, $M_2(CO)_6(\eta^5\text{-Cp})_2$.

The reaction of $Co_3(\mu_3\text{-CR})(CO)_9$ with $M(CO)_3(AsMe_2)(\eta^5\text{-Cp})$ leads to arsenic

Table 2
Compilation of group 6–group 9 mixed-metal cluster syntheses[a]

Compound	Type[b]	Reactants	Yield (%)	Other data	Reference
A. Trinuclear μ_3-alkylidyne clusters					
$CrCo_2(\mu_3\text{-}CH)(CO)_8(\eta^5\text{-}Cp)$	A	$Co_3(\mu_3\text{-}CH)(CO)_8\{AsMe_2Cr(CO)_3(\eta^5\text{-}Cp)\}$	45	IR, ^1H	[24,25]
	A	$Co_3(\mu_3\text{-}CCl)(CO)_9$, $Na[Cr(CO)_3(\eta^5\text{-}Cp)]$	20	IR, ^1H	[65]
$CrCo_2(\mu_3\text{-}CMe)(CO)_8(\eta^5\text{-}Cp)$	A	$Co_3(\mu_3\text{-}CMe)(CO)_8\{AsMe_2Cr(CO)_3(\eta^5\text{-}Cp)\}$	21	IR, ^1H	[24,25]
$CrCo_2(\mu_3\text{-}CPh)(CO)_8(\eta^5\text{-}Cp)$	A	$Co_3(\mu_3\text{-}CPh)(CO)_8\{AsMe_2Cr(CO)_3(\eta^5\text{-}Cp)\}$	17	IR, ^1H	[24,25]
$CrCo_2(\mu_3\text{-}CTol)(CO)_8(\eta^5\text{-}Cp)$	A	$Co_3(\mu_3\text{-}CTol)(CO)_8\{AsMe_2Cr(CO)_3(\eta^5\text{-}Cp)\}$	17	IR, ^1H	[24]
	C	$Cr(\equiv CTol)(CO)_2(\eta^5\text{-}Cp)$, $Co_2(CO)_8$	51	IR, ^1H, ^{13}C	[66]
$CrCo_2(\mu_3\text{-}CF)(CO)_8(\eta^5\text{-}Cp)$	A	$Co_3(\mu_3\text{-}CF)(CO)_8\{AsMe_2Cr(CO)_3(\eta^5\text{-}Cp)\}$	26	IR, ^1H, ^{19}F	[24]
$CrCo_2(\mu_3\text{-}CCl)(CO)_8(\eta^5\text{-}Cp)$	A	$Co_3(\mu_3\text{-}CCl)(CO)_9$, $[PPN][Cr(CO)_3(\eta^5\text{-}Cp)]$	20	IR, ^1H	[65]
$MoCo_2(\mu_3\text{-}CH)(CO)_8(\eta^5\text{-}Cp)$	A	$Co_3(\mu_3\text{-}CH)(CO)_8\{AsMe_2Mo(CO)_3(\eta^5\text{-}Cp)\}$	48	IR, ^1H	[24,25]
	A	$Co_3(\mu_3\text{-}CH)(CO)_9$, $Mo(CO)_3(AsMe_2)(\eta^5\text{-}Cp)$	62		[62]
	A	$Co_3(\mu_3\text{-}CH)(CO)_9$, $Mo(CO)_3H(\eta^5\text{-}Cp)$	17		[62]
	A	$Co_3(\mu_3\text{-}CBr)(CO)_9$, $Mo(CO)_3H(\eta^5\text{-}Cp)$	11		[62]
	A	$Co_3(\mu_3\text{-}CBr)(CO)_9$, $Mo(CO)_3Cl(\eta^5\text{-}Cp)$	7		[62]
	A	$Co_3(\mu_3\text{-}CH)(CO)_9$, $Na[Mo(CO)_3(\eta^5\text{-}Cp)]$	13		[62]
	A	$Co_3(\mu_3\text{-}CBr)(CO)_9$, $Na[Mo(CO)_3(\eta^5\text{-}Cp)]$	17		[62]
	A	$Co_3(\mu_3\text{-}CCl)(CO)_9$, $K[Mo(CO)_3(\eta^5\text{-}Cp)]$	20	IR, ^1H	[65]
	A	$Co_3(\mu_3\text{-}CBr)(CO)_9$, $[PPN][Mo(CO)_3(\eta^5\text{-}Cp)]$	27		[65]
	A	$Co_3(\mu_3\text{-}CCl)(CO)_9$, $[PPN][Mo(CO)_3(\eta^5\text{-}Cp)]$, $Me_3NO{\cdot}2H_2O$	82		[65]
$MoCo_2(\mu_3\text{-}CMe)(CO)_8(\eta^5\text{-}Cp)$	A	$Co_3(\mu_3\text{-}CMe)(CO)_8\{AsMe_2Mo(CO)_3(\eta^5\text{-}Cp)\}$	75	IR, ^1H	[24,25]
	A	$Co_3(\mu_3\text{-}CMe)(CO)_9$, $Mo_2(CO)_6(\eta^5\text{-}Cp)_2$	17		[67,68]
	A	$MoCo_3(\mu_3\text{-}CMe)(CO)_8(\mu\text{-}AsMe_2)(\eta^5\text{-}Cp)$, CO	92		[69]
	A	$Co_3(\mu_3\text{-}CMe)(CO)_9$, $Mo(CO)_3H(\eta^5\text{-}Cp)$	63		[62]
	A	$Co_3(\mu_3\text{-}CMe)(CO)_9$, $Mo(CO)_3Cl(\eta^5\text{-}Cp)$	8		[62]
$MoCo_2(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_2(\eta^5\text{-}Cp)_3$	R	$MoCo_2(\mu_3\text{-}CMe)(CO)_8(\eta^5\text{-}Cp)$, $(C_5H_6)_2$	19	IR, ^1H	[44]
	D	$Co_2(\mu\text{-}CCH_2)(CO)_2(\eta^5\text{-}Cp)_2$, $Mo(CO)_3H(\eta^5\text{-}Cp)$	76	XR, IR, ^1H, ^{13}C	[43]
$MoCo_2(\mu_3\text{-}CCO_2Me)(CO)_8(\eta^5\text{-}Cp)$	A	$Co_3(\mu_3\text{-}CCO_2Me)(CO)_9$, $Mo(CO)_3(AsMe_2)(\eta^5\text{-}Cp)$	36	IR, ^1H	[44]
	A	$Co_3(\mu_3\text{-}CCO_2Me)(CO)_9$, $Na[Mo(CO)_3(\eta^5\text{-}Cp)]$	56		[44]
$MoCo_2(\mu_3\text{-}CCO_2CHMe_2)(CO)_8(\eta^5\text{-}Cp)$	A	$Co_3(\mu_3\text{-}CCO_2CHMe_2)(CO)_9$, $Mo_2(CO)_6(\eta^5\text{-}Cp)_2$	33	IR, ^1H, ^{13}C	[61]
$MoCo_2(\mu_3\text{-}CCO_2CHMe_2)(CO)_8(\eta^5\text{-}Cp^*)$	A	$Co_3(\mu_3\text{-}CCO_2CHMe_2)(CO)_9$, $Mo_2(CO)_6(\eta^5\text{-}Cp^*)_2$	30	IR, ^1H, ^{13}C	[55]
$MoCo_2(\mu_3\text{-}CCO_2CHMe_2)(\mu\text{-}CO)(CO)_2(\eta^5\text{-}Cp)_3$	R	$MoCo_2(\mu_3\text{-}CCO_2CHMe_2)(CO)_8(\eta^5\text{-}Cp)$, C_5H_6	22	IR, ^1H, ^{13}C	[61]
$MoCo_2(\mu_3\text{-}CC(O)Ph)(CO)_8(\eta^5\text{-}Cp)$	A	$Co_3(\mu_3\text{-}CC(O)Ph)(CO)_9$, $Mo(CO)_3(AsMe_2)(\eta^5\text{-}Cp)$	31	IR, ^1H	[44]
	A	$Co_3(\mu_3\text{-}CC(O)Ph)(CO)_9$, $Na[Mo(CO)_3(\eta^5\text{-}Cp)]$	52		[44]
$MoCo_2(\mu_3\text{-}CCO_2Ph)(CO)_8(\eta^5\text{-}Cp)$	A	$Co_3(\mu_3\text{-}CCO_2Ph)(CO)_9$, $Na[Mo(CO)_3(\eta^5\text{-}Cp)]$	61	IR, ^1H	[44]
$MoCo_2(\mu_3\text{-}CC(Me){=}CH_2)(CO)_8(\eta^5\text{-}Cp)$	A	$Co_3(\mu_3\text{-}CC(Me){=}CH_2)(CO)_9$, $Na[Mo(CO)_3(\eta^5\text{-}Cp)]$	61	IR, ^1H, ^{13}C	[53]
$MoCo_2(\mu_3\text{-}CCH_2CMe_3)(CO)_8(\eta^5\text{-}Cp)$	D	$Co_2(\mu_2\text{-}\eta^2\text{-}HC_2CMe_3)(CO)_6$, $Mo(CO)_3H(\eta^5\text{-}Cp)$	75	^1H	[42]
$MoCo_2(\mu_3\text{-}CC{\equiv}C^tBu)(CO)_8(\eta^5\text{-}Cp)$	C	$Mo(\equiv CC{\equiv}C^tBu)(CO)_2(\eta^5\text{-}Cp)$, $Co_2(CO)_8$	96	IR, ^1H, ^{13}C	[29]
$MoCo_2(\mu_3\text{-}CPh)(CO)_8(\eta^5\text{-}Cp)$	A	$Co_3(\mu_3\text{-}CPh)(CO)_8\{AsMe_2Mo(CO)_3(\eta^5\text{-}Cp)\}$	32	XR, IR, ^1H	[24,25]

	A	$MoCo_3(\mu_3\text{-CPh})(CO)_8(\mu\text{-}AsMe_2)(\eta^5\text{-Cp})$, CO	91		[69]
	A	$Co_3(\mu_3\text{-CPh})(CO)_9$, $Na[Mo(CO)_3(\eta^5\text{-Cp})]$	61		[44]
$MoCo_2(\mu_3\text{-CPh})Br(CO)_8(py)_2$	C	$Mo(\equiv CPh)(CO)_2Br(py)_2$, $Co_2(CO)_8$	97	IR, ^1H, ^{13}C	[70]
$MoCo_2(\mu_3\text{-CPh})Br(CO)_8(bipy)$	C	$Mo(\equiv CPh)(CO)_2Br(bipy)$, $Co_2(CO)_8$	95	XR, IR, ^1H, ^{13}C	[70]
$MoCo_2(\mu_3\text{-CTol})(CO)_8(\eta^5\text{-Cp})$	A	$Co_3(\mu_3\text{-CTol})(CO)_8\{AsMe_2Mo(CO)_3(\eta^5\text{-Cp})\}$	27	IR, ^1H	[24,25]
	C	$MoW(\equiv CTol)(CO)_7(\eta^5\text{-Cp})$, $Co_2(CO)_8$	90	IR, ^1H, ^{13}C	[19]
$MoCo_2(\mu_3\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_8(\eta^5\text{-Cp})$	C	$Mo(\equiv CC_6H_3Me_2\text{-}2,6)(CO)_2(\eta^5\text{-Cp})$, $Co_2(CO)_8$	82	IR, ^1H, ^{13}C	[71]
$MoCo_2(\mu_3\text{-}CSiEt_3)(CO)_8(\eta^5\text{-Cp})$	A	$Co_3(\mu_3\text{-}CSiEt_3)(CO)_9$, $Na[Mo(CO)_3(\eta^5\text{-Cp})]$	63	IR, ^1H	[62]
	R	$MoCo_2(\mu_3\text{-CH})(CO)_8(\eta^5\text{-Cp})$, $HSiEt_3$	32		[62]
$MoCo_2(\mu_3\text{-CF})(CO)_8(\eta^5\text{-Cp})$	A	$Co_3(\mu_3\text{-CF})(CO)_8\{AsMe_2Mo(CO)_3(\eta^5\text{-Cp})\}$	83	IR, ^1H, ^{19}F	[24]
$MoCo_2(\mu_3\text{-CCl})(CO)_8(\eta^5\text{-Cp})$	A	$Co_3(\mu_3\text{-CCl})(CO)_9$, $Mo(CO)_3H(\eta^5\text{-Cp})$	NA	IR, ^1H	[62]
	A	$Co_3(\mu_3\text{-CCl})(CO)_9$, $Mo(CO)_3Cl(\eta^5\text{-Cp})$	NA		[62]
	A	$Co_3(\mu_3\text{-CCl})(CO)_9$, $[PPN][Mo(CO)_3(\eta^5\text{-Cp})]$	40	XR, IR, ^1H	[65]
$CrMoCo_2\{\mu_3\text{-}\sigma, \sigma', \sigma'':\eta^6\text{-}CC_6H_4(OMe)\text{-}2\}(CO)_{11}(\eta^5\text{-Cp})$	C	$CrMo\{\mu\text{-}\sigma:\eta^6\text{-}CC_6H_4(OMe)\text{-}2\}(CO)_5(\eta^5\text{-Cp})$, $Co_2(CO)_8$	75	IR, ^1H, ^{13}C	[16]
$MoCo_2(\mu_3\text{-CTol})(CO)_8[Co\{P(O)(OCH_3)_2\}_3(\eta^5\text{-Cp})]$	C	$Mo(\equiv CTol)(CO)_2[Co\{P(O)(OCH_3)_2\}_3(\eta^5\text{-Cp})]$, $Co_2(CO)_8$	73	IR, ^1H, ^{13}C	[17]
$MoRh_2(\mu_3\text{-}CC{\equiv}C^tBu)(\mu\text{-CO})(CO)_2(\eta^5\text{-Cp})(\eta^5\text{-}C_9H_7)_2$	C	$Mo(\equiv CC{\equiv}C^tBu)(CO)_2(\eta^5\text{-Cp})$, $Rh(CO)_2(\eta^5\text{-}C_9H_7)$	90	IR, ^1H, ^{13}C	[32]
$MoRh_2(\mu_3\text{-CTol})(\mu\text{-CO})(CO)_2(\eta^5\text{-Cp})(\eta^5\text{-}C_9H_7)_2$	C	$MoW(\equiv CTol)(CO)_7(\eta^5\text{-Cp})$, $Rh(CO)_2(\eta^5\text{-}C_9H_7)$	41	IR, ^1H, ^{13}C	[19]
$Mo_2Co(\mu_3\text{-CH})(CO)_7(\eta^5\text{-Cp})_2$	A	$Co_3(\mu_3\text{-CBr})(CO)_9$, $Mo_2(CO)_6(\eta^5\text{-Cp})_2$	9	IR, ^1H	[62]
	A	$Co_3(\mu_3\text{-CCl})(CO)_9$, $K[Mo(CO)_3(\eta^5\text{-Cp})]$	15	XR, IR, ^1H	[65,72]
$Mo_2Co(\mu_3\text{-CMe})(CO)_7(\eta^5\text{-Cp})_2$	A	$MoCo_2(\mu_3\text{-CMe})(CO)_8(\eta^5\text{-Cp})$, $Mo_2(CO)_6(\eta^5\text{-Cp})_2$	26	XR, IR, ^1H	[44,67]
$Mo_2Co(\mu_3\text{-CPh})(CO)_7(\eta^5\text{-Cp})_2$	A	$Co_3(\mu_3\text{-CPh})(CO)_9$, $Na[Mo(CO)_3(\eta^5\text{-Cp})]$	47	IR, ^1H	[44]
$Mo_2Co(\mu_3\text{-}CCO_2Me)(CO)_7(\eta^5\text{-Cp})_2$	A	$Co_3(\mu_3\text{-}CCO_2Me)(CO)_9$, $Mo(CO)_3(AsMe_2)(\eta^5\text{-Cp})$	7	IR, ^1H	[44]
	A	$Co_3(\mu_3\text{-}CCO_2Me)(CO)_9$, $Na[Mo(CO)_3(\eta^5\text{-Cp})]$	58		[44]
	A	$MoCo_2(\mu_3\text{-}CCO_2Me)(CO)_8(\eta^5\text{-Cp})$, $Mo_2(CO)_6(\eta^5\text{-Cp})_2$	37		[44]
$Mo_2Co(\mu_3\text{-CC(O)Ph})(CO)_7(\eta^5\text{-Cp})_2$	A	$Co_3(\mu_3\text{-CC(O)Ph})(CO)_9$, $Mo(CO)_3(AsMe_2)(\eta^5\text{-Cp})$	7	IR, ^1H	[44]
$MoWCo(\mu_3\text{-CH})(CO)_7(\eta^5\text{-Cp})_2$	A	$MoCo_2(\mu_3\text{-CCl})(CO)_8(\eta^5\text{-Cp})$, $Na[W(CO)_3(\eta^5\text{-Cp})]$	19	IR, ^1H	[65]
$WCo_2(\mu_3\text{-CH})(CO)_8(\eta^5\text{-Cp})$	A	$Co_3(\mu_3\text{-CH})(CO)_8\{AsMe_2W(CO)_3(\eta^5\text{-Cp})\}$	60	IR, ^1H	[24,25]
	A	$Co_3(\mu_3\text{-CH})(CO)_9$, $W(CO)_3(AsMe_2)(\eta^5\text{-Cp})$	56		[62]
	A	$Co_3(\mu_3\text{-CH})(CO)_9$, $Na[W(CO)_3(\eta^5\text{-Cp})]$	19		[62]
$WCo_2(\mu_3\text{-CMe})(CO)_8(\eta^5\text{-Cp})$	A	$Co_3(\mu_3\text{-CMe})(CO)_8\{AsMe_2W(CO)_3(\eta^5\text{-Cp})\}$	70	IR, ^1H	[24,25]
	A	$WCo_3(\mu_3\text{-CMe})(CO)_8(\mu\text{-}AsMe_2)(\eta^5\text{-Cp})$, CO	77		[69]
	A	$Co_3(\mu_3\text{-CMe})(CO)_9$, $Na[W(CO)_3(\eta^5\text{-Cp})]$	44		[44]
	A	$Co_3(\mu_3\text{-CMe})(CO)_9$, $Na[W(CO)_3(\eta^5\text{-Cp})]$	68		[62]
	A	$Co_3(\mu_3\text{-CMe})(CO)_9$, $W_2(CO)_6(\eta^5\text{-Cp})_2$	4		[67,68]
$WCo_2(\mu_3\text{-CMe})(CO)_8(\eta^5\text{-Cp*})$	C	$W(\equiv CMe)(CO)_2(\eta^5\text{-Cp*})$, $Co_2(CO)_8$	95	IR, ^1H, ^{13}C	[66]
$[WCo_2(\mu_3\text{-CMe})(CO)_6(\eta^5\text{-}C_2B_9H_9Me_2)][NEt_4]$	C	$[NEt_4][W(\equiv CMe)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$, $Co_2(CO)_8$	10	IR	[13]
$[WCo_2(\mu_3\text{-CMe})(CO)_8(\eta^5\text{-}C_2B_9H_9Me_2)][NEt_4]$	C	$[NEt_4][W(\equiv CMe)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$, $Co_2(CO)_8$	18	IR, ^1H, ^{13}C, ^{11}B	[13]
$WCo_2(\mu_3\text{-CMe})(CO)_8\{HB(pz)_3\}$	C	$W(\equiv CMe)(CO)_2\{HB(pz)_3\}$, $Co_2(CO)_8$	82	IR, ^1H, ^{13}C	[73,74]
$[WCo_2(\mu_3\text{-CMe})(CO)_8\{HC(pz)_3\}][BF_4]$	C	$[W(\equiv CMe)(CO)_2\{HC(pz)_3\}][BF_4]$, $Co_2(CO)_8$	43	IR, ^1H, ^{13}C	[14]
$WCo_2(\mu_3\text{-CMe})(CO)_8\{(C_6F_5)AuC(pz)_3\}$	C	$W(\equiv CMe)(CO)_2\{(C_6F_5)AuC(pz)_3\}$, $Co_2(CO)_8$	39	IR, ^1H, ^{13}C	[15]
$WCo_2(\mu_3\text{-}CCO_2Ph)(CO)_8(\eta^5\text{-Cp})$	A	$Co_3(\mu_3\text{-}CCO_2Ph)(CO)_9$, $W(CO)_3(AsMe_2)(\eta^5\text{-Cp})$	24	IR, ^1H	[44]
$WCo_2(\mu_3\text{-}CC{\equiv}C^tBu)(CO)_8(\eta^5\text{-Cp})$	C	$W(\equiv CC{\equiv}C^tBu)(CO)_2(\eta^5\text{-Cp})$, $Co_2(CO)_8$	96	IR, ^1H, ^{13}C	[29]
$WCo_2(\mu_3\text{-CPh})(CO)_8(\eta^5\text{-Cp})$	A	$Co_3(\mu_3\text{-CPh})(CO)_8\{AsMe_2W(CO)_3(\eta^5\text{-Cp})\}$	28	IR, ^1H	[24,25]
	A	$MoCo_3(\mu_3\text{-CPh})(CO)_8(\mu\text{-}AsMe_2)(\eta^5\text{-Cp})$, CO	84		[69]

