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Alkyne-Substituted Homo- and Heterometallic Carbonyl Clusters of the Iron, Cobalt, and Nickel Triads

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I. Introduction

This review deals with the alkyne-substituted carbonyl cluster complexes of the iron, cobalt, and nickel

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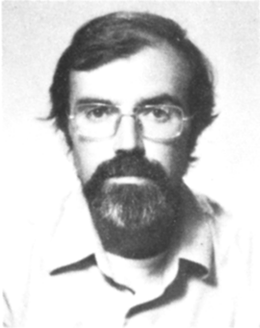

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triads, and with some related clusters obtained by reactions of alkenes, dienes, and isonitriles. Also some clusters containing *alkyne-derived* ligands, such as acetylide-, alkenylidene-, and alkylidyne-substituted complexes, will be considered. These can be formed, indeed, upon reaction of the alkynes coordinated to the clusters.

The chemistry of these derivatives has been developed in recent years and considerable material is now available to attempt systematic discussion.

Several review articles, and books dealing with related aspects of this chemistry have recently been published; some of these take into account alkyne derivatives. Thus, metal–metal bonding,[1] metal–cluster preparation,[2] growth, and stoichiometry,[3] and chemistry[4] have been recently reviewed, as well as the alkyne–cobalt chemistry.[5]

The interest in the alkyne–cluster chemistry is due to two main reasons, which will certainly influence the general setting of this work.

The first one is the wish of gaining a better knowledge of the interactions of small molecules with metal clusters—the alkyne complexes (and in particular the monoalkyne derivatives) being considered as useful "models" for the chemisorption of small molecules on metal surfaces[6]—and for the carbon–carbon triple-bond "activation" and reduction.[7] Also considerable analogies can be found between the coordination modes of alkynes and of carbon monoxide to several metal centers; in particular, the alkynes show a greater variety of interactions resulting from the possibility of varying the substituents, and hence the polarity of the triple bond.

The other main reason for interest in the alkyne–cluster chemistry is the importance of acetylene as feedstock for industrial organic chemistry. Indeed, after a period of predominant importance followed by a sharp decline of interest due to the availability of "cheaper, more readily accessible and workable olefins",[8] acetylene is slowly becoming again an attractive source of chemicals in view of the present shortage in oil supplies.

New interest in coal is presently shown by many countries; thus the CO/H_2 mixture from coal gasification[9] and the acetylene obtained either by conventional or by new methods[10] are at present of great importance.

In this light, the activation and reactions of CO[11] and of alkynes on metal clusters is already considered of great importance for a better understanding of catalytic processes and for the development of new catalysts. In particular, the pre-World War Two acetylene chemistry was based mainly on heterogeneous or on homogeneous monometallic catalysts and only a few studies on the reactivity of acetylene coordinated to clusters had been made until recently.

At present a considerable number of alkyne-substituted clusters is known; those reported, until the end 1981 are given in Table I together with some chemically or structurally related complexes.

Often clusters containing a different number of metals or a different number of alkyne (or alkyne-derived) ligands are structurally related. This makes it difficult to order the complexes on the basis of structural analogies.

For this reason we preferred an ordering based on increasing cluster nuclearity; in each triad the metals are disposed in order of increasing weight. The homometallic complexes precede the heterometallic ones; in the formula of the latter the metals are ordered on the basis of increasing weight. Finally, the number of alkyne substituents has been considered.

Noncluster, polymetallic alkyne derivatives are also known; some of these contain acetylides or alkynes bonded to several metallic centers in the same way as found for the cluster complexes, and in some instances these will be considered in the following discussion.

Examples of these complexes are given in references.[160,161]

As a preliminary comment, Table I shows that the greater part of the alkyne clusters are trinuclear or tetranuclear; few examples are known of 5- and 6-atom clusters, and only one 7-atom derivative is known. At the present state of the art a considerable number of structural studies is available, which allows a discussion based on well-established parameters for the solid state. On the other hand, a considerable lack of fluxionality and mass spectrometric studies is still observed.

Some isonitrile (or isonitrile-derived) complexes that show comparable bonding characteristics are listed in Table II.

II. Synthesis of the Complexes

The preparative methods are the usual ones for substituted carbonyl clusters, e.g.: CO substitution (thermal or photochemical, assisted by Me_3NO), rearrangement or reactions of the coordinated ligands, reaction of "closo" tetrahedral clusters with alkynes, and "metal fragment condensation" induced by alkynes, ligand or metal exchange between complexes, oxidative addition–reductive elimination of C–H and H_2, M–H addition to unsaturated molecules, protonation of neutral complexes, reaction of carbonyl anions towards organic substrates, pyrolysis, metal vapor syntheses, etc.