Table 2 (*continued*)

Compound	Type[b]	Reactants	Yield (%)	Other data	Reference
$[WCo_2(\mu_3\text{-}CPh)(CO)_6(\eta^5\text{-}C_2B_9H_9Me_2)][NEt_4]$	C	$[NEt_4][W(\equiv CPh)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$, $Co_2(CO)_8$	39	IR, ^1H, ^{13}C, ^{11}B	[13]
$[WCo_2(\mu_3\text{-}CPh)(CO)_8(\eta^5\text{-}C_2B_9H_9Me_2)][NEt_4]$	C	$[NEt_4][W(\equiv CPh)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$, $Co_2(CO)_8$	60	IR, ^1H, ^{13}C, ^{11}B	[13]
$[WCo_2(\mu_3\text{-}CPh)(CO)_6(\eta^5\text{-}C_2B_9H_9Me_2)][PPh_4]$	C	$[PPh_4][W(\equiv CPh)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$, $Co_2(CO)_8$	20	IR	[13]
$[WCo_2(\mu_3\text{-}CPh)(CO)_8(\eta^5\text{-}C_2B_9H_9Me_2)][PPh_4]$	C	$[PPh_4][W(\equiv CPh)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$, $Co_2(CO)_8$	40	XR, IR	[13]
$WCo_2(\mu_3\text{-}CTol)(CO)_8(\eta^5\text{-}Cp)$	A	$Co_3(\mu_3\text{-}CTol)(CO)_8\{AsMe_2W(CO)_3(\eta^5\text{-}Cp)\}$	26	IR, ^1H	[24,25]
	C	$W(\equiv CTol)(CO)_2(\eta^5\text{-}Cp)$, $Co_2(CO)_8$	95	XR, IR, ^1H, ^{13}C	[22,23]
$WCo_2(\mu_3\text{-}CTol)(CO)_8(\eta^5\text{-}Cp^*)$	C	$W(\equiv CTol)(CO)_2(\eta^5\text{-}Cp^*)$, $Co_2(CO)_8$	76	IR, ^1H, ^{13}C	[75]
$WCo_2(\mu_3\text{-}CTol)(CO)_8(\eta^5\text{-}C_5H_4SiMe_3)$	C	$W(\equiv CTol)(CO)_2(\eta^5\text{-}C_5H_4SiMe_3)$, $Co_2(CO)_8$	80	^{13}C	[22]
$WCo_2(\mu_3\text{-}CTol)(CO)_7(PMe_3)(\eta^5\text{-}Cp)$	C	$W\{\eta^2\text{-}C(Tol)C(O)\}(CO)(PMe_3)(\eta^5\text{-}Cp)$, $Co_2(CO)_8$	85	IR, ^1H, ^{13}C, ^{31}P	[28]
$[WCo_2(\mu_3\text{-}CTol)(CO)_6(\eta^5\text{-}C_2B_9H_9Me_2)][NEt_4]$	C	$[NEt_4][W(\equiv CTol)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$, $Co_2(CO)_8$	17	IR, ^1H, ^{13}C, ^{11}B	[13]
$[WCo_2(\mu_3\text{-}CTol)(CO)_8(\eta^5\text{-}C_2B_9H_9Me_2)][NEt_4]$	C	$[NEt_4][W(\equiv CTol)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$, $Co_2(CO)_8$	60	IR	[13]
$WCo_2(\mu_3\text{-}CTol)(CO)_9\{H_2B(pz)_2\}$	C	$W(\equiv CTol)(CO)_3\{H_2B(pz)_2\}$, $Co_2(CO)_8$	85	IR, ^1H, ^{13}C	[76]
$WCo_2(\mu_3\text{-}CTol)(CO)_8\{HB(pz)_3\}$	C	$W(\equiv CTol)(CO)_2\{HB(pz)_3\}$, $Co_2(CO)_8$	95	IR, ^1H, ^{13}C	[73,74]
$WCo_2(\mu_3\text{-}CTol)(CO)_8\{B(pz)_4\}$	C	$W(\equiv CTol)(CO)_2\{B(pz)_4\}$, $Co_2(CO)_8$	92	IR, ^1H, ^{13}C	[73,74]
$[WCo_2(\mu_3\text{-}CTol)(CO)_8\{HC(pz)_3\}][BF_4]$	C	$[W(\equiv CTol)(CO)_2\{HC(pz)_3\}][BF_4]$, $Co_2(CO)_8$	37	IR, ^1H, ^{13}C	[14]
$WCo_2(\mu_3\text{-}CTol)(CO)_8\{(C_6F_5)AuC(pz)_3\}$	C	$W(\equiv CTol)(CO)_2\{(C_6F_5)AuC(pz)_3\}$, $Co_2(CO)_8$	32	IR, ^1H, ^{13}C	[15]
$WCo_2(\mu_3\text{-}CTol)(CO)_8(dmpe)Cl$	C	$W(\equiv CTol)(CO)_2(dmpe)Cl$, $Co_2(CO)_8$	71	IR, ^1H, ^{13}C, ^{31}P	[77]
$WCo_2(\mu_3\text{-}CTol)(CO)_8(dmpe)Br$	C	$W(\equiv CTol)(CO)_2(dmpe)Br$, $Co_2(CO)_8$	60	XR, IR, ^1H, ^{31}P	[77]
$[WCo_2(\mu_3\text{-}CC_6H_4Me\text{-}2)(CO)_6(\eta^5\text{-}C_2B_9H_9Me_2)][NEt_4]$	C	$[NEt_4][W(\equiv CC_6H_4Me\text{-}2)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$, $Co_2(CO)_8$	40	IR, ^1H, ^{13}C, ^{11}B	[13]
$[WCo_2(\mu_3\text{-}CC_6H_4Me\text{-}2)(CO)_8(\eta^5\text{-}C_2B_9H_9Me_2)][NEt_4]$	C	$[NEt_4][W(\equiv CC_6H_4Me\text{-}2)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$, $Co_2(CO)_8$	60	IR, ^1H, ^{13}C, ^{11}B	[13]
$WCo_2(\mu_3\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_8(\eta^5\text{-}Cp)$	C	$W(\equiv CC_6H_3Me_2\text{-}2,6)(CO)_2(\eta^5\text{-}Cp)$, $Co_2(CO)_8$	87	IR, ^1H, ^{13}C	[71]
$WCo_2(\mu_3\text{-}CSiMe_3)(CO)_8(\eta^5\text{-}Cp)$	A	$Co_3(\mu_3\text{-}CSiMe_3)(CO)_9$, $Na[W(CO)_3(\eta^5\text{-}Cp)]$	47	IR, ^1H	[62]
	R	$WCo_2(\mu_3\text{-}CH)(CO)_8(\eta^5\text{-}Cp)$, $HSiEt_3$	38		[62]
$WCo_2(\mu_3\text{-}CF)(CO)_8(\eta^5\text{-}Cp)$	A	$Co_3(\mu_3\text{-}CF)(CO)_8\{AsMe_2W(CO)_3(\eta^5\text{-}Cp)\}$	46	IR, ^1H	[24]
$WCo_2(\mu_3\text{-}CCl)(CO)_8(\eta^5\text{-}Cp)$	A	$Co_3(\mu_3\text{-}CCl)(CO)_9$, $[PPN][W(CO)_3(\eta^5\text{-}Cp)]$	12	IR, ^1H	[65]
$CrWCo_2\{\mu_3\text{-}\sigma, \sigma', \sigma'':\eta^6\text{-}CC_6H_4(OMe)\text{-}2\}(CO)_{11}(\eta^5\text{-}Cp)$	C	$CrW\{\mu\text{-}\sigma\text{:}\eta^6\text{-}CC_6H_4(OMe)\text{-}2\}(CO)_5(\eta^5\text{-}Cp)$, $Co_2(CO)_8$	78	IR, ^1H, ^{13}C	[16]
$WCo_2(\mu_3\text{-}CPh)(CO)_8[Co\{P(O)(O\text{-}i\text{-}C_3H_7)_2\}_3(\eta^5\text{-}Cp)]$	C	$W(\equiv CPh)(CO)_2[Co\{P(O)(O\text{-}i\text{-}C_3H_7)_2\}_3(\eta^5\text{-}Cp)]$, $Co_2(CO)_8$	76	IR, ^1H, ^{13}C	[17]
$WCo_2(\mu_3\text{-}CTol)(CO)_8[Co\{P(O)(OCH_3)_2\}_3(\eta^5\text{-}Cp)]$	C	$W(\equiv CTol)(CO)_2[Co\{P(O)(OCH_3)_2\}_3(\eta^5\text{-}Cp)]$, $Co_2(CO)_8$	60	IR, ^1H, ^{13}C	[17]
$WCo_2(\mu_3\text{-}CTol)(CO)_8[Co\{P(O)(O\text{-}i\text{-}C_3H_7)_2\}_3(\eta^5\text{-}Cp)]$	C	$W(\equiv CTol)(CO)_2[Co\{P(O)(O\text{-}i\text{-}C_3H_7)_2\}_3(\eta^5\text{-}Cp)]$, $Co_2(CO)_8$	74	IR, ^1H, ^{13}C	[17]
$WCoRh(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_2(\eta^5\text{-}Cp)(\eta^5\text{-}Cp^*)_2$	C	$W(\equiv CMe)(CO)_2(\eta^5\text{-}Cp)$, $CoRh(\mu\text{-}CO)_2(\eta^5\text{-}Cp^*)_2$	38	IR, ^1H, ^{13}C	[26]
$WCoRh(\mu_3\text{-}CC{\equiv}C^tBu)(\mu\text{-}CO)(CO)_2(\eta^5\text{-}Cp)(\eta^5\text{-}Cp^*)(\eta^5\text{-}C_9H_7)$	C	$WRh(\mu\text{-}CC{\equiv}{}^tBu)(CO)_3(\eta^5\text{-}Cp)(\eta^5\text{-}C_9H_7)$, $Co(C_2H_4)_2(\eta^5\text{-}Cp^*)$	49	IR, ^1H, ^{13}C	[32]
$WRh_2(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_2(\eta^5\text{-}Cp)(\eta^5\text{-}Cp^*)_2$	C	$W(\equiv CMe)(CO)_2(\eta^5\text{-}Cp)$, $Rh_2(\mu\text{-}CO)_2(\eta^5\text{-}Cp^*)_2$	35	XR, IR, ^1H, ^{13}C	[26]
$WRh_2(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_2(\eta^5\text{-}Cp^*)_3$	C	$W(\equiv CMe)(CO)_2(\eta^5\text{-}Cp^*)$, $Rh_2(\mu\text{-}CO)_2(\eta^5\text{-}Cp^*)_2$	51	IR, ^1H, ^{13}C	[66]
$WRh_2(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_2(\eta^5\text{-}C_9H_7)_2\{HB(pz)_3\}$	C	$W(\equiv CMe)(CO)_2\{HB(pz)_3\}$, $Rh(CO)_2(\eta^5\text{-}C_9H_7)$	73	IR, ^1H, ^{13}C	[73,74]
$WRh_2(\mu_3\text{-}CC{\equiv}C^tBu)(\mu\text{-}CO)(CO)_2(\eta^5\text{-}Cp)(\eta^5\text{-}C_9H_7)_2$	C	$W(\equiv CC{\equiv}C^tBu)(CO)_2(\eta^5\text{-}Cp)$, $Rh(CO)_2(\eta^5\text{-}C_9H_7)$	86	IR, ^1H, ^{13}C	[32]
$WRh_2(\mu_3\text{-}CTol)(\mu\text{-}CO)(CO)_2(acac)_2(\eta^5\text{-}Cp)$	C	$WRh(CO)_2(\mu\text{-}CTol)(acac)(CO)_3(\eta^5\text{-}Cp)$, $Rh(acac)(C_2H_4)_2$	68	XR, IR, ^1H, ^{13}C	[23]
$WRh_2(\mu_3\text{-}CTol)(\mu\text{-}CO)(CO)_2(\eta^5\text{-}Cp)(\eta^5\text{-}Cp^*)_2$	C	$W(\equiv CTol)(CO)_2(\eta^5\text{-}Cp)$, $Rh_2(\mu\text{-}CO)_2(\eta^5\text{-}Cp^*)_2$	55	IR, ^1H, ^{13}C	[22,78]
$WRh_2(\mu_3\text{-}CTol)(\mu\text{-}CO)(CO)_2(\eta^5\text{-}Cp)(\eta^5\text{-}C_9H_7)_2$	C	$WRh(CO)_2(\mu\text{-}CTol)(CO)_3(\eta^5\text{-}Cp)(\eta^5\text{-}C_9H_7)$, $Rh(CO)_2(\eta^5\text{-}C_9H_7)$	94	IR, ^1H, ^{13}C	[78]
$WRh_2(\mu_3\text{-}CTol)(\mu\text{-}CO)(CO)_2(\eta^5\text{-}Cp^*)(\eta^5\text{-}C_9H_7)_2$	C	$W(\equiv CTol)(CO)_2(\eta^5\text{-}Cp^*)$, $Rh(CO)_2(\eta^5\text{-}C_9H_7)$	26	IR, ^1H, ^{13}C	[19]
$WRh_2(\mu_3\text{-}CTol)(\mu\text{-}CO)(CO)_3(\eta^5\text{-}C_9H_7)_2\{H_2B(pz)_2\}$	C	$W(\equiv CTol)(CO)_3\{H_2B(pz)_2\}$, $Rh(CO)_2(\eta^5\text{-}C_9H_7)$	66	IR, ^1H, ^{13}C	[76]

$WRh_2(\mu_3\text{-CTol})(\mu\text{-CO})(CO)_2(\eta^5\text{-}C_9H_7)_2\{HB(pz)_3\}$	C	$W(\equiv CTol)(CO)_2\{HB(pz)_3\}$, $Rh(CO)_2(\eta^5\text{-}C_9H_7)$	90	XR, IR, ^1H, ^{13}C	[73,74]
$WRh_2(\mu_3\text{-CSMe})(\mu\text{-CO})(CO)_2(\eta^5\text{-}C_9H_7)_2\{HB(pz)_3\}$	C	$W(\equiv CSMe)(CO)_2\{HB(pz)_3\}$, $Rh(CO)_2(\eta^5\text{-}C_9H_7)$	91	IR, ^1H, ^{13}C	[54]
$WRhIr(\mu_3\text{-CTol})(\mu\text{-CO})(CO)_2(\eta^5\text{-Cp})(\eta^5\text{-}C_9H_7)_2$	C	$WRh(\mu\text{-CTol})(CO)_3(\eta^5\text{-Cp})(\eta^5\text{-}C_9H_7)$, $Ir(CO)_2(\eta^5\text{-}C_9H_7)$	10	IR, ^1H, ^{13}C	[19]
$W_2Co(\mu_3\text{-CH})(CO)_7(\eta^5\text{-Cp})_2$	A	$Co_3(\mu_3\text{-CBr})(CO)_9$, $W_2(CO)_6(\eta^5\text{-Cp})_2$	8	IR, ^1H	[62]
$W_2Co(\mu_3\text{-CMe})(CO)_7(\eta^5\text{-Cp})_2$	A	$Co_3(\mu_3\text{-CMe})(CO)_9$, $Na[W(CO)_3(\eta^5\text{-Cp})]$	41	IR, ^1H	[44]
B. Other trinuclear clusters					
$CrCo_2\{\mu_3\text{-}\eta^4\text{-}(CC(OEt)\text{=}CPhC(O)\}(\mu\text{-CO})_2(CO)_7$	D	$Cr\text{=}C(OEt)(C\text{=}CPh)(CO)_5$, $Co_2(CO)_8$	20	XR, IR, ^1H, ^{13}C	[31]
$CrRh_2(\mu\text{-CO})_2(CO)_5(\eta^5\text{-Cp*})_2$	D	$Rh_2(\mu\text{-CO})_2(\eta^5\text{-Cp*})_2$, $Cr(thf)(CO)_5$	94	IR, ^1H, ^{13}C	[35]
$MoCoRh(\mu\text{-CO})_2(CO)_5(\eta^5\text{-Cp*})_2$	D	$CoRh(\mu\text{-CO})_2(\eta^5\text{-Cp*})_2$, $Mo(thf)(CO)_5$	90	XR, IR, ^1H, ^{13}C	[33,34]
$MoRh_2(\mu\text{-CO})_2(CO)_5(\eta^5\text{-Cp*})_2$	D	$Rh_2(\mu\text{-CO})_2(\eta^5\text{-Cp*})_2$, $Mo(CH_3CN)(CO)_5$	96	XR, IR, ^1H, ^{13}C	[33–35]
$MoRh_2(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(\mu\text{-CO})_2(CO)(\eta^5\text{-Cp})(\eta^5\text{-}C_9H_7)_2$	C	$Mo(\equiv CC_6H_3Me_2\text{-}2,6)(CO)_2(\eta^5\text{-Cp})$, $Rh(CO)_2(\eta^5\text{-}C_9H_7)$	44	IR, ^1H, ^{13}C	[79]
$Mo_2Rh(CO)_5(\eta^5\text{-Cp})_3$	D	$Mo_2(CO)_6(\eta^5\text{-Cp})_2$, $Rh(C_2H_4)_2(\eta^5\text{-Cp})$	28	XR, IR, ^1H, ^{13}C	[36,37]
$Mo_2Rh\{\mu_3\text{-}\eta^2\text{-}C_2(C\equiv C^tBu)_2\}(CO)_4(\eta^5\text{-Cp})_2(\eta^5\text{-}C_9H_7)$	C	$Mo(\equiv CC\equiv C^tBu)(CO)_2(\eta^5\text{-Cp})$, $Rh(CO)_2(\eta^5\text{-}C_9H_7)$	14	IR, ^1H, ^{13}C	[32]
$MoWRh\{\mu_3\text{-}\eta^2\text{-}C_2(C\equiv C^tBu)_2\}(CO)_4(\eta^5\text{-Cp})_2(\eta^5\text{-}C_9H_7)$	C	$W(\equiv CC\equiv C^tBu)(CO)_2(\eta^5\text{-Cp})$, $MoRh(\mu\text{-}CC\equiv C^tBu)(CO)_3(\eta^5\text{-Cp})(\eta^5\text{-}C_9H_7)$	15	IR, ^1H, ^{13}C	[32]
$WCo_2\{\mu_3\text{-}\eta^4\text{-}(CC(OEt)\text{=}CPhC(O)\}(\mu\text{-CO})_2(CO)_7$	D	$W\text{=}C(OEt)(C\equiv CPh)(CO)_5$, $Co_2(CO)_8$	25	IR, ^1H, ^{13}C	[31]
$WCo_2(\mu_3\text{-}\eta^3\text{-PhCCHCTol})(\mu\text{-CO})(CO)_5(\eta^5\text{-Cp})$	C	$W(\equiv CTol)(CO)_2(\eta^5\text{-Cp})$, $Co_2(\mu_2\text{-}\eta_2\text{-}PhC_2H)(CO)_6$	72	XR, IR, ^1H, ^{13}C	[80]
$WCo_2(\mu_2\text{-}\eta^2\text{-}C_2Et_2)(\mu_2\text{-}\eta^4\text{-}C_4Et_4)(CO)_8$	D	$W(CO)(C_2Et_2)_3$, $Co_2(C)_8$	68	XR, IR, ^1H, ^{13}C	[40,41]
$WCo_2(\mu_2\text{-}\eta^2\text{-}C_2Pr_2)(\mu_2\text{-}\eta^4\text{-}C_4Pr_4)(CO)_8$	D	$W(CO)(C_2Pr_2)_3$, $Co_2(CO)_8$	NA	IR, ^1H, ^{13}C	[41]
$WRh_2(\mu\text{-CO})_2(CO)_5(\eta^5\text{-Cp*})_2$	D	$Rh_2(\mu\text{-CO})_2(\eta^5\text{-Cp*})_2$, $W(thf)(CO)_5$	90	IR, ^1H, ^{13}C	[35]
$WRh_2(\mu_3\text{-C(O)CMe})(\mu\text{-CO})(\mu_3\text{-CO})(CO)_2(\eta^5\text{-Cp})(\eta^5\text{-Cp*})_2$	C	$W(\equiv CMe)(CO)_2(\eta^5\text{-Cp})$, $Rh_2(\mu\text{-CO})_2(\eta^5\text{-Cp*})_2$	41	IR, ^1H, ^{13}C	[26]
$W_2Co(OCH_2{}^tBu)_6(\eta^5\text{-Cp})$	D	$W_2(OCH_2{}^tBu)_6(py)_2$, $Co(C_2H_4)_2(\eta^5\text{-Cp})$	49	XR, ^1H, ^{13}C	[39]
$W_2Rh(CO)_5(\eta^5\text{-Cp})_3$	D	$W_2(CO)_6(\eta^5\text{-Cp})_2$, $Rh(C_2H_4)_2(\eta^5\text{-Cp})$	27	XR, IR, ^1H, ^{13}C	[36,37]
$W_2Ir(\mu_3\text{-}\eta^2\text{-}C_2Tol_2)Cl(CO)_4(\eta^5\text{-Cp})_2$	C	$W(\equiv CTol)(CO)_2(\eta^5\text{-Cp})$, $Ir_2Cl_2(CO)_2(\eta^2\text{-}C_8H_{14})_4$	15	XR, IR, ^1H, ^{13}C	[20]
$W_2Ir(\mu\text{-CTol})(\mu_3\text{-CTol})Cl(CO)_4(\eta^5\text{-Cp})_2$[c]	C	$W(\equiv CTol)(CO)_2(\eta^5\text{-Cp})$, $Ir_2Cl_2(CO)_2(\eta^2\text{-}C_8H_{14})_4$	36	XR, IR, ^1H, ^{13}C	[20]
C. Tetranuclear clusters					
$MoCo_3(\mu\text{-CO})_3(CO)_8(\eta^5\text{-Cp})$	B	$MoCo(CO)_7(\eta^5\text{-Cp})$	77	XR, IR, ^1H	[9]
	B	$MoCo(CO)_7(\eta^5\text{-Cp})$, $Co_2(CO)_8$	19		[9]
	A	$Co_4(CO)_{12}$, $Mo(CO)_3H(\eta^5\text{-Cp})$, $Me_3NO{\cdot}2H_2O$	72		[5]
	A	$Co_4(CO)_9(\eta^6\text{-}Me_3C_6H_3)$, $Mo_2(CO)_6(\eta^5\text{-Cp})_2$	16	XR, IR, ^1H, ^{13}C	[6]
	B	$Co_2(CO)_8$, $Mo_2(CO)_6(\eta^5\text{-Cp})_2$	25		[6]
$MoCo_3(\mu\text{-CO})_3(CO)_8(\eta^5\text{-MeCp})$	B	$MoCo(CO)_7(\eta^5\text{-MeCp})$, $Co_2(CO)_8$	NA	IR, ^1H	[8]
$MoCo_3(\mu\text{-CO})_3(CO)_8(\eta^5\text{-}C_5H_4SiMe_3)$	B	$Mo_2(CO)_6(\eta^5\text{-}C_5H_4SiMe_3)_2$, $Co_2(CO)_8$	18	IR, ^1H	[81]
$MoCo_3(\mu\text{-CO})_3(CO)_8(\eta^5\text{-}C_5H_4CO_2Me)$	B	$Mo_2(CO)_6(\eta^5\text{-}C_5H_4CO_2Me)_2$, $Co_2(CO)_8$	27	IR, ^1H	[81]
$MoCo_3(\mu\text{-CO})_3(CO)_8(\eta^5\text{-}C_5H_4CO_2Et)$	B	$Mo_2(CO)_6(\eta^5\text{-}C_5H_4CO_2Et)_2$, $Co_2(CO)_8$	20	IR, ^1H	[81]
$MoCo_3(\mu_3\text{-CMe})(\mu\text{-CO})_2(CO)_5(\eta^5\text{-Cp})_2$	R	$MoCo_2(\mu_3\text{-CMe})(CO)_8(\eta^5\text{-Cp})$, $Mo_2(CO)_6(\eta^5\text{-Cp})_2$	5	XR, IR, ^1H	[44]
	R	$MoCo_2(\mu_3\text{-CMe})(CO)_8(\eta^5\text{-Cp})$, $(C_5H_6)_2$	12		[44]
$MoCo_3(\mu_3\text{-}CCO_2Me)(\mu\text{-CO})_2(CO)_5(\eta^5\text{-Cp})_2$	R	$MoCo_2(\mu_3\text{-}CCO_2Me)(CO)_8(\eta^5\text{-Cp})$, $Mo_2(CO)_6(\eta^5\text{-Cp})_2$	1	IR, ^1H	[44]
$MoRh_3(\mu_3\text{-CO})(CO)_3(PPh_3)_3(\eta^5\text{-Cp})$	B	$MoRh(\mu\text{-CO})_2(CO)(PPh_3)_2(\eta^5\text{-Cp})$, $Fe_2(CO)_9$	27	XR, IR, ^1H, ^{13}C, ^{31}P	[82]
$MoIr_3(\mu\text{-CO})_3(CO)_8(\eta^5\text{-Cp})$	B	$IrCl(CO)_2NH_2Tol)$, $(\eta^5\text{-Cp})Mo(CO)_3H$	60	XR, IR, ^1H	[5]
$Mo_2Co_2(\mu\text{-CO})_3(CO)_7(\eta^5\text{-MeCp})_2$	B	$MoCo(CO)_7(\eta^5\text{-MeCp})$, $Co_2(CO)_8$	NA	IR, ^1H	[8]
$Mo_2Co_2(\mu\text{-CO})_3(CO)_7(\eta^5\text{-Cp})_2$	A	$Co_4(CO)_9(\eta^6\text{-}Me_3C_6H_3)$, $Mo_2(CO)_6(\eta^5\text{-Cp})_2$	11	XR, IR	[6]
	B	$Co_2(CO)_8$, $Mo_2(CO)_6(\eta^5\text{-Cp})_2$	1		[6]
$Mo_2Co_2(\mu_4\text{-}\eta^2\text{-}C_2Me_2)(\mu\text{-CO})_4(CO)_4(\eta^5\text{-Cp})_2$	R	$MoCo_2(\mu_3\text{-CMe})(CO)_8(\eta^5\text{-Cp})$, $Na_2Ru(CO)_4$	7	XR, IR, ^1H	[50]
$Mo_2Co_2(\mu\text{-CO})_3(\mu_4\text{-CO})(\eta^5\text{-Cp})_2(\eta^5\text{-Cp*})_2$	D	$Co(C_2H_4)_2(\eta^5\text{-Cp*})$, $Mo_2(CO)_6(\eta^5\text{-Cp})_2$	20	XR, IR, ^1H, ^{13}C	[38]

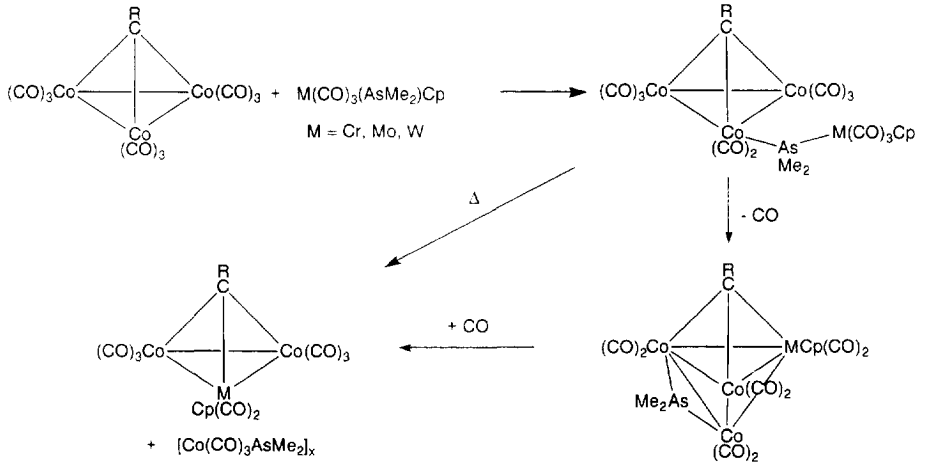
Table 2 (*continued*)