A. Substitution of the CO Groups

1. Thermal Substitution

For the trimetallic carbonyls of the iron triad this is usually the first reaction step (in hydrocarbons: refluxing pentane to octane temperature). Complexes of general formula $M_3(CO)_{10}L$ or $HM_3(CO)_{10}(L\text{–}H)$ and $M_3(CO)_9L$ or $HM_3(CO)_9(L\text{–}H)$ are usually obtained; the alkyne acts as a 4- to 6-electron donor, depending upon its substitution.

When considering the CO-substitution reactions four "basic" types of alkynes should be considered, namely:

"Symmetrical" alkynes, with aromatic substituents such as C_2Ph_2, are coordinated without rearrangement.

Alkyl-substituted internal alkynes, such as C_2Et_2 or C_2MeEt, which in some instances are coordinated without drastic change (on iron), but usually isomerize to "allenyl" and "allylic" ligands, with transfer of one hydrogen on the cluster.

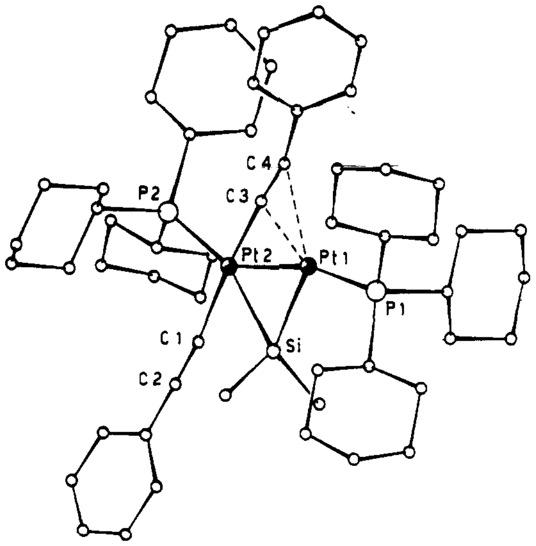
Terminal alkynes, HC_2R, which usually split into bridging hydride and multisite bound acetylides. Similar behavior has also been observed for ClC_2Ph.[176]

Phosphinoalkynes, Ph_2PC_2R, which split into bridging phosphido ligands, and multisite bound acetylides.

Functionalized alkynes also give oxidative addition to $Ru_3(CO)_{12}$; in particular $MeC{\equiv}CCH_2NMe_2$ gives high yields of the "allenic" $HRu_3(CO)_9(MeC{=}C{=}CHNMe_2)$ and of the "allylic" $HRu_3(CO)_9(MeC{\cdots}CH{\cdots}CNMe_2)$ clusters.[177]

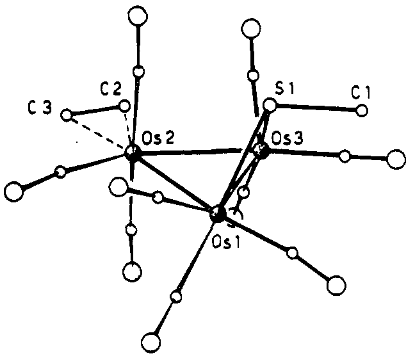
The behavior of the hydroxyalkynes is discussed in the section on the reactivity.

CO substitution also occurs on phosphine-substituted ruthenium clusters. Thus, $Ru_3(CO)_9(PMe_3)_3$ reacts with $HC_2CBu\text{-}t$ to give $HRu_3(CO)_7(PMe_3)_3(C_2Bu\text{-}t)$.[178] Whereas on the unsubstituted carbonyl cluster three CO's were displaced, in the substituted cluster only two are removed.



$Pt_2(C_2Ph)_2(SiMe_2)(PR_3)_2$ (ref. 179)

1



$HOs_3(CO)_9(C_2H_4)(SMe)$ (ref. 79)

2

Figure 1. Complexes in which acetylide or alkene interact with one metal atom (bonding modes A and B).

Usually, the interaction of the alkyne occurs with more than one metal atom: no example of a "linear" acetylide on a cluster is known, and one only has been reported for a bimetallic complex[179] (Figure 1, 1). On the contrary, the isonitriles apparently show a greater tendency to coordinate linearly. For both the alkynes and the isonitriles, it is difficult to stop the reactions at the stage of simple substitution: with alkynes usually oligomerization occurs; few examples of complexes containing two independently coordinated alkynes are known. Among these are $Fe_3(CO)_8(C_2Ph_2)_2$ (violet isomer),[19] $Pt_3(PEt_3)_4(C_2Ph_2)_2$ (Figure 2, 6),[105] and $Fe_4(CO)_{11}(HC_2Et)_2$ (Figure 9, 28).[125] The isonitriles rearrange, especially in the presence of hydrogen, to more complex ligands (Table II).