Compound	Type[b]	Reactants	Yield (%)	Other data	Reference
$Mo_2Ir_2(CO)_{10}(\eta^5\text{-Cp})$	B	$IrCl(CO)_2(NH_2Tol)$, $Na[Mo(CO)_3(\eta^5\text{-Cp})]$	79	IR, ^1H	[10]
$MoW_2Co(CO)_9(\eta^5\text{-MeCp})_3$	B	$MoCo(CO)_7(\eta^5\text{-MeCp})$, $W_2(CO)_4(\eta^5\text{-MeCp})_2$	12	IR, ^1H, ^{13}C	[8]
$WCo_3(\mu\text{-CO})_3(CO)_8(\eta^5\text{-Cp})$	B	$WCo(CO)_7(\eta^5\text{-Cp})$, $Co_2(CO)_8$	22	IR, ^1H	[9]
	A	$Co_4(CO)_{12}$, $W(CO)_3H(\eta^5\text{-Cp})$, $Me_3NO{\cdot}2H_2O$	80		[5]
	R	$Co_3(\mu_3\text{-CMe})(CO)_9$, $Na[W(CO)_3(\eta^5\text{-Cp})]$	5	XR, IR, ^1H	[62]
$WCo_3(\mu\text{-CO})_3(CO)_8(\eta^5\text{-MeCp})$	B	$WCo(CO)_7(\eta^5\text{-MeCp})$, $Co_2(CO)_8$	19	IR, ^1H	[8]
	B	$W_2(CO)_4(\eta^5\text{-MeCp})_2$, $Co_2(CO)_8$	3		[8]
	B	$MoCo(CO)_7(\eta^5\text{-Cp})$	NA		[8]
$WCo_3(\mu\text{-CO})_3(CO)_8(\eta^5\text{-}C_5H_4C(O)Me)$	B	$W_2(CO)_6(\eta^5\text{-}C_5H_4C(O)Me)_2$, $Co_2(CO)_8$	24	IR, ^1H	[81]
$WCo_3(\mu\text{-CO})_3(CO)_8(\eta^5\text{-}C_5H_4CO_2Me)$	B	$W_2(CO)_6(\eta^5\text{-}C_5H_4CO_2Me)_2$, $Co_2(CO)_8$	29	XR, IR, ^1H	[81]
$WCo_3(\mu\text{-CO})_3(CO)_8(\eta^5\text{-}C_5H_4CO_2Et)$	B	$W_2(CO)_6(\eta^5\text{-}C_5H_4CO_2Et)_2$, $Co_2(CO)_8$	32	IR, ^1H	[81]
	A	$W_2(CO)_6(\eta^5\text{-}C_5H_4CO_2Et)_2$, $Co_4(CO)_{12}$	14		[81]
$WRh_3(\mu_3\text{-CO})(CO)_3(PPh_3)_3(\eta^5\text{-Cp})$	B	$WRh(\mu\text{-CO})_2(CO)(PPh_3)_2(\eta^5\text{-Cp})$, $Fe_2(CO)_9$	12	IR, ^1H, ^{13}C, ^{31}P	[82]
$WIr_3(CO)_{11}(\eta^5\text{-Cp})$	B	$IrCl(CO)_2(NH_2Tol)$, $W(CO)_3H(\eta^5\text{-Cp})$	71	XR, IR, ^1H, ^{13}C	[5,11,83]
$W_2Co_2(\mu\text{-CO})_3(CO)_7(\eta^5\text{-MeCp})_2$	B	$WCo(CO)_7(\eta^5\text{-MeCp})$, $W_2(CO)_4(\eta^5\text{-MeCp})_2$	5	IR, ^1H	[8]
	B	$MoCo(CO)_7(\eta^5\text{-MeCp})$, $W_2(CO)_4(\eta^5\text{-MeCp})_2$	5		[8]
	B	$WCo(CO)_7(\eta^5\text{-MeCp})$, $Co_2(CO)_8$	NA		[8]
	B	$W_2(CO)_4(\eta^5\text{-MeCp})_2$, $Co_2(CO)_8$	17		[8]
$W_2Co_2(\mu_4\text{-}\eta^2\text{-}C_2Me_2)(\mu\text{-CO})_4(CO)_4(\eta^5\text{-Cp})_2$	R	$WCo_2(\mu_3\text{-CMe})(CO)_8(\eta^5\text{-Cp})$, $Na_2Ru(CO)_4$	4	IR, ^1H	[50]
$W_2Ir_2(CO)_{10}(\eta^5\text{-Cp})_2$	B	$IrCl(CO)_2(NH_2Tol)$, $Na[W(CO)_3(\eta^5\text{-Cp})]$	85	XR, IR, ^1H	[11,84]
$W_2Ir_2(\mu_4\text{-}\eta^2\text{-}C_2Tol_2)(\mu\text{-CO})_2(CO)_6(\eta^5\text{-Cp})_2$	C	$W(\equiv CTol)(CO)_2(\eta^5\text{-Cp})$, $Ir_2Cl_2(CO)_2(\eta^2\text{-}C_8H_{14})_4$	4	IR, ^1H, ^{13}C	[20]
$W_3Co(CO)_9(\eta^5\text{-MeCp})_3$	B	$WCo(CO)_7(\eta^5\text{-MeCp})$, $W_2(CO)_4(\eta^5\text{-MeCp})_2$	23	XR, IR, ^1H, ^{13}C	[8]
	B	$MoCo(CO)_7(\eta^5\text{-MeCp})$, $W_2(CO)_4(\eta^5\text{-MeCp})_2$	6		[8]
D. Higher nuclearity clusters					
$Mo_4Co_3(\mu_3\text{-OH})(\mu_3\text{-CPh})_2(\mu_6\text{-C})(\mu\text{-CO})_3(CO)_3(\eta^5\text{-Cp})_4$	B	$Co_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C_2Ph_2)$, $Mo_2(CO)_6(\eta^5\text{-Cp})_2$	NA	XR, ^1H	[85]

[a] The following abbreviations are used throughout Table 2: acac ≡ acetylacetonate, bipy ≡ bipyridyl, Cp ≡ C_5H_5, Cp* ≡ C_5Me_5, dmpe ≡ $Me_2PCH_2CH_2PMe_2$, MeCp ≡ C_5H_4Me, NA ≡ not available, PPN ≡ $Ph_2PNPPh_2^+$, py ≡ pyridine, pz ≡ pyrazolyl, IR ≡ infrared spectroscopy, XR ≡ X-ray crystallography. The following abbreviations refer to the various NMR spectroscopies: ^1H, ^{13}C, ^{19}F, ^{11}B, ^{31}P.

[b] Entries in this column refer to general synthetic methods A–D as defined in Section 2. The entry of an R denotes the reaction of a mixed-metal cluster leading to ligand replacement or formation of higher nuclearity products and is discussed in Section 3.4.

[c] Isomeric mixture. See text.



Scheme II.

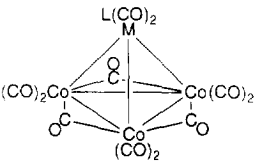
substituted tricobalt clusters with pendant $M(CO)_3(\eta^5\text{-Cp})$ moieties, while further loss of CO provides tetranuclear products with μ-$AsMe_2$ moieties (see Scheme II). Thermolysis of the former or introduction of CO to the latter promotes loss of a Co–As fragment in the form of oligomeric $[Co(CO)_3AsMe_2]_x$, and the mixed-metal cluster $MCo_2(\mu_3\text{-CR})(CO)_8(\eta^5\text{-Cp})$ is formed. The reactions of $Co_3(\mu_3\text{-CR})(CO)_9$ with metal exchange reagents can lead to replacement of one, two, or all three $Co(CO)_3$ vertices with $M(CO)_2(\eta^5\text{-Cp})$ fragments. This topic has been reviewed [1g].

An alternative route to $MCo_2(\mu_3\text{-CR})(CO)_8(\eta^5\text{-Cp})$ (M ≡ Cr, Mo, W; R ≡ Me, Ph, H) clusters involved electron transfer catalysis [4]. The addition of a catalytic amount of benzophenone ketyl to a solution of $Co_3(\mu_3\text{-CR})(CO)_9$ and $[M(CO)_3(\eta^5\text{-Cp})^-]$ generated the radical cluster anion, and subsequent attack of the metal carbonylate provided the mixed-metal clusters with the loss of the good leaving group $[Co(CO)_4^-]$.

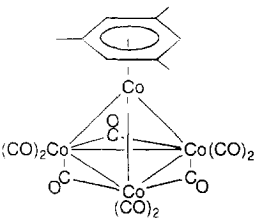
Metal exchange can also be effective in tetranuclear cluster synthesis. The reaction of $Co_4(CO)_{12}$ with $M(CO)_3H(\eta^5\text{-Cp})$ led to $MCo_3(\mu\text{-CO})_3(CO)_8(\eta^5\text{-Cp})$ (M ≡ Mo, **1**; M ≡ W, **2**) in high yield [5]. The tetracobalt arene cluster, $Co_4(CO)_9(\eta^6\text{-}Me_3C_6H_3)$, **3**, reacted with $Mo_2(CO)_6(\eta^5\text{-Cp})_2$ to give the heterometallic clusters **1** and $Mo_2Co_2(\mu\text{-CO})_3(CO)_7(\eta^5\text{-Cp})_2$, **4** [6].

2.2. *Type B: reactions between dinuclear species*

The reactions between homo- and heterometallic dinuclear species can lead to tetranuclear mixed-metal clusters. In some cases these appear formally as condensations of unsaturated dimers. That is, an $M_2M'_2$ cluster can be viewed as the product of M≡M and M′≡M′ units, or similarly, as the dimer of two M≡M′ units. Triply



	M	L
1	Mo	Cp
2	W	Cp
6	W	MeCp
7	Mo	MeCp



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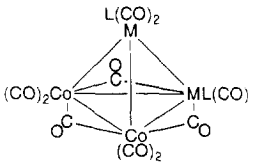
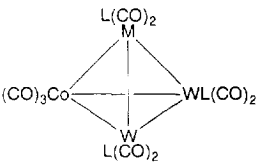


	M	L
4	Mo	Cp
5	W	MeCp
10	Mo	MeCp

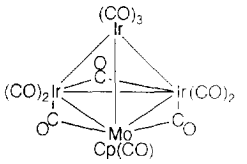


	M	L
8	W	MeCp
9	Mo	MeCp

bonded precursors have been employed explicitly as synthons [7], however singly bonded M–M or M–M′ dinuclear compounds are more common starting materials. These may provide triply bonded species in situ which then lead to the observed tetranuclear clusters.

The reaction between $W_2(CO)_4(\eta^5\text{-MeCp})_2$ and $Co_2(CO)_8$ produced $W_2Co_2(\mu\text{-CO})_3(CO)_7(\eta^5\text{-MeCp})_2$, **5**, as well as $WCo_3(\mu\text{-CO})_3(CO)_8(\eta^5\text{-MeCp})$, **6** [8]. Furthermore, the reaction of the saturated dimolybdenum compound, $Mo_2(CO)_6(\eta^5\text{-Cp})_2$, with $Co_2(CO)_8$ resulted in the formation of **1** and **4** [6]. Compound **1** and the η^5-MeCp analog, $MoCo_3(\mu\text{-CO})_3(CO)_8(\eta^5\text{-MeCp})$, **7**, have also been prepared by thermolysis of the heterodinuclear compounds, $MoCo(CO)_7(\eta^5\text{-}C_5H_4R)$ ($R \equiv H$, Me) [8,9]. The heterometallic dinuclear reagent $WCo(CO)_7(\eta^5\text{-MeCp})$ yielded W_xCo_{4-x} ($x \equiv 1$, **6**; $x \equiv 2$, **5**; $x \equiv 3$, **8**) tetranuclear clusters when reacted with $Co_2(CO)_8$ or $W_2(CO)_4(\eta^5\text{-MeCp})_2$ [8]. The reaction of $MoCo(CO)_7(\eta^5\text{-MeCp})$ with $W_2(CO)_4(\eta^5\text{-MeCp})_2$ formed the heterotrimetallic tetranuclear cluster, $MoW_2Co(CO)_9(\eta^5\text{-MeCp})_3$, **9**, as one product, while reaction with $Co_2(CO)_8$ led to **7** and $Mo_2Co_2(\mu\text{-CO})_3(CO)_7(\eta^5\text{-MeCp})_2$, **10** [8].

The reactions of $IrCl(CO)_2(NH_2Tol)$ with $Na[M(CO)_3(\eta^5\text{-Cp})]$ or $M(CO)_3H(\eta^5\text{-Cp})$ led to tetranuclear mixed-metal clusters, $MIr_3(CO)_{11}(\eta^5\text{-Cp})$ ($M \equiv Mo$, **11**; $M \equiv W$, **12**) and $M_2Ir_2(CO)_{10}(\eta^5\text{-Cp})_2$ ($M \equiv Mo$, **13**; $M \equiv W$, **14**) under a range of reaction conditions [5,10,11]. Although mononuclear precursors were employed, the initial reaction products are very likely dinuclear Ir–M or Ir–Ir species that dimerize to form the observed products.



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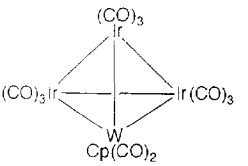

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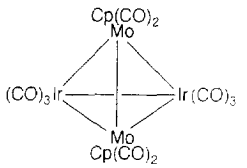

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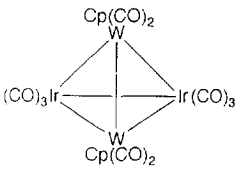

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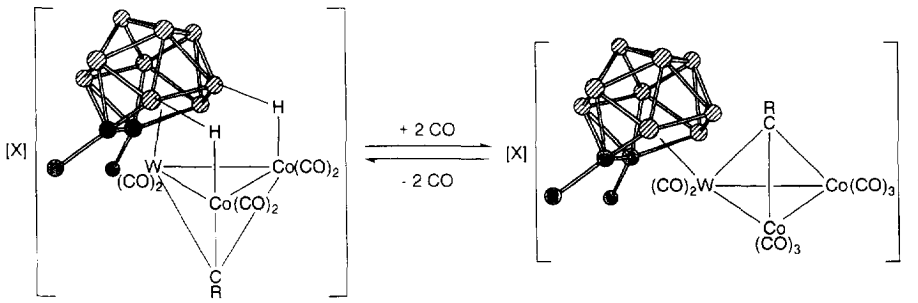
2.3. *Type C: reactions utilizing mononuclear metal alkylidynes*

Mononuclear metal alkylidynes, such as $W(\equiv CTol)(CO)_2(\eta^5\text{-Cp})$, have proved to be versatile coupling reagents in cluster synthesis [12]. The metal–carbon triple bond is isolobal to alkynes and follows similar reaction patterns in reactions with other transition metal compounds. A wide array of metal alkylidynes have been employed in the synthesis of group 6–group 9 mixed-metal clusters. Early work with compounds of the type $M(\equiv CR)(CO)_2(\eta^5\text{-L})$ contained cyclopentadienyl ligands, or derivatives thereof; more recently, however, isolobal ligands such as η^5-carboranes, have been introduced. The carborane ligand $\eta^5\text{-}C_2B_9H_9Me_2$ has been shown to adopt more than a simple spectator role in that it exhibits reversible three-center two-electron B–H–Co linkages in the dicobalt tungsten clusters, $[X][WCo_2(\mu_3\text{-CR})(CO)_6(\eta^5\text{-}C_2B_9H_9Me_2)]$, **15** [13]. Upon introduction of CO to the system, the latter form the compounds $[X][WCo_2(\mu_3\text{-CR})(CO)_8(\eta^5\text{-}C_2B_9H_9Me_2)]$, **16** ($X \equiv NEt_4$; $R \equiv$ Me, Ph, Tol, 2-C_6H_4Me; $X \equiv PPh_4$; $R \equiv$ Ph), which do not contain the novel B–H–Co interactions (Scheme III). Reagents of the form $M(\equiv CR)(CO)_xL_y$ including compounds containing nitrogen donors such as pyridine, 2, 2′-dipyridyl, or pyrazol-1-yl borates have also been employed in cluster synthesis. Also, several cluster compounds have been prepared from the alkylidyne precursors $[W(\equiv CR)(CO)_2\{R'C(pz)_3\}][BF_4]$ ($R \equiv$ Me, Tol; $R' \equiv$ H, Au(C_6F_5), Me) [14,15]. Other novel alkylidyne precursors employed in cluster synthesis contained pendant organometallic groups. In **17** a $Cr(CO)_3$ fragment was bonded to the arene ring of the alkylidyne C_6H_4OMe-2 substituent [16] and in **18** the oxygen ligands of the $[Co\{P(O)R_2\}_3(\eta^5\text{-Cp})^-]$ moiety were bound to the M≡CR unit [17].

The reaction of mononuclear alkylidynes with mononuclear reagents leads initially to dinuclear species containing bridging alkylidynes. While these compounds are usually isolable, they often react readily with another mole of reagent to give



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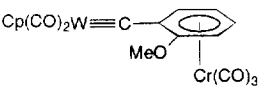
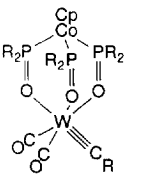
X = NEt_4; R = Me, Ph, Tol, 2-C_6H_4Me
X = PPh_4; R = Ph

Scheme III.



17 M = Mo, W



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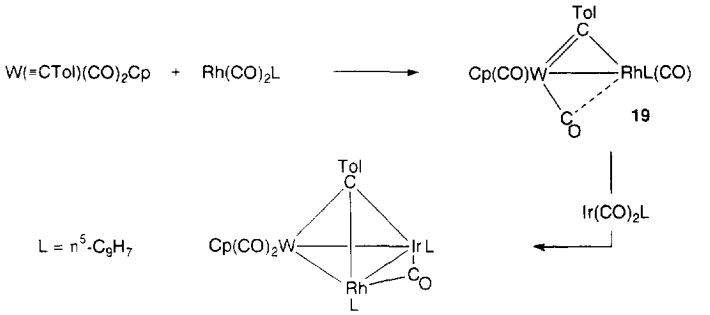
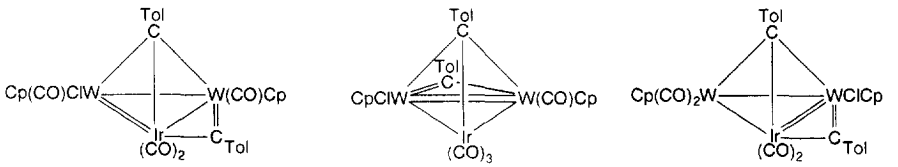
R = OCH_3, O-i-C_3H_7
R' = Ph, Tol
M = Mo, W

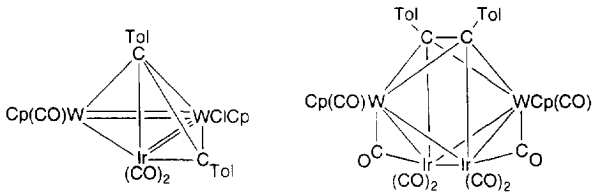
trinuclear μ_3-alkylidyne clusters. These reactions, conducted stepwise can lead to compounds containing three different metal atoms. For example, the reaction of $W(\equiv CTol)(CO)_2(\eta^5\text{-Cp})$ with $Rh(CO)_2(\eta^5\text{-}C_9H_7)$ provided the dinuclear species, $WRh(\mu\text{-CTol})(CO)_3(\eta^5\text{-Cp})(\eta^5\text{-}C_9H_7)$, **19** [18]. The subsequent reaction of **19** with $Ir(CO)_2(\eta^5\text{-}C_9H_7)$ gave $WRhIr(\mu_3\text{-CTol})(\mu\text{-CO})(CO)_2(\eta^5\text{-Cp})(\eta^5\text{-}C_9H_7)_2$, **20**, as one product (Scheme IV) [19].

While the reactions of mononuclear alkylidynes with mononuclear reagents are fairly general, leading to many analogous compounds, some exceptions have been discussed. For example, the reaction of $W(\equiv CTol)(CO)_2(\eta^5\text{-Cp})$ with the 16 electron iridium species, $IrCl(CO)(\eta^2\text{-}C_8H_{14})_2$ led to a separable mixture of products [20]. Three products were an isomeric mixture of 46 electron, unsaturated clusters with the composition, $W_2Ir(\mu\text{-CTol})(\mu_3\text{-CTol})Cl(CO)_4(\eta^5\text{-Cp})_2$, **21**, **22**, **23** that differed in the position of the μ_2-bridging alkylidyne and the localization of the unsaturation. Two other products, $W_2Ir(\mu_3\text{-}\eta^2\text{-}C_2Tol_2)Cl(CO)_4(\eta^5\text{-Cp})_2$, **24**, and $W_2Ir_2(\mu_4\text{-}\eta^2\text{-}C_2Tol_2)(\mu\text{-CO})_2(CO)_6(\eta^5\text{-Cp})_2$, **25**, contained bridging ditolylacetylene ligands that formed through alkylidyne–alkylidyne coupling. The latter compound is analogous to the diphenylacetylene compound $W_2Ir_2(\mu_4\text{-}\eta^2\text{-}C_2Ph_2)(\mu\text{-CO})_2(CO)_6(\eta^5\text{-Cp})_2$, **57**,



Scheme IV.





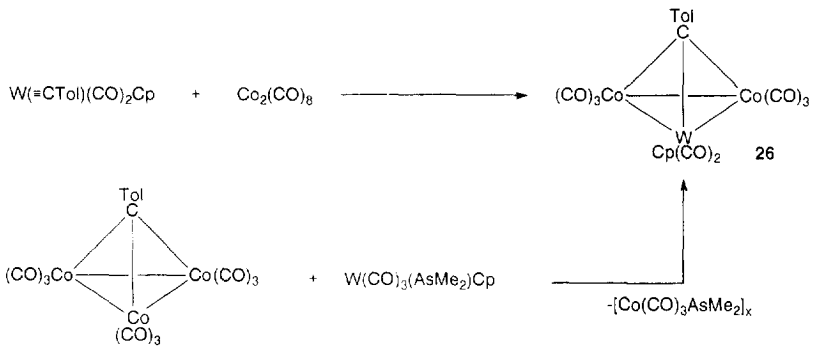
that was formed by the reaction of the tetranuclear cluster $W_2Ir_2(CO)_{10}(\eta^5\text{-Cp})_2$ with C_2Ph_2 [21].

Reaction of mononuclear alkylidynes with dinuclear reagents such as $Co_2(CO)_8$ or $MRh(\mu\text{-CO})_2(\eta^5\text{-Cp*})_2$ (M ≡ Co, Rh), can lead to μ_3-alkylidyne clusters. For example, W(≡CTol)$(CO)_2(\eta^5$-Cp) reacted with $Co_2(CO)_8$ to provide $WCo_2(\mu_3$-CTol$)(CO)_8(\eta^5$-Cp), **26**, [22,23] a compound that was also prepared by metal exchange with $Co_3(\mu_3$-CTol$)(CO)_9$ and the reagent $W(CO)_3(AsMe_2)(\eta^5$-Cp) (Scheme V) [24,25]. The reaction of W(≡CMe)$(CO)_2(\eta^5$-Cp) with $Rh_2(\mu\text{-CO})_2(\eta^5\text{-Cp*})_2$ gave $WRh_2(\mu_3$-CMe$)(\mu$-CO$)(CO)_2(\eta^5$-Cp$)(\eta^5$-Cp*$)_2$, **27** [26].

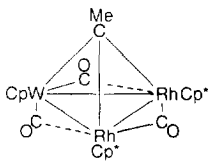
The tungsten alkylidyne, W(≡CTol)$(CO)_2(\eta^5$-Cp), reacts with phosphines to give compounds with an η^2-C(Tol)C(O) ketenyl ligand [27]. The trimethylphosphine derivative, W$\{\eta^2$-C(Tol)C(O)$\}$(CO)$(PMe_3)(\eta^5$-Cp), **28**, reacted with $Co_2(CO)_8$ to give the phosphine-substituted μ_3-alkylidyne cluster, $WCo_2(\mu_3$-CTol$)(CO)_7(PMe_3)(\eta^5$-Cp), **29** (Scheme VI) [28]. Initially, the phosphine was coordi-

nated to the tungsten; however, over the course of 48 h the phosphine migrated to a cobalt atom. Interestingly, this latter product, **30**, is analogous to the compound isolated from the reaction of $WCo_2(\mu_3\text{-}CTol)(CO)_8(\eta^5\text{-}Cp)$ and PMe_2Ph, **75** [23].

The alkynyl alkylidyne compounds, $M(\equiv CC\equiv C^tBu)(CO)_2L$ ($M \equiv Mo$, $L \equiv \eta^5$-Cp, $HB(dmpz)_3$; $M \equiv W$, $L \equiv \eta^5$-Cp, $HB(pz)_3$), have two reactive sites. The reactions with $Co_2(CO)_8$ led to attack at the $M\equiv C$ bond in the cyclopentadienyl compounds, but attack at the $C\equiv C$ bond in the pyrazolyl compounds, leading to $MCo_2(\mu_3\text{-}CC\equiv C^tBu)(CO)_8(\eta^5\text{-}Cp)$, **31** ($M \equiv Mo$, W) and $Co_2\{\mu_2\text{-}\eta^2\text{-}{}^tBuC_2C\equiv M(CO)_2L\}(CO)_6$, **32** ($M \equiv Mo$, $L \equiv HB(dmpz)_3$; $M \equiv W$, $HB(pz)_3$) respec-



Scheme V.



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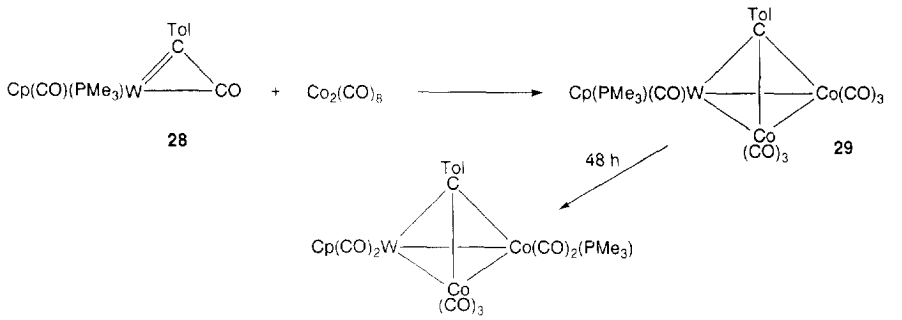
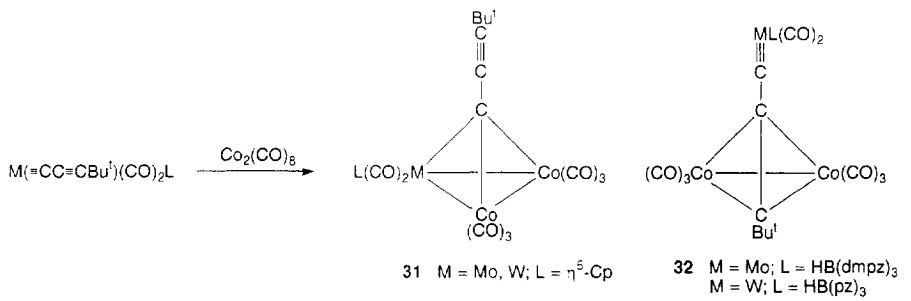


Scheme VI.

tively (Scheme VII) [29]. The reactions forming the latter species are similar to those of the metal propargyl compounds, $M(CH_2C{\equiv}CR)(CO)_3(\eta^5\text{-Cp})$ ($M \equiv Mo$, $R \equiv Ph$; $M \equiv W$, $R \equiv Me$, Ph) with $Co_2(CO)_8$ [30] forming $Co_2(\mu_2\text{-}\eta^2\text{-}C_2R_2)$ products, **33**, rather than clusters, and are therefore not included in Table 2 (Scheme VIII). However the related compounds, $Co_2\{\mu_2\text{-}\eta^2\text{-}PhC_2C(OEt){=}M(CO)_5\}(CO)_6$, **34**, formed from $M{=}C(OEt)(C{\equiv}CPh)(CO)_5$ and $Co_2(CO)_8$, rearranged in boiling hexane to give the clusters $MCo_2(CO)_7(\mu\text{-}CO)_2\{\mu_3\text{-}\eta^4\text{-}CC(OEt){=}CPhC(O)\}$ ($M \equiv Cr$, W) **35** and the less stable isomers $MCo_2(CO)_7(\mu\text{-}CO)_2\{\mu_3\text{-}\eta^4\text{-}CCPh{=}C(OEt)C(O)\}$ ($M \equiv Cr$, W) **36** (Scheme IX) [31]. The reactions of $M(\equiv CC{\equiv}C^tBu)(CO)_2(\eta^5\text{-Cp})$ with $Rh(CO)_2(\eta^5\text{-}C_9H_7)$ gave a mixture of di- and trimetal products [32]. One type of product, $MRh_2(\mu_3\text{-}CC{\equiv}C^tBu)(\mu\text{-}CO)(CO)_2(\eta^5\text{-Cp})(\eta^5\text{-}C_9H_7)_2$, **37**, ($M \equiv Mo$, W), is analogous to the μ_3-alkylidyne cluster, **27**, discussed above. Another product, $M_2Rh\{\mu_3\text{-}\eta^2\text{-}C_2(C{\equiv}C^tBu)_2\}(CO)_4(\eta^5\text{-Cp})_2(\eta^5\text{-}C_9H_7)$, **38**, ($M \equiv Mo$), incorporated a triyne ligand that formed through the coupling of two alkylidyne moieties. The further reaction of the dimetal product, $WRh(\mu\text{-}CC{\equiv}C^tBu)(CO)_3(\eta^5\text{-Cp})(\eta^5\text{-}C_9H_7)$ with $Co(\eta^2\text{-}C_2H_4)_2(\eta^5\text{-Cp*})$, provided the heterotrimetallic cluster, $WCoRh(\mu_3\text{-}CC{\equiv}C^tBu)(\mu\text{-}CO)(CO)_2(\eta^5\text{-Cp})(\eta^5\text{-Cp*})(\eta^5\text{-}C_9H_7)$, **39**.

2.4. Type D: condensation reactions with other mononuclear species

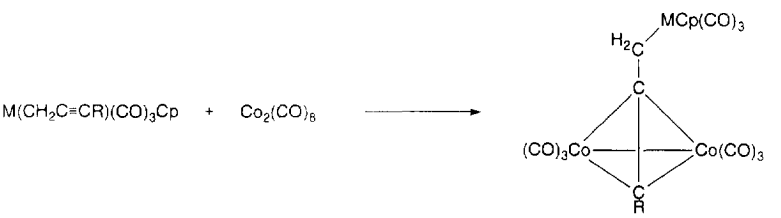
The reactions of both saturated and unsaturated dinuclear species with mononuclear reagents are included under this heading. The most rational syntheses dis-



31 M = Mo, W; L = η^5-Cp

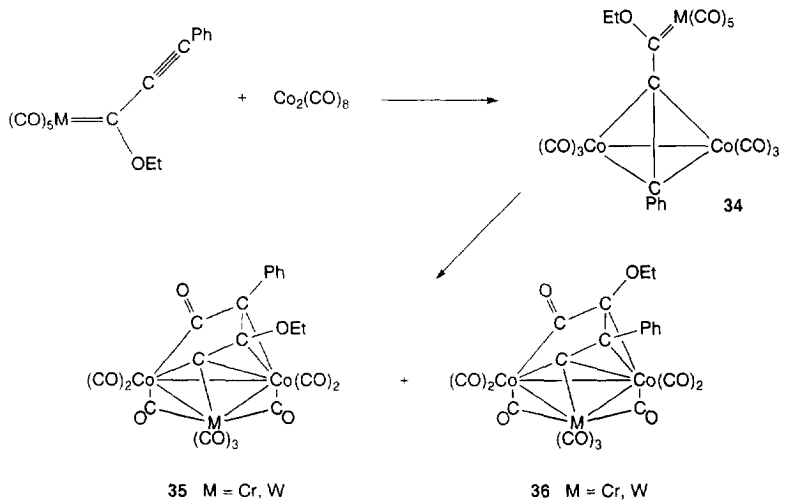
32 M = Mo; L = HB(dmpz)$_3$
M = W; L = HB(pz)$_3$

Scheme VII.

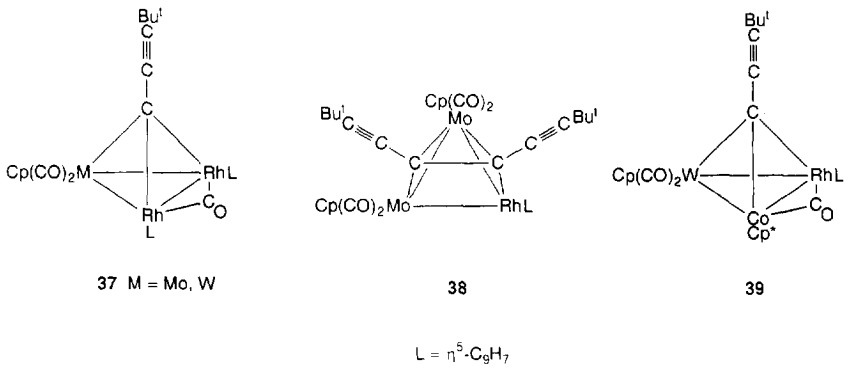


33 M = Mo; R = Ph
M = W; R = Me, Ph

Scheme VIII.

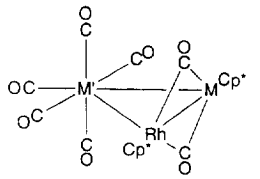


Scheme IX.