2. Photochemical or "Assisted" Substitutions

Until now, very few photochemical experiments have been performed; there is, however, an increasing interest toward the photochemical syntheses of clusters, hence it is predictable that this method will soon be used to

TABLE I. Alkyne-Substituted Carbonyl Clusters of the Iron, Cobalt, and Nickel Triads

		references			
entry	complex	prepn, IR ^{1}H NMR	^{13}C NMR^{a}	mass spectrum^{a}	X-ray (or neutron) structure
	A. Trinuclear Complexes				
	Iron				
1	$Fe_3(CO)_{10}(C_2H_2)$	12			
2	$Fe_3(CO)_9(C_2Ph_2)$	13, 14			15
3	$Fe_3(CO)_9(C_2Et_2)$	16		16	
4	$(Cp)Fe_3(CO)_7(C_2Ph)$	17			17
5	$Fe_3(CO)_8(C_2Ph_2)_2$, violet isomer	13	18		19
6	$Fe_3(CO)_8(C_2Ph_2)_2$, black isomer	13	18	20	19
7	$Fe_3(CO)_8(RC_2R')$, black isomer	21, 22		20	
8	$Fe_3(CO)_8(R''C_2R'')_2$	23			
9	$Fe_3(CO)_8(L_2\text{-}H_2O)$	24			
10	$Fe_3(CO)_7C_4(CF_3)_2(COOMe)L_2$	25			25
11	$Fe_3(CO)_8(HC_2Me)_3$	22	22	20	22
12	$Fe_3(CO)_8(HC_2R)_4$	26	26	27	26
13	$Fe_3(CO)_7(HC_2Et)_4$	28			28
14	$(Cp)Fe_2Ru(CO)_6(PPh_3)(C_2Ph)$	108			
15	$FeRu_2(CO)_8(C_2Ph_2)_2$	110		110	
16	$(Cp)FeCo_2(CO)_6(C_2R)$	111			
17	$FeCo_2(CO)_9(C_2Ph_2)$	112			
18	$FeCo_2(CO)_9(C_2Et_2)$	113			113
19	$HFeCo_2(CO)_9CR^{c}$	114			
20	$H_2Fe_2Co(CO)_9CR^{c}$	114			
21	$(Cp)FeCoNi(CO)_6(PhC_2COOR)$	115			115
22	$(Cp)(C_7H_9)FeRhW(CO)_6(CR)^{c,d}$	116			116
23	$(Cp)_2FeNiMo(CO)_3(PhC_2COOR)$	115	115		115
24	$(Cp)Fe_2Ni(CO)_6(C_2R)$	62, 118		117	118
25	$[(Cp)Fe_2Ni(CO)_6(C_2R_2)]^-$	119			119
26	$(Cp)_2FeNi_2(CO)_3(RC_2R')$	120			120
27	$(Cp)_2FeNi_2(CO)_3(RC_2COOR)$	115			
28	$(Cp)Fe_2Ni(CO)_7(CCH_2R)$	62, 120			
29	$(Cp)(PEt_3)FePtW(CO)_6(CR)^{c,d}$	116			116
30	$(Cp)Fe_2W(CO)_7(CC_6H_4Me\text{-}4)(Me_3SiC_2SiMe_3)$	332			332