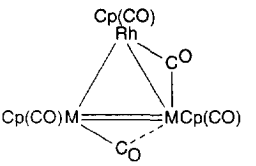


cussed in this section incorporate the use of metal–metal double bonds as coupling units, leading to clusters that are the isolobal analogies of metal olefin compounds. The dinuclear compounds $M_2(CO)_n(\eta^5\text{-}Cp)_2$ ($M \equiv Mo$, W; $n = 4,6$), as well as the unsaturated compound $W_2(OCH_2{}^tBu)_6(py)_2$, have also been used in reactions with mononuclear group 9 compounds leading to mixed-metal clusters. Other syntheses discussed in this section utilize alkynes or vinylidenes as coupling units.

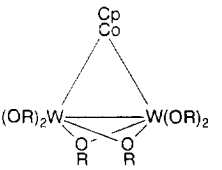
Unsaturated dinuclear compounds of the form $MRh(\mu\text{-}CO)_2(\eta^5\text{-}Cp^*)_2$ ($M \equiv Co$, Rh) reacted with the solvated pentacarbonyls $M'(CO)_5(L)$, ($M' \equiv Cr$, Mo, W, $L \equiv thf$; $M' \equiv Mo$, $L \equiv MeCN$) to form compounds of the form, $M'MRh(\mu\text{-}CO)_2(CO)_5(\eta^5\text{-}Cp^*)_2$ ($M \equiv Co$, $M' \equiv Mo$, **40**; $M \equiv Rh$, $M' \equiv Cr$, **41**; $M \equiv Rh$, $M' \equiv Mo$, **42**; $M \equiv Rh$, $M' \equiv W$, **43**) [33–35]. Rotation of the Co=Rh moiety in **40** about the axis through the Mo and the midpoint of the CoRh vector was examined by variable temperature NMR. The barrier to rotation was similar to that observed for some isolobal d^6



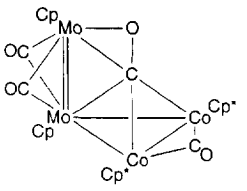
	M	M'
40	Co	Mo
41	Rh	Cr
42	Rh	Mo
43	Rh	W



44 M = Mo, W



46 R = CH_2Bu^t



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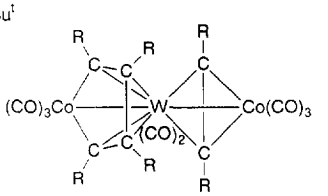

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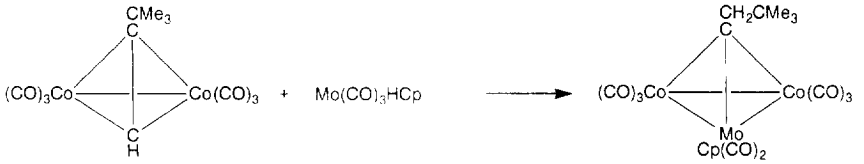
ML_5 alkene compounds; however, EHMO calculations suggest a different balance between electronic and steric contributions in the two cases [34].

The reactions of the saturated dinuclear compounds $M_2(CO)_6(\eta^5\text{-Cp})_2$ with $Rh(\eta^2\text{-}C_2H_4)_2(\eta^5\text{-Cp})$ resulted in the unsaturated trinuclear clusters $M_2Rh(CO)_5(\eta^5\text{-Cp})_3$, **44**, (M ≡ Mo, W). X-ray crystallography indicated the unsaturation was localized at the M–M bond [36,37]. The synthesis of a tetranuclear cluster, $Mo_2Co_2(\mu\text{-CO})_3(\mu_4\text{-}\eta^2\text{-CO})(\eta^5\text{-Cp})_2(\eta^5\text{-Cp*})_2$, **45**, from $Mo_2(CO)_4(\eta^5\text{-Cp})_2$ and $Co(\eta^2\text{-}C_2H_4)_2(\eta^5\text{-Cp*})$ was reported and structurally characterized. The molecule was formally unsaturated, with a Mo–Mo double bond, and contained a CO ligand showing a novel μ_4, η^2-bonding mode [38]. In contrast, the reaction of the unsaturated compound $W_2(OCH_2{}^tBu)_6(py)_2$ with $Co(\eta^2\text{-}C_2H_4)(\eta^5\text{-Cp})$ led to the trinuclear compound $W_2Co(OCH_2{}^tBu)_6(\eta^5\text{-Cp})$, **46** [39].

The reaction of $Co_2(CO)_8$ with $W(CO)(C_2R_2)_3$ led to the linear trinuclear clusters, $WCo_2(\mu_2\text{-}\eta^2\text{-}C_2R_2)(\mu_2\text{-}\eta^4\text{-}C_4R_4)(CO)_8$ (R ≡ Et, Pr), **47**, products that necessitate C–C bond formation through alkyne coupling [40,41]. The reaction of $Co_2(CO)_6(\mu_2\text{-}\eta^2\text{-}HC_2CMe_3)$ with $Mo(CO)_3H(\eta^5\text{-Cp})$ led to a trinuclear μ_3-alkylidyne cluster, $MoCo_2(\mu_3\text{-}CCH_2CMe_3)(CO)_8(\eta^5\text{-Cp})$, **48** (Scheme X) [42]. A similar compound was obtained through the reaction of the dicobalt μ-vinylidene compound, $Co_2(\mu\text{-}CCH_2)(CO)_2(\eta^5\text{-Cp})_2$, with $Mo(CO)_3H(\eta^5\text{-Cp})$ leading to the trinuclear μ_3-ethylidyne cluster, $MoCo_2(\mu_3\text{-CMe})(CO)_3(\eta^5\text{-Cp})_3$, **49** (Scheme XI) [43]. Interestingly, **49** was also prepared from $MoCo_2(\mu_3\text{-CMe})(CO)_8(\eta^5\text{-Cp})$ and excess dicyclopentadiene in toluene at reflux [44].



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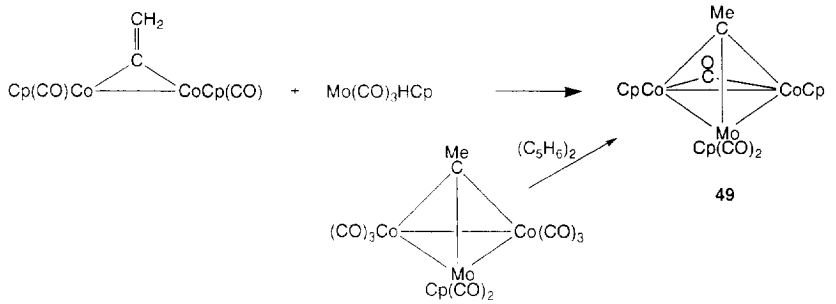
Scheme X.



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Scheme XI.

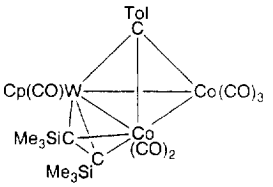
3. Reactivity

The reactivity of heterometallic clusters is often discussed in terms of site-selectivity. The concept that different metals incorporated in a polynuclear cluster may react preferentially with certain types of ligands is integral to the study of the reactions of mixed-metal clusters. The reactions of group 6–group 9 heterometallic clusters with alkynes, protons and carbon electrophiles, and other related substitution reactions will be summarized.

3.1. Reactions with alkynes

The reactions of group 6–group 9 mixed-metal clusters with alkynes can provide products involving both C–C formation and C≡C scission. Both trinuclear μ_3-alkylidyne and tetranuclear heterometallic clusters have been studied. The analysis of these reactions may provide insight into the fate of hydrocarbons on heterogeneous catalysts.

The reaction of $WCo_2(\mu_3\text{-CTol})(CO)_8(\eta^5\text{-Cp})$ with $C_2(SiMe_3)_2$ led to $WCo_2(\mu_3\text{-CTol})\{\mu_2\text{-}\eta^2\text{-}C_2(SiMe_3)_2\}(CO)_6(\eta^5\text{-Cp})$, **50** [23]. ^{13}C NMR spectroscopy indicated the inequivalence of the two $CSiMe_3$ carbons, and the structure was proposed to incorporate the alkyne ligand bridging a Co–W bond in a perpendicular fashion. Analogies were drawn to the structurally characterized compound, $WFe_2(\mu_3\text{-CTol})\{\mu_2\text{-}\eta^2\text{-}C_2(SiMe_3)_2\}(\mu\text{-CO})(CO)_6(\eta^5\text{-Cp})$, **51**, which has been shown to contain the alkyne ligand bridging an Fe–W bond in this manner [45].



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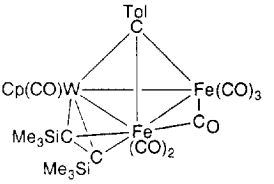

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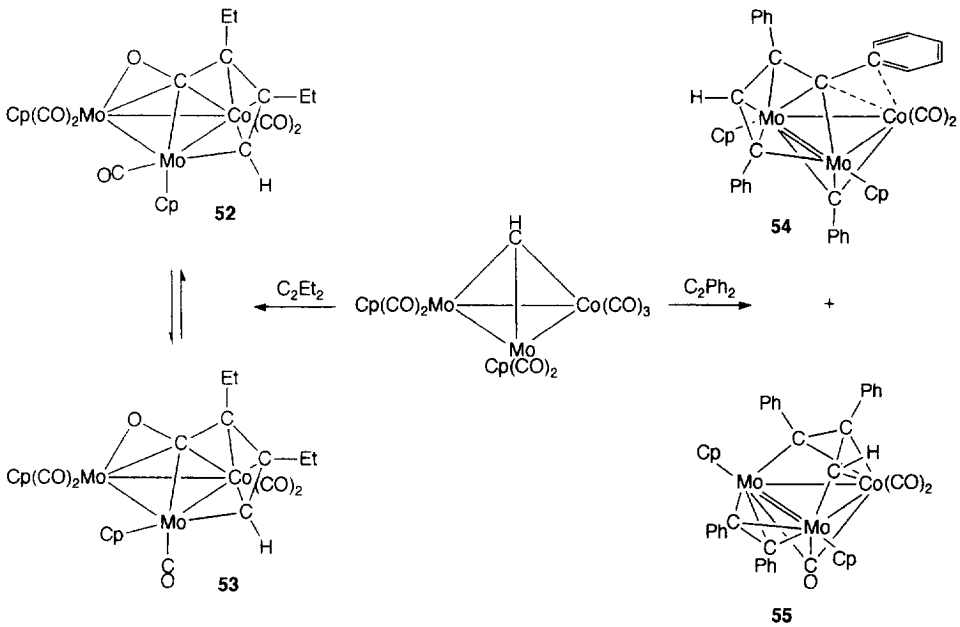
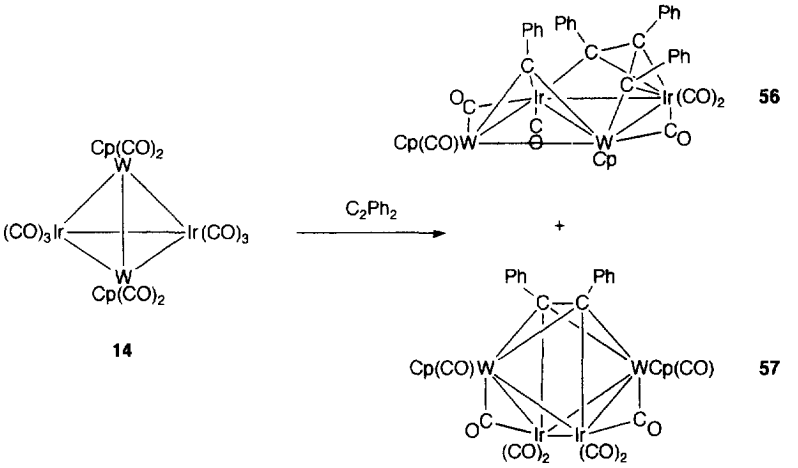
The reactions of $Mo_2Co(\mu_3\text{-}CH)(CO)_7(\eta^5\text{-}Cp)_2$ with C_2Et_2 and C_2Ph_2 were explored and led to trimetallic products derived from alkyne–methylidyne coupling [46]. Interestingly, the analogous reactions with $Co_3(\mu_3\text{-}CH)(CO)_9$ led to cluster fragmentation and formation of dinuclear $Co_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C_2R_2)$ ($R \equiv Et$, Ph) compounds [46,47]. The reactions with C_2Et_2 gave a mixture of separable isomers with the formulation, $Mo_2Co\{\mu_3\text{-}OCC(Et)C(Et)CH\}(CO)_5(\eta^5\text{-}Cp)_2$, **52** and **53**, that could be interconverted by the formal rotation of one $Mo(CO)(\eta^5\text{-}Cp)$ fragment. Both isomers exhibited the same general structure and contained a triply bridging OCC(Et)C(Et)CH group that was derived from the coupling of the alkyne with the methylidyne and one CO ligand (Scheme XII). The reaction of $Mo_2Co(\mu_3\text{-}CH)(CO)_7(\eta^5\text{-}Cp)_2$ with C_2Ph_2 led to the isolation of two products that each incorporated two equivalents of the alkyne (Scheme XII). The first, $Mo_2Co\{\mu_3\text{-}C(Ph)C(H)C(Ph)C(Ph)\}(\mu_3\text{-}CPh)(CO)_2(\eta^5\text{-}Cp)_2$, **54**, contained a μ_3-CPh group and



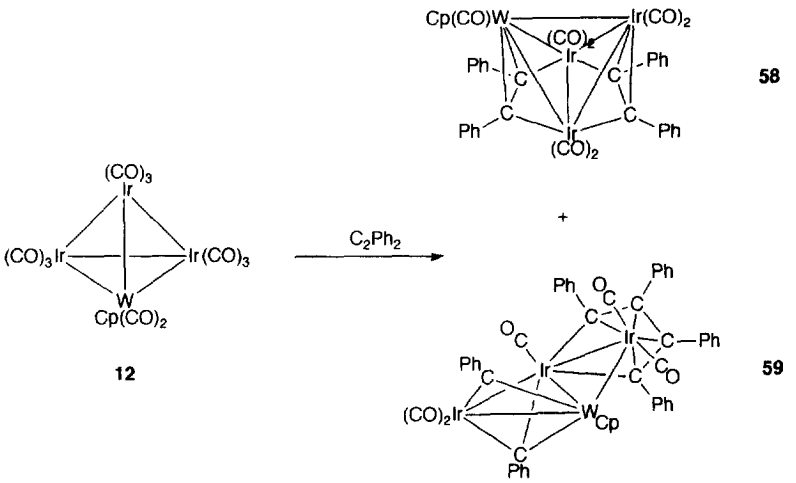
Scheme XII.

a dimetallatriphenylbutadiene ligand. These were suggested to arise from the coupling of two alkynes with the methylidyne group together with the separation of one CPh group. The cluster contains 44 valence electrons, and is therefore electronically unsaturated. The shortness of the Mo–Mo bond suggested some degree of unsaturation, and a short phenyl–cobalt distance suggested a weak interaction. If the latter interaction is taken into account the valence electron count becomes 46 electrons. The second reaction product, $Mo_2Co\{\mu_3\text{-}C(H)C(Ph)C(Ph)\}(\mu_2\text{-}\eta^2\text{-}C_2Ph_2)(\mu_3\text{-}CO)(CO)_2(\eta^5\text{-}Cp)_2$, **55**, contained a triply bridging dimetalladiphenylallyl ligand that resulted from the coupling of one alkyne with the methylidyne group. This compound is also formally electronically unsaturated with 46 valence electrons. The other alkyne bridged the short, and presumably unsaturated, Mo–Mo bond, in a perpendicular mode.

The reactions of the tetranuclear bimetallic clusters $WIr_3(CO)_{11}(\eta^5\text{-}Cp)$, **12**, and $W_2Ir_2(CO)_{10}(\eta^5\text{-}Cp)_2$, **14**, with alkynes were reported [2,21]. In both cases, two products were obtained, one that resulted from both alkyne scission and C–C bond formation, and one that did not. The reaction of $W_2Ir_2(CO)_{10}(\eta^5\text{-}Cp)_2$, **14**, with C_2Ph_2 proceeded in two independent reaction pathways to $W_2Ir_2(\mu_3\text{-}CPh)(\mu_3\text{-}\eta^3\text{-}C_3Ph_3)(CO)_6(\eta^5\text{-}Cp)_2$, **56**, and $W_2Ir_2(\mu_4\text{-}\eta^2\text{-}C_2Ph_2)(CO)_8(\eta^5\text{-}Cp)_2$, **57** (Scheme XIII). Both ^1H and ^{13}C NMR spectra were consistent with the conclusion that the structure of **57** was a closo-octahedral framework with a butterfly arrangement of the W_2Ir_2 moiety, and CPh groups at the other two vertices. The compound resulted from formal insertion of the alkyne into the W–W bond and apparently has the same structure later determined for **25**. The other compound, $W_2Ir_2(\mu_3\text{-}CPh)(\mu_3\text{-}\eta^3\text{-}C_3Ph_3)(CO)_6(\eta^5\text{-}Cp)_2$, **56**, was crystallographically characterized and consisted of an almost flat W_2Ir_2 core with the W_2Ir triangular face capped with a μ_3-CPh group and the WIr_2 triangular face bridged by a $\mu_3\text{-}\eta^3$-dimetallatriphenylallyl group [48].



Scheme XIII.

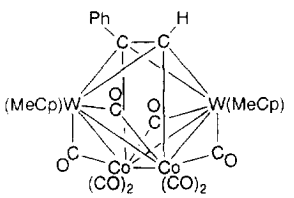


Scheme XIV.

This compound resulted from cleavage of a W–Ir bond, the scission of one C≡C bond and the consequent condensation of one of the resulting alkylidyne fragments with a second alkyne.

The reaction of $WIr_3(CO)_{11}(\eta^5\text{-Cp})$, **12**, with C_2Ph_2 led to both structurally characterized compounds $WIr_3(\mu_3\text{-}\eta^2\text{-}C_2Ph_2)_2(CO)_7(\eta^5\text{-Cp})$, **58**, and $WIr_3(\mu\text{-CPh})(\mu_3\text{-CPh})(\mu_3\text{-}\eta^4\text{-}C_4Ph_4)(CO)_5(\eta^5\text{-Cp})$, **59** (Scheme XIV). The first compound exhibited a closed WIr_3 tetrahedral core containing two $\mu_3\text{-}\eta^2$-alkyne ligands bound on both a WIr_2 face and the Ir_3 face. The second compound, resulting from cleavage of an Ir–Ir bond, had a WIr_3 butterfly core and contained two CPh ligands; one triply bridging a WIr_2 face and one doubly bridging a W–Ir bond on the same face. The molecule also incorporated an iridacyclopentadienyl group that bridged the Ir–Ir bond of the other WIr_2 face. Interestingly, in both the reactions of **12** and **14** with C_2Ph_2 the products resulting from C≡C scission and C–C formation contained tungsten in the hinge position of a butterfly WIr_3 or W_2Ir_2 core.

The reactions of PhC_2H with **5**–**8** were reported [49]. Both $W_2Co_2(\mu\text{-CO})_3(CO)_7(\eta^5\text{-MeCp})_2$, **5**, and $MoCo_3(\mu\text{-CO})_3(CO)_8(\eta^5\text{-MeCp})$, **7**, gave



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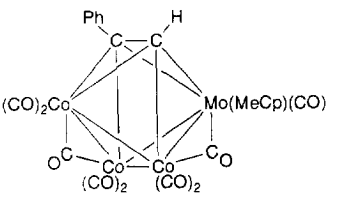

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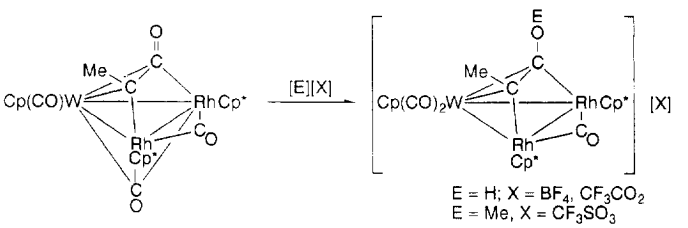
tetranuclear clusters with $W_2Co_2C_2$, and $MoCo_3C_2$ butterfly cores respectively, each incorporating a μ_4-η^2-PhC_2H ligand. The compound, $W_2Co_2(\mu_4$-η^2-$PhC_2H)(\mu$-$CO)_4(CO)_4(\eta^5$-$MeCp)_2$, **60**, had both tungsten atoms in wing-tip positions, and $MoCo_3(\mu_4$-η^2-$PhC_2H)(\mu$-$CO)_2(CO)_7(\eta^5$-MeCp), **61**, contained the molybdenum atom in a wing-tip position. The related compounds $M_2Co_2(\mu_4$-η^2-$C_2Me_2)(\mu$-$CO)_4(CO)_4(\eta^5$-$Cp)_2$ (M ≡ Mo, W) were isolated as byproducts in metal exchange reactions and exhibited a similar cluster core [50]. The reactions of $WCo_3(\mu$-$CO)_3(CO)_8(\eta^5$-MeCp), **6**, and $W_3Co(CO)_9(\eta^5$-$MeCp)_3$, **8**, with PhC_2H led to cluster fragmentation, PhC_2H oligomerization, and the isolation of dinuclear WCo species.

3.2. *Reactions with protons and carbon electrophiles*

The reaction of $W(\equiv CMe)(CO)_2(\eta^5$-Cp) with $Rh_2(\mu$-$CO)_2(\eta^5$-$Cp^*)_2$ formed the trinuclear compound, $WRh_2(\mu_3$-$CMe)(\mu$-$CO)(CO)_2(\eta^5$-$Cp)(\eta^5$-$Cp^*)_2$, **27**, and $WRh_2(\mu$-$CO)(\mu_3$-$CO)\{\mu_3$-η^2-C(O)CMe$\}$(CO)$(\eta^5$-$Cp)(\eta^5$-$Cp^*)_2$, **62**, which contained a triply bridging ketenyl ligand. Elaboration of this ligand was affected through reaction with $HBF_4 \cdot Et_2O$, CF_3CO_2H or CF_3SO_3Me, leading to cationic alkyne clusters, $[WRh_2(\mu$-$CO)\{\mu_3$-η^2-C(OE)CMe$\}$(CO)$_2(\eta^5$-$Cp)(\eta^5$-$Cp^*)_2][X]$, **63** (E ≡ H, X ≡ BF_4 or CF_3CO_2; E ≡ Me, X ≡ CF_3SO_3) (Scheme XV) [26].

The protonation of $WCoRh(\mu_3$-$CMe)(\mu$-$CO)(CO)_2(\eta^5$-$Cp)(\eta^5$-$Cp^*)_2$ with HBF_4 provided two isomers with the formula $[WCoRh(\mu_3$-$CMe)(\mu$-$H)(\mu$-$CO)(CO)_2(\eta^5$-$Cp)(\eta^5$-$Cp^*)_2][BF_4]$, with the hydride bridging the W–Co bond in the major isomer, **64**, and the W–Rh bond in the minor isomer, **65** [26]. Protonation of $WRh_2(\mu_3$-$CR)(\mu$-$CO)(CO)_2(\eta^5$-$Cp)(\eta^5$-$Cp^*)_2$ with HBF_4 led to an isomeric mixture



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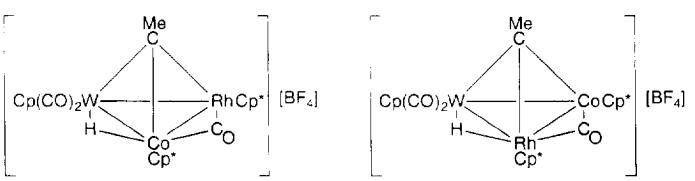
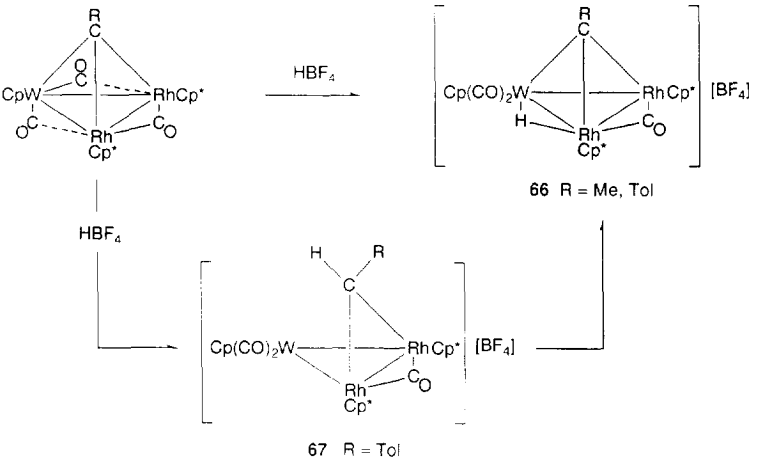
Scheme XV.



64 65



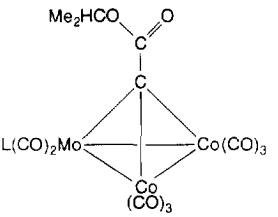
Scheme XVI.

of two compounds with the formula $[WRh_2(\mu_3\text{-}CR)(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(\eta^5\text{-}Cp)(\eta^5\text{-}Cp^*)_2][BF_4]$, **66** (R ≡ Me, Tol) (Scheme XVI) [26]. The isomers corresponded to different rotational orientations of the $W(CO)_2(\eta^5\text{-}Cp)$ moiety with respect to the axis defined by the tungsten atom and the centroid of the CRh_2 plane. An intermediate, **67**, observed in the reaction with R ≡ Tol indicated initial attack of the proton at the alkylidyne carbon. It has been reported, however, that protonation of $M_3(\mu_3\text{-}CR)(\mu\text{-}H)_3(CO)_9$ (M ≡ Ru, R ≡ Et, $CHPhCH_2Ph$; M ≡ Os, R ≡ Me) involved attack at the M–C bond and the formation of an agostic hydrogen interaction [51]. This suggests the possibility that initial attack at the W–C bond upon protonation of $WRh_2(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_2(\eta^5\text{-}Cp)(\eta^5\text{-}Cp^*)_2$ formed an analogous agostic interaction, rather than the intermediate proposed, which rearranged to give the isolable product, **66**.

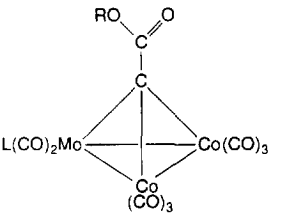
The addition of HPF_6 to propionic anhydride solutions of $MoCo_2(\mu_3\text{-}CCO_2CHMe_2)(CO)_8(\eta^5\text{-}L)$, **68**, led to the isolation of the cationic ketenylidene clusters, $[MoCo_2(\mu_3\text{-}CCO)(CO)_8(\eta^5\text{-}L)][PF_6]$, (L ≡ Cp, Cp*), the structure of which was not totally clear [52]. The treatment of these cations with ROH or diethylamine led to the esters $MoCo_2(\mu_3\text{-}CCO_2R)(CO)_8(\eta^5\text{-}L)$, **69**, (L ≡ Cp, Cp*; R ≡ Me, Et), or the amide $MoCo_2(\mu_3\text{-}CC(O)NEt_2)(CO)_8(\eta^5\text{-}Cp)$, **70**, respectively. These clusters also reacted with *N,N*-dimethylaniline, indole or pyrrole to give Friedel–Crafts type products, such as $MoCo_2(\mu_3\text{-}CC(O)\text{-}p\text{-}C_6H_4NMe_2)(CO)_8(\eta^5\text{-}Cp)$, **71**, in which the acylium species attacked the *para* position on the aniline ring.

Metal exchange, using the tricobalt cluster, $Co_3(\mu_3\text{-}CC(Me)=CH_2)(CO)_9$ and $Na[Mo(CO)_3(\eta^5\text{-}Cp)]$ provided the mixed-metal cluster $MoCo_2(\mu_3\text{-}CC(Me)=CH_2)(CO)_8(\eta^5\text{-}Cp)$, **72**. The subsequent reaction with HPF_6 in propionic anhydride solution resulted in the cationic vinylidene cluster, $[MoCo_2(\mu_3\text{-}C=CMe_2)(CO)_8(\eta^5\text{-}Cp)][PF_6]$, **73** (Scheme XVII) [53].

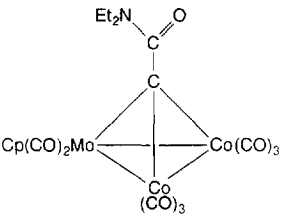
The μ_3-thiocarbyne cluster, $WRh_2(\mu_3\text{-}CSMe)(\mu\text{-}CO)(CO)_2\{HB(pz)_3\}(\eta^5\text{-}C_9H_7)_2$



68 L = Cp, Cp*



69 L = Cp, Cp*; R = Me, Et



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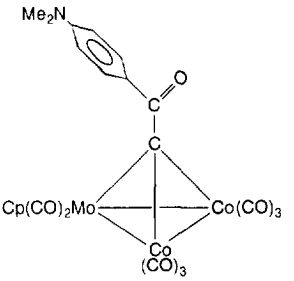

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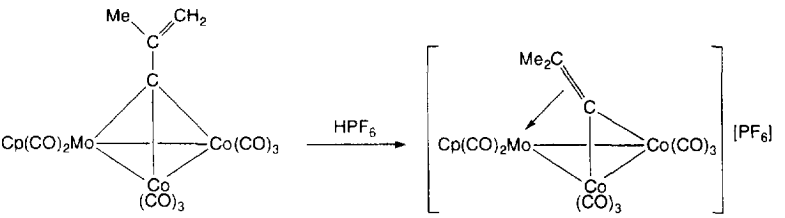


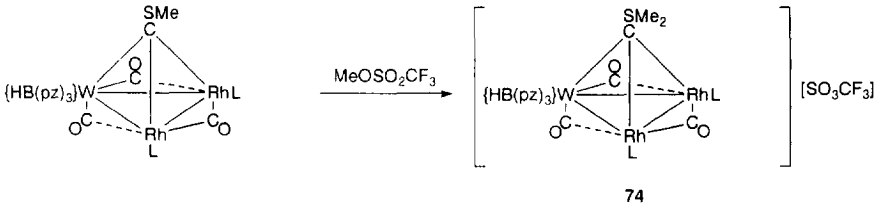
72 73

Scheme XVII.

reacted with $MeOSO_2CF_3$, resulting in methylation of the μ_3-CSMe moiety to give $[WRh_2(\mu_3\text{-}CSMe_2)(\mu\text{-}CO)(CO)_2\{HB(pz)_3\}(\eta^5\text{-}C_9H_7)_2][SO_3CF_3]$, **74** (Scheme XVIII) [54].

3.3. Carbonyl substitution reactions

The reaction of trinuclear alkylidyne clusters with mono- and bidentate phosphines and arsines generally proceeds without cluster fragmentation to give substituted clusters. Although the resulting phosphorus or arsenic-containing compounds do not fall strictly under the heading of this review, it is useful to consider these reactions as indicators of possible reactive sites in the parent clusters. The reactions of the compounds, $MCo_2(\mu_3\text{-}CR)(CO)_8(\eta^5\text{-}C_5H_4R')$ (M ≡ Mo, W; R ≡ Me, Tol; R′ ≡ H, $SiMe_3$) with PMe_3, PMe_2Ph, $P(OMe)_3$, dppm (dppm ≡ $Ph_2PCH_2PPh_2$) and diars

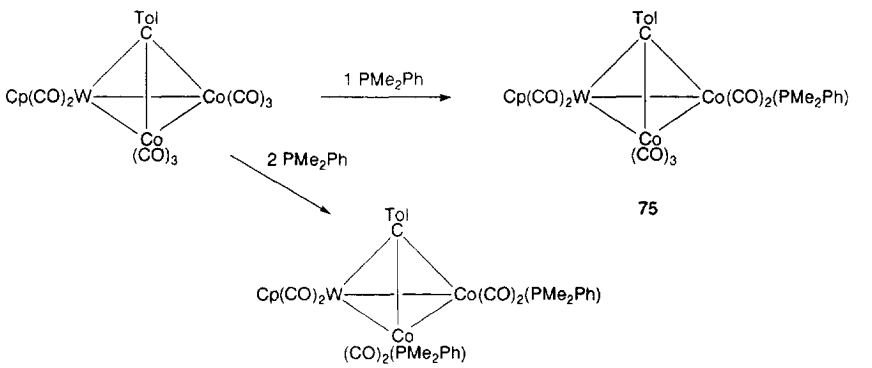


74

L = η^5-C_9H_7

Scheme XVIII.