31	$(Cp)_2FeW_2(CO)_6[C_2(C_6H_4Me)_2]$	327			327
	Ruthenium^{e}				
32	$Ru_3(CO)_{11}(PPh_2C_2R)$	29			
33	$Ru_3(CO)_{10}(C_2Ph_2)$	52			
34	$Ru_3(CO)_9(C_2Ph_2)$	30			
35	$Ru_3(CO)_9(RC_2R')$	31, 32			
36	$HRu_3(CO)_9C_2\text{-Bu-}t$	33	34		35, 36
37	$HRu_3(CO)_9C_2R$	33			
38	$HRu_3(CO)_7(C_6H_{10})(C_2\text{Bu-}t)$	235			235
39	$(PPh_2)Ru_3(CO)_9(C_2R)$	29			29
40	$Ru_3(CO)_8(PPh_2)(C_2\text{Bu-}t)$	29			29
41	$HRu_3(CO)_9(RCHCCR')$	39	39		40
42	$HRu_3(CO)_9(RCCHCR')$	37	37		38
43	$HRu_3(CO)_9(C_nH_m)^{c}$	41			41
44	$HRu_3(CO)_9(PhC{\cdot}C_6H_4)^{c}$	42			42
45	$HRu_3(CO)_9(C_5H_5)^{c}$	43	43		
46	$HRu_3(CO)_9(C_5H_7)^{c}$	43	43		
47	$HRu_3(CO)_9[HCCHCC(=O)OH]$	44	44		44
48	$HRu_3(CO)_9[HCCHCCH_2OH]$	44	44		
49	$HRu_3(CO)_9[C_2RR'(OH)]$	44	44		
50	$HRu_3(CO)_9[C_2C(=CH_2)Ph]$	45			45
51	$HRu_3(CO)_{9-n}(C_2R)(PR_3)_n$	67, 68	67		67
52	$HRu_3(CO)_{9-n}(RCCHCR')(PR_3)_n$	70^{b}	70^{b}		
53	$H_2Ru_3(CO)_9(C_2H_2)$	46			
54	$H_2Ru_3(CO)_9(HC_2\text{Bu-}t)$	47			
55	$H_2Ru_3(CO)_9(C_nH_m)^{c}$	41, 48	48		
56	$H_3Ru_3(CO)_9CMe$	49	50		51
57	$H_3Ru_3(CO)_9CCH_2\text{Bu-}t$	47		47	47
58	$(Cp)Ru_3(CO)_8CCH_2R$	62			
59	$Ru_3(CO)_8(C_2Ph_2)_2$, violet isomer	30			
60	$Ru_3(CO)_8(C_2Ph_2)_2$, orange isomer	30			
61	$Ru_3(CO)_8(L_2\text{-}H_2O)$	24			
62	$Ru_3(CO)_8(C_5H_6)_2$	53			53
63	$Ru_3(CO)_8[(CF_2)Ph_2PC{=}CPPh_2]_2$	54			
64	$Ru_3(CO)_9(C_2Ph_2)_3$	30, 31			
65	$Ru_3(CO)_8(HC_2\text{Bu-}t)_3$	57			57
66	$Ru_3(CO)_8(C_{10}H_{15})$	56			56
67	$Ru_3(CO)_8(HC_2\text{Bu-}t)(C_5H_6)_2$	55			55
68	$Ru_3(CO)_6(C_2\text{Bu-}t)_2(PPh_2)_2(Ph_2PC_2\text{Bu-}t)$	58			58
69	$Ru_3(CO)_7(C_2\text{Bu-}t)[PhC_2(H)Ph](C_2Ph_2)$	59			59
70	$Ru_3(CO)_6(C_{12}H_{20})(C_{13}H_{20}O)$	60			60
71	$Ru_3(CO)_5(C_{12}H_{20})(C_{19}H_{30}O)$	61			61