(diars ≡ 1,2-$C_6H_4(AsMe_2)_2$) were studied [23,24]. As a representative example, $WCo_2(\mu$-CTol)$(CO)_8(\eta^5$-Cp) reacted with one or two equivalents of PMe_2Ph to give the mono- and disubstituted clusters $WCo_2(\mu$-CTol)$(CO)_7(PMe_2Ph)(\eta^5$-Cp), **75**, and $WCo_2(\mu$-CTol)$(CO)_6(PMe_2Ph)_2(\eta^5$-Cp), **76**, respectively (Scheme XIX) [23]. In both cases, the presence of many rapidly interconverting isomers was observed by infrared and NMR spectroscopy. ^{31}P NMR indicated, however, that the phosphines were coordinated to cobalt atoms only, due to lack of ^{31}P–^{183}W coupling. Similarly, the bidentate reagents, dppm and diars also coordinated exclusively to the Co_2 moiety to give $WCo_2(\mu_3$-CTol$)(CO)_6(\mu$-dppm$)(\eta^5$-Cp), **77**, and $WCo_2(\mu_3$-CTol$)(CO)_6(\mu$-diars$)(\eta^5$-Cp), **78**, respectively. The related molybdenum compound, $MoCo_2(\mu_3$-CC≡C^{t}Bu$)(CO)_6(\mu$-dppm$)(\eta^5$-Cp), **79**, synthesized analogously [29], had differences in both ^{31}P and IR spectra that suggested the μ-dppm ligand occupied different coordination sites than in **77**. Steric considerations led to the suggestion that in **79** the diphosphine lies on the same side of the MCo_2 plane as the alkylidyne, while in **77** the diphosphine lies on the opposite side of the MCo_2 plane. The reaction of $MoCo_2(\mu_3$-$CCO_2CHMe_2)(CO)_8(\eta^5$-Cp*) with dppe (dppe ≡ $Ph_2PCH_2CH_2PPh_2$) or



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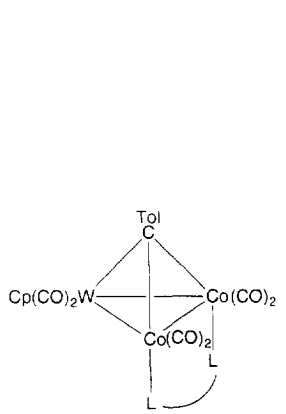
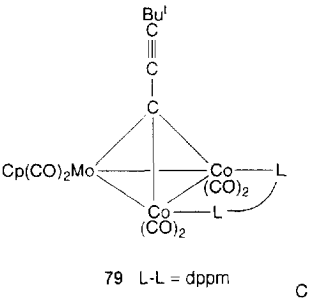
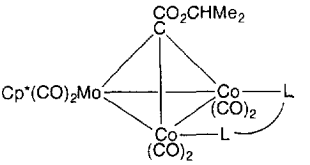
Scheme XIX.



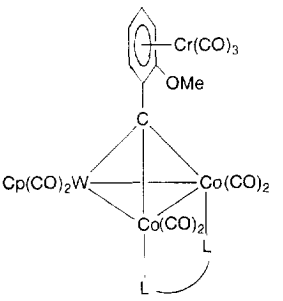
77 L-L = dppm
78 L-L = diars



79 L-L = dppm



80 L-L = dppe
81 L-L = arphos

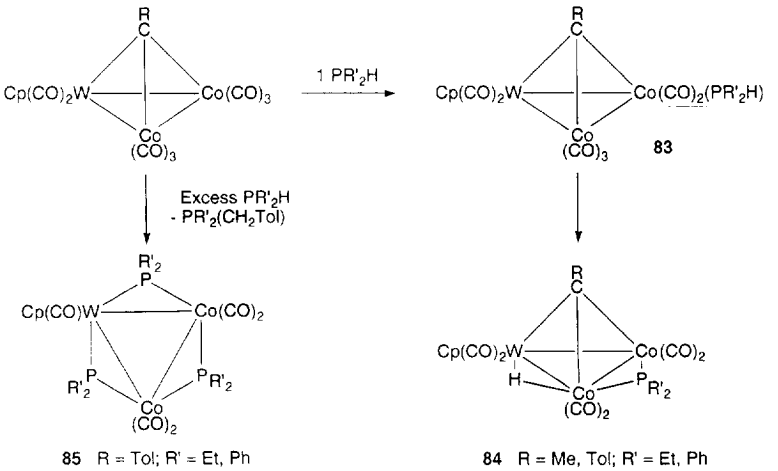


82 L-L = dppm

arphos (arphos ≡ $Ph_2AsCH_2CH_2PPh_2$) led to substitution of two carbonyls and the formation of $MoCo_2(\mu_3\text{-}CCO_2CHMe_2)(CO)_6(\mu\text{-dppe})(\eta^5\text{-Cp*})$, **80**, or $MoCo_2(\mu_3\text{-}CCO_2CHMe_2)(CO)_6(\mu\text{-arphos})(\eta^5\text{-Cp*})$, **81**, respectively [55]. The bidentate ligands in both compounds were thought to bridge the two Co atoms in equatorial sites, on the same side of the $MoCo_2$ triangle as the μ_3-CR moiety, by comparison to the analogous structurally characterized tricobalt μ_3-CCO_2CHMe_2, μ-arphos compound. The compound $CrMoCo_2\{\mu_3\text{-}\sigma, \sigma', \sigma'':\eta^6\text{-}2\text{-}CC_6H_4(OMe)\}(\mu\text{-dppm})(CO)_9(\eta^5\text{-Cp})$, **82**, containing a μ_3-aryl alkylidyne η^6-bonded to a $Cr(CO)_3$ moiety was also reported [16]. While the orientation of the diphos ligand with respect to the $MoCo_2$ plane was not discussed, based on similar steric arguments, the dppm ligand most likely coordinates in axial sites similar to **77**.

As described in Section 2.1, the reactions of trinuclear alkylidyne clusters containing cobalt with the organometallic dimethylarsenides, $ML_n\text{-}AsMe_2$, lead to the arsenic substituted clusters with a pendant ML_n group. Compounds of this type can be isolated before metal exchange is affected. For example, the reaction of $WCo_2(\mu_3\text{-}CMe)(CO)_8(\eta^5\text{-Cp})$ with $Fe(CO)_2(AsMe_2)(\eta^5\text{-Cp})$ led to a 71% yield of the arsenic substituted cluster containing a pendant iron moiety, $WCo_2(\mu_3\text{-}CMe)(CO)_7\{AsMe_2Fe(CO)_2(\eta^5\text{-Cp})\}(\eta^5\text{-Cp})$ [24].

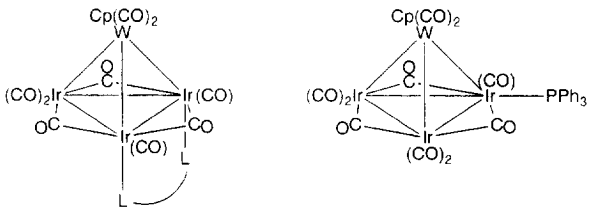
The reaction of $WCo_2(\mu_3\text{-CR})(CO)_8(\eta^5\text{-Cp})$ (R ≡ Me, Tol) with one equivalent of PR'_2H (R′ ≡ Ph, Et) led initially to the monosubstituted compounds $WCo_2(\mu_3\text{-CR})(CO)_7(PR'_2H)(\eta^5\text{-Cp})$, **83**, which rearranged to give μ-phosphido, μ-hydrido alkylidyne compounds, $WCo_2(\mu\text{-H})(\mu_3\text{-CR})(\mu\text{-}PR'_2)(CO)_6(\eta^5\text{-Cp})$, **84**. The reactions of $WCo_2(\mu_3\text{-CTol})(CO)_8(\eta^5\text{-Cp})$ or $WCo_2(\mu_3\text{-CTol})(CO)_7(PR'_2H)(\eta^5\text{-Cp})$



Scheme XX.

with excess PR'_2H ($R' \equiv Ph,Et$) led to the tris-phosphido bridged compounds, $WCo_2(\mu\text{-}PR'_2)_3(CO)_5(\eta^5\text{-}Cp)$, **85**, with loss of the alkylidyne as $PR'_2(CH_2Tol)$ (Scheme XX) [56].

The reactions of heterometallic tetranuclear clusters with phosphines have not been as thoroughly explored. The reactions of $WIr_3(CO)_{11}(\eta^5\text{-}Cp)$, **12**, with PPh_3, dppm ($dppm \equiv Ph_2PCH_2PPh_2$), dppe ($dppe \equiv Ph_2PCH_2CH_2PPh_2$), and dppa ($dppa \equiv Ph_2PC{\equiv}CPPh_2$) have recently been reported [57]. The products of the reactions with diphos reagents, $WIr_3(\mu\text{-diphos})(\mu\text{-}CO)_3(CO)_6(\eta^5\text{-}Cp)$ (diphos ≡ dppm, **86**; diphos ≡ dppe, **87**; diphos ≡ dppa, **88**), were structurally characterized and contained the bidentate ligands bonded to two iridium atom in axial positions. The solid state structures of all three compounds, and the solution infrared spectra for the dppm and dppe adducts, indicated carbonyl ligands bridging each of the three Ir–Ir bonds. The dppa adduct, **88**, did not display a solution infrared spectrum consistent with bridging CO ligands, suggesting it adopted a different structure in solution. Similarly, the solution infrared spectrum of the PPh_3 adduct, $WIr_3(\mu\text{-}CO)_3(CO)_7(PPh_3)(\eta^5\text{-}Cp)$, **89**, suggested only terminal CO ligands; however,



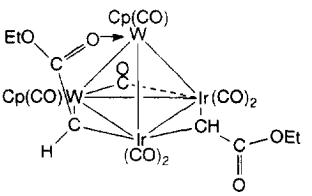
an incomplete X-ray analysis suggested it adopts a solid-state structure with bridging carbonyls about the Ir_3 plane. Furthermore, the phosphine ligand was coordinated in a radial rather than axial site, an observation that was supported by ^{31}P NMR data [58].

The tetranuclear heterometallic cluster $W_2Ir_2(CO)_{10}(\eta^5\text{-Cp})_2$, **14**, reacted with alkyl diazocarboxylates, N_2CHCO_2R (R ≡ Me, Et), to form the dicarbene species, $W_2Ir_2(CHCO_2R)_2(CO)_7(\eta^5\text{-Cp})_2$, **90** [59]. The R ≡ Et analog was structurally characterized and contained two distinct ethylcarboxylatocarbene ligands [60]. One carbene bridged the Ir–Ir bond, while the other bridged an Ir–W bond and also formed a donor bond from a carbonyl oxygen atom to the second tungsten atom.

3.4. Other substitution or condensation reactions

The syntheses of mixed-metal clusters denoted with an R in the reaction type column of Table 2 do not fall under any of the general reaction types discussed in Section 2 and are more adequately described in a reactivity section. These include thermolysis reactions in the presence of C_5H_6 or $(C_5H_6)_2$, formation of higher nuclearity clusters rather than vertex replacement in metal exchange reactions, and replacement of the R substituent in μ_3-CR alkylidyne clusters.

The thermolysis of $MoCo_2(\mu_3\text{-CR})(CO)_8(\eta^5\text{-Cp})$ in the presence of C_5H_6 or $(C_5H_6)_2$ led to loss of CO and formation of $MoCo_2(\mu_3\text{-CR})(\mu\text{-CO})(CO)_2(\eta^5\text{-Cp})_3$ (R ≡ Me, **49**; R ≡ CO_2CHMe_2) in moderate yields [44,61]. As mentioned in Section 2.4, **49** was also obtained by another route [43]. In the R ≡ Me case, the formation of a tetranuclear alkylidyne cluster $MoCo_3(\mu_3\text{-CMe})(\mu\text{-CO})_2(CO)_5(\eta^5\text{-Cp})_2$, **91**, was also observed.



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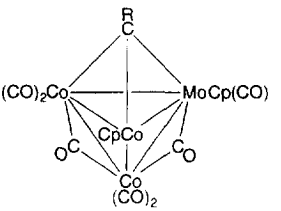

91 R = Me
92 R = CO_2Me

In some cases, metal exchange reactions provide products resulting from condensation of the cluster starting material with the metal exchange reagent rather than vertex replacement. For example, the tetranuclear clusters $MoCo_3(\mu_3\text{-}CR)(\mu\text{-}CO)_2(CO)_5(\eta^5\text{-}Cp)_2$ ($R \equiv Me$, **91**; $R \equiv CO_2Me$, **92**) were obtained in low yields along with metal exchange products $Mo_2Co(\mu_3\text{-}CR)(CO)_7(\eta^5\text{-}Cp)_2$ through reaction of $MoCo_2(\mu_3\text{-}CR)(CO)_8(\eta^5\text{-}Cp)$ with $Mo_2(CO)_6(\eta^5\text{-}Cp)_2$ [44]. More interestingly, the reaction of $Co_3(\mu_3\text{-}CMe)(CO)_9$ with $Na[W(CO)_3(\eta^5\text{-}Cp)]$ provided the tetranuclear cluster $WCo_3(\mu\text{-}CO)_3(CO)_8(\eta^5\text{-}Cp)$, **1**, lacking an alkylidyne ligand, as well as the metal exchange product, $W_2Co(\mu_3\text{-}CMe)(CO)_7(\eta^5\text{-}Cp)$ [62]. The reactions of $MCo_2(\mu_3\text{-}CMe)(CO)_8(\eta^5\text{-}Cp)$ ($M \equiv Mo$, W) with $Na_2[Ru(CO)_4]$ or $Na_2[Os(CO)_4]$ provided the tetranuclear $\mu_4\text{-}\eta^2$-alkyne clusters $M_2Co_2(\mu_4\text{-}\eta^2\text{-}C_2Me_2)(\mu\text{-}CO)_4(CO)_4(\eta^5\text{-}Cp)_2$ as minor products as well as the metal exchange products containing the group 8 metals [50]. As discussed in Section 3.1, the analogous cluster, **60**, was obtained through reaction of a tetranuclear W_2Co_2 cluster with PhC_2H [49].

The elaboration of alkylidyne functionalities on trinuclear μ_3-alkylidyne clusters was discussed in Section 3.2. However, the reaction of the methylidyne clusters, $MCo_2(\mu_3\text{-}CH)(CO)_8(\eta^5\text{-}Cp)$ with $HSiEt_3$ led to replacement of the H substituent by a silyl group, forming $MCo_2(\mu_3\text{-}CSiEt_3)(CO)_8(\eta^5\text{-}Cp)$ ($M \equiv Mo$, W) [62]. While the same compounds were obtained through reaction of $Co_3(\mu_3\text{-}CSiEt_3)(CO)_9$ with $Na[M(CO)_3(\eta^5\text{-}Cp)]$, both routes provided moderate yields of the silyl alkylidyne products.

3.5. Catalytic and related studies

The reaction of $MoCo_2(\mu_3\text{-}CCH_2CMe_3)(CO)_8(\eta^5\text{-}Cp)$, **48**, with 3–4 atm of H_2 in benzene led to hydrogenolysis and the formation $CH_2{=}CHCMe_3$. Data was presented that suggested the product was formed through radical organic intermediates [42].

The hydrogenation of CO over the supported clusters $M_2Rh(CO)_5(\eta^5\text{-}Cp)_3$, **44** ($M \equiv Mo$, W) led to methanol and other oxygen containing products more selectively than other conventionally prepared catalysts [36,63].

The hydroformylation of pent-1-ene was explored using $MoCo_2(\mu_3\text{-}CMe)(CO)_8(\eta^5\text{-}Cp)$ as a catalyst precursor [64]. Facile isomerization of pent-1-ene to internal olefins was seen, but moderate normal-to-branched selectivity was observed for the hydroformylation product.

The tetranuclear clusters, $MIr_3(CO)_{11}(\eta^5\text{-}Cp)$, $M_2Ir_2(CO)_{10}(\eta^5\text{-}Cp)_2$, **11–14** ($M \equiv Mo$, W), were studied as precursors to alumina supported heterometallic catalysts [2,11]. Evidence for heterobimetallic interactions maintained in the activated materials was adduced from selectivity ratios observed for n-butane hydrogenolysis and in part from EXAFS [2b] analysis.

4. Summary and conclusions

A large number of synthetic methods are available for the synthesis of heterometallic group 6–group 9 cluster compounds. While the methods discussed provide the

desired mixed-metal clusters, the reactions are often not very selective for one product and adequate separation schemes are a necessity. Of all the synthetic methods, the use of mononuclear alkylidyne precursors leads to heteronuclear clusters most cleanly and consistently. It is interesting that there is no reported example of a tetranuclear mixed-metal group 6–group 9 cluster containing rhodium or chromium, so specific synthetic targets remain.

Studies of the reactivity of group 6–group 9 clusters provide many opportunities for further exploration. While the reactions of tetranuclear clusters with alkynes have been reported in several cases, similar reactions with trinuclear alkylidyne clusters have been much less explored. The protonation of some trinuclear alkylidyne clusters has been reported, and it would be of interest to extend the study to the isolobal electrophiles from the copper subgroup, $M(PPh_3)^+$ ($M \equiv Cu$, Ag, Au). In this regard, it appears that no reactions of these tetranuclear clusters with electrophiles have been reported.

Acknowledgments

M.C.C. thanks the Department of Chemistry for a fellowship funded by the Lubrizol Corporation. This work was also supported by a grant from the Inorganic, Bioinorganic, and Organometallic Chemistry program of the National Science Foundation.

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