TABLE I (*Continued*)

entry	complex	references			
		prepn, IR ^1H NMR	^{13}C NMR^a	mass spectrum^a	X-ray (or neutron) structure
72	$[(Ru_3(CO)_9(C_2Bu\text{-}t)(HgBr)]_2$	121			121
	Osmium				
73	$Os_3(CO)_{10}(HC_2Ph)$	63			
74	$Os_3(CO)_{10}(C_2Ph_2)$	64			64
75	$Os_3(CO)_{10}(C_4H_6)$	65			
76	$Os_3(CO)_{10}(RC_2R')$	66			
77	$HOs_3(CO)_{10}(RC{=}CHR)$	69, 74, 75			
78	$HOs_3(CO)_{10}(C_2Ph)$	74			
79	$H_2Os_3(CO)_{10}(C_2Ph)$	74			
80	$HOs_3(CO)_{10}R^c$	69			
81	$HOs_3(CO)_{10}(CH{=}CH_2)^c$	68			68
82	$HOs_3(CO)_{10}(CH{=}CHEt)$	317			317
83	$HOs_3(CO)_{10}(CCF_3{=}CHCF_3)(PEt_3)$	72			72
84	$HOs_3(CO)_{10}(CPh{=}CHPh)$	326	326		326
85	$HOs_3(CO)_{10}(CF_3C_2HCF_3)$	218			218
86	$HOs_3(CO)_{10}(CHCH{=}NEt_2)^c$	70,^{a} 73			70, 73
87	$HOs_3(CO)_{10}(CHCH_2PMe_2Ph)$	71			71
88	$HOs_3(CO)_9(C_3H_2OR)$	331			331
89	$HOs_3(CO)_9(C_6H_7)$	76			
90	$HOs_3(CO)_9(C_2R)$	32, 63, 75			
91	$HOs_3(CO)_9(C\cdot CH_2Ph)$	63			
92	$HOs_3(CO)_9(C{=}CH_2)$	74, 75			
93	$HOs_3(CO)_9(RCH{=}CHR)^c$	74			
94	$HOs_3(CO)_9(C_4H_5)$	74			
95	$HOs_3(CO)_9(AsMe_2)(C_6H_4)$	325	325		325
96	$HOs_3(CO)_9(C_6H_3Me)^c$	77			
97	$HOs_3(CO)_9(C_9H_{13})^c$	78			78
98	$HOs_3(CO)_9(C_2H_4)(SMe)^c$	79			79
99	$H_2Os_3(CO)_9(C{=}CHPh)$	69, 75			
100	$H_2Os_3(CO)_9(HC{=}CMe)$	69, 75			
101	$H_2Os_3(CO)_9(RC{=}CR)$	69, 75			
102	$H_2Os_3(CO)_9(CCH_2)^c$	80			80
103	$H_2Os_3(CO)_9(C_nH_m)^c$	80			
104	$H_2Os_3(CO)_9(C_5H_4)^c$	43			
105	$H_2Os_3(CO)_9(C_2RR')^c$	81			
106	$H_3Os_3(CO)_9CMe$	82	50		
107	$Os_3(CO)_9(RC_2R')$	32, 63			63
108	$Os_3(CO)_9(HC_2Bu\text{-}t)$	32			
109	$Os_3(CO)_9(C_2Ph_2)(CH_2)$	330			330
110	$Os_3(CO)_9[(HC_2R)_2(CO)]$	63			83
111	$Os_3(CO)_9[(RC_2R')_2(CO)]$	74, 84			
112	$Os_3(CO)_9(C_2Ph_2)_2$	85			86
113	$Os_3(CO)_9(RC_2R')_2$	63, 74			
114	$HOs_3(CO)_8(C_2Ph_2)(PhC_2C_6H_4)$	87			88
115	$HOs_3(CO)_8L$	89			
116	$Os_3(CO)_7(C_2Ph_2)_3$	85			90
117	$Os_3(CO)_7(RC_2R')_3$	63, 85			
118	$OsPt_2(CO)_5(PPh_3)_2(C_2Me_2)$	329			329
119	$(Cp)_2W_2Os(CO)_7[C_2(C_6H_4Me)_2]$, two isomers	327, 328			327, 328
	Cobalt^f				
120	$Co_3(CO)_9CR^b$	91	92	93	91, 221
121	$Co_3(CO)_{9-n}(L_n)(CR)$	91, 95, 96			91, 95
122	$Co_3(CO)_9C\cdot CHR^+$	94			
123	$(Cp)_2Co_3(CO)_4(CMe)$	97			97
124	$(Cp)_3Co_3(CR)(CR')$	98			98
125	$(Cp)_3Co_3(CR)_2$	101	101		
126	$(Cp)_3Co_3(C_4F_6)$	99		99	
127	$(Cp)_3Co_3(C_4F_6)(CO)$	99		99	
128	$(Cp)_3Co_3(CO)(C_{14}H_{20})$	100	100		
129	$(Cp)Co_2M(CO)_8(CPh)$,^{c} M = Cr, Mo, W	122			122
	Rhodium^g				
130	$(Cp)_3Rh_3(CR)_2$	101	101		
131	$(Cp)_3Rh_3(CO)(C_2Ph_2)$	106			106
132	$(Cp)_3Rh_3(CO)[C_2(C_6F_5)_2]$	106, 107			106
133	$RhAg_2(PPh_3)(C_2C_6F_5)_5$	124			124
	Iridium				
134	$Ir_3(CO)_9(CR)$	102			
	Nickel^h				
135	$(Cp)_3Ni_3(CR)$	103, 104			
136	$(C_8H_8)Ni_3(CO)_3[C_2(CF_3)_2]$	109	109		109
137	$(Cp)NiRu_2(CO)_6(C_2R)$	120			
138	$(Cp)NiRu_2(CO)_7(C\cdot CH_2R)$	120			
139	$(Cp)_2Ni_2Ru(CO)_3(C_2Ph_2)$	120			120
140	$(Cp)_2NiRu_2(CO)_4(C_2Ph_2)$	123			123
	Palladium				

TABLE I (*Continued*)

		references			
entry	complex	prepn, IR ^1H NMR	^{13}C NMR[a]	mass spectrum[a]	X-ray (or neutron) structure
	Platinum[i]				
141	$Pt_3(Et_3P)_4(C_2Ph_2)_2$	105			105
	B. Tetranuclear Complexes				
	Iron				
142	$Fe_4(CO)_{11}(HC_2Et)_2$	125			125
143	$FeRu_3(CO)_{12}(C_2Ph_2)$	127			127
144	$FeRu_3(CO)_{12}(RC_2R')$	127			
145	$HFeCo_3(CO)_9(C_2Ph_2)$	128			
146	$(Cp)_2Fe_2Ni_2(CO)_6(RC_2R')$	62, 115, 274		129	274
147	$FeCo_3(CO)_9(C_2Ph_2)(CPh{=}CHPh)$	298	298	298	298
	Ruthenium[j]				
148	$Ru_4(CO)_{12}(C_2Ph_2)$	130			131
149	$Ru_4(CO)_{12}[MeC_2C(H)Me_2]$	56			
150	$Ru_4(CO)_{12}(C_nH_m)$[c]	132, 133, 134			133, 134
151	$(OR)Ru_4(CO)_{10}(PPh_2)[C_2(H)Pr\text{-}i]$, R = H, Et	135			135
152	$Ru_4(CO)_{11}(RC_2R')(R''C_2R''')$	130			
153	$Ru_4(CO)_{11}(C_8H_{10})$[c]	136			136
154	$Ru_4(CO)_9(C_6H_6)(C_6H_8)$[c]	137			137
155	$Ru_4(CO)_9(C_{13}H_{14})$[c]	138			139
	Osmium				
156	$Os_4(CO)_{12}(C_2H_2)$	140			140
157	$Os_4(CO)_{12}(HC_2Et)$	140			140
158	$H_2Os_4(CO)_{11}(HC_2R)$	141			
159	$H_3Os_4(CO)_{11}(HC_2HR)$	141			
160	$H_3Os_4(CO)_{11}(RC_2R')$	142			142
	Cobalt[k]				
161	$Co_4(CO)_{10}(RC_2R)$	143	18		143
162	$Co_4(CO)_9(C_6H_6)$[c]	144			144
163	$Co_3Ru(CO)_9(PPh_2)(HC_2Bu\text{-}t)$	145			145
	Rhodium				
164	$Rh_4(CO)_{10}(RC_2R)$	26			
	Iridium				
165	$H_4Ir_4(CO)_4(HC_2Me)$	146			146
166	$Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$	147			147
167	$Ir_4(CO)_8[C_2(COOMe)_2]_4$	148			148
	Nickel[l]				
168	$Ni_4(CO)_4[C_2(CF_3)_2]_3$	109			109
169	$Ni_4(CHR)_4(RC_2R)_3$	149			149, 150
170	$Ni_4(CHR)_6(RC_2R)$	149			149
171	$(Cp)NiRu_3(H)(CO)_9[C_2(H)R]$	151, 152			151, 152
172	$(Cp)NiRu_3(CO)_8(C_nH_m)$	153			153
173	$(Cp)NiRu_3(CO)_9(C_2Ph_2)$	120			
174	$(Cp)_2Ni_2Ru_2(CO)_6(C_5H_6)$	154			154
	C. Pentanuclear and Higher Nuclearity Derivatives				
175	$Ru_5(CO)_{13}(PPh_2)(C_2Ph)$	155			155
176	$NiRu_4(CO)_9(PPh_2)_2(C_2Pr\text{-}i)_2$	156			156
177	$Ru_6(C)(CO)_{15}[Me(CH_2)_4Me]$	134			134
178	$Os_6(CO)_{16}(C_2Me_2)C$[c]	157			157
179	$Os_6(CO)_{16}(CMe)_2$	157			157
180	$[Co_3(CO)_9C]_xL$[c]	91			91
181	$Ir_2Cu_4(PPh_3)_2(C_2Ph)_8$	158			158
182	$Ir_7(CO)_{12}(C_8H_{12})(C_8H_{11})(C_8H_{10})$	159			159

[a] References are reported only for the papers particularly concerning ^{13}C NMR or mass spectral studies of the complexes. [b] Series of complexes with different R groups, only in part obtained from alkynes. [c] Complexes containing ligands different from the alkynes, or obtained from other starting ligands, but showing close structural properties with the alkyne clusters. [d] Obtained from metal carbynes. [e] See also entries 14, 15, and 137-140. [f] See also entries 16-21. [g] See also entry 22. [h] See also entries 21 and 23-28. [i] See also entries 29 and 118. [j] See also entries 143-144, 163 and 171-174. [k] See also entries 145 and 147. [l] See also entry 146.

a greater extent with the alkyne derivatives.

CO substitution under mild conditions, in the presence of anhydrous Me_3NO, has been shown to occur by Carty and co-workers,[29] who obtained $Ru_3(CO)_{11}(PPh_2C_2R)$ monosubstituted derivatives, in which the alkyne acts as a formal 2-electron donor; this complex is one of few examples of such behavior. The monosubstituted derivative, upon thermal rearrangement, gives an interesting series of trimetallic clusters characterized by different modes of coordination of the alkyne, and a pentanuclear complex.[58,155] When hydrated (or moist) Me_3NO is used a surprising tetrametallic cluster with a vinylidene substitutent as well as a triply bridging OH substitutent is obtained.[135]

This examplifies the great potential of this method, which also allows greater selectivity in the product distribution with respect to the simple thermal substitutions.

The reaction scheme for the synthesis of the above products is given in Scheme I.

Scheme I

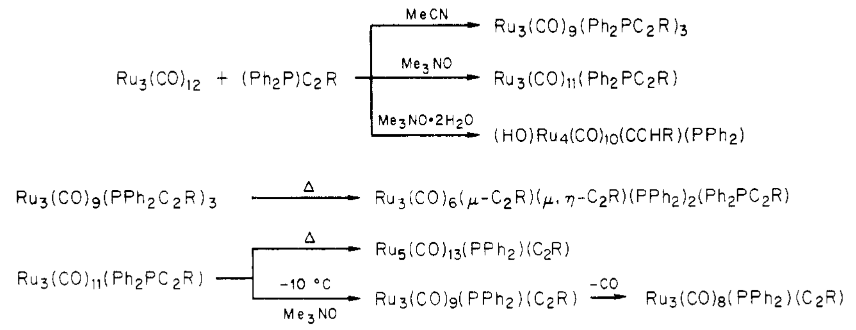


TABLE II. Nitrile and Isonitrile (or Derived therefrom) Complexes Structurally Related to the Alkyne-Carbonyl Derivatives

complex	ref prepn, IR, ^{1}H NMR	 X-ray (or neutron) structure
$Ru_3(CO)_{11}(CNBu\text{-}t)$	162	
$Fe_3(CO)_9(NCCH_3)$	163	
$HFe_3(CO)_9(HNCCH_3)$	163	
$HFe_3(CO)_9(NC(H)CH_3)$	163	
$H_2Fe_3(CO)_9(NCH_2CH_3)$	163	
$HRu_3(CO)_9(HC{=}NBu\text{-}t)$	162	
$H_2Os_3(CO)_{10}(CNBu\text{-}t)$	164	164
$H_2Os_3(CO)_9(CNBu\text{-}t)$	164	164, 166
$H_2Os_3(CO)_9(HC{=}NPh)$	164	164, 166
$HOs_3(CO)_9(HC{=}NPh)[P(OMe)_3]$	164	164
$HOs_3(CO)_{10}(C{=}N(H)Bu\text{-}t)$	165	165
$HFe_3(CO)_{10}(CNMe_2)$	167	167
$HRu_3(CO)_{10}(CNMe_2)$	168	168
$Fe_3(CO)_{10}(CNBu\text{-}t)_2$	170	170
$Pt_3(CNR)_6$	171	171
$Ir_4(CO)_{11}(CNBu\text{-}t)$	172	172
$Ni_4(CNBu\text{-}t)_7$	173	173
$Os_6(CO)_{16}(CNBu\text{-}t)_2$	174	174
$Os_6(CO)_{18}(CNR)_2$	175	175

B. Rearrangements and Reactions of the Coordinated Alkynes

Two separate cases have to be considered, namely, the rearrangement of a single alkyne molecule, after CO substitution and coordination to the cluster, and the reaction of a coordinated alkyne with other alkynes or ligands.

"Ligand tautomerism" can be observed when C_2Et_2 is reacted with $Ru_3(CO)_{12}$; the first reaction product is an "allenic" hydride obtained upon isomerization of the alkyne.[39,40] Moderate warming of this cluster leads to the "allylic" isomer (Figure 6, 18, 17).[37,38]

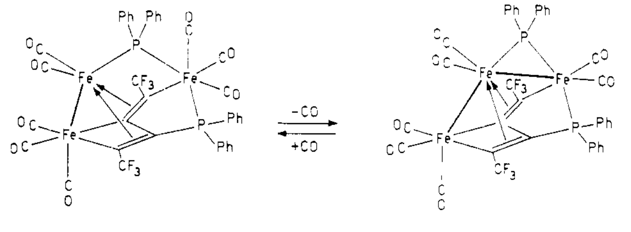
By reaction of $HRu_3(CO)_9C_2Bu\text{-}t$ with the cyclopentadiene ligand, $(Cp)Ru_3(CO)_8CCH_2Bu\text{-}t$ is obtained, which shows another alkyne-to-cluster bonding and, moreover, the alkyne itself has been hydrogenated.[62]

Reaction with excess alkyne usually leads to polysubstituted products and finally to complexes of lower nuclearity. The main reactions on clusters are formation of 5- and 6-membered metallacycles, sometimes with cluster opening,[13,19] activation and cleavage of a C≡C bond,[28,98] insertion of an alkyne into a M–C(σ) bond already formed[57] or nucleophilic addition of an alkyne on the C(σ).[59]

All these processes will be discussed in detail when considering the reactivity of the coordinated alkynes.

Cluster formation or opening can be favored by the presence of ligands; an example of formation of an open cluster in the presence of an organic ligand is found in Scheme II; displacement of a CO molecule and formation of a new metal–metal bond are observed.[312] On the other hand, phosphine substitution on a closed metal cluster can induce a cluster opening, either in case of homometallic derivatives[72] or heterometallic clusters.[180]

Scheme II



C. Reactions of Tetrahedral Clusters with Alkynes and Condensation of "Metal Fragments" Induced by Alkynes

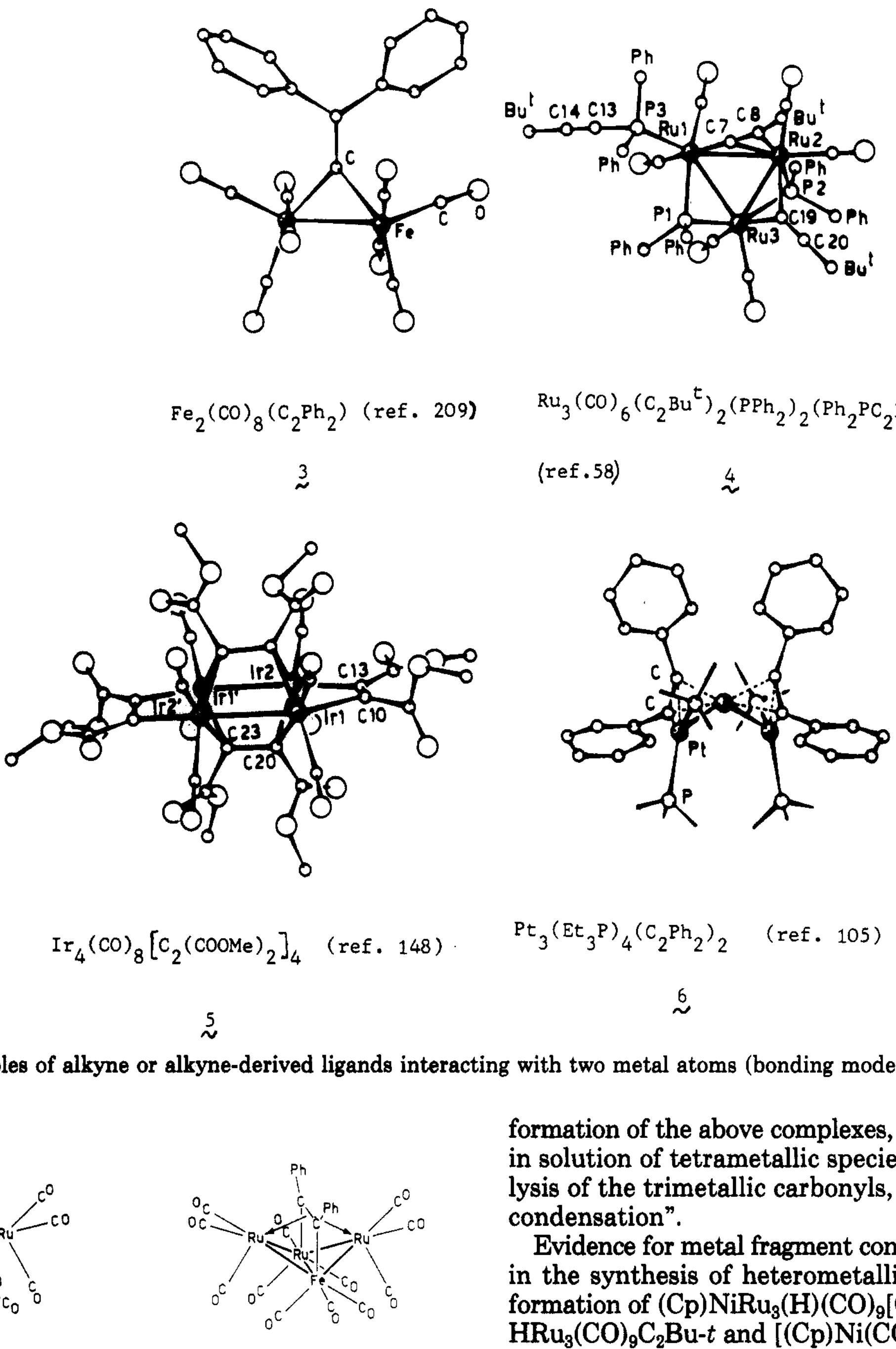
Whereas tetrahedral clusters can react with isonitriles by simply substituting CO ligands, and with cyclic dienes in the same way,[180,181] the common reaction pattern in the presence of alkynes is a cluster opening to give butterfly structures.[2]

Indeed, tetrahedral alkyne-substituted clusters are not common and are usually obtained by indirect reaction pathways.[109,143,150] Cluster opening to butterfly structures was first observed by treating $Co_4(CO)_{12}$ with stoichiometric amounts of alkynes; complexes $Co_4(CO)_{10}(RC_2R')$ were obtained,[143] the yields depending upon the substituents R and R′.[182] Excess of alkynes results in the formation of $Co_2(CO)_6(C_2RR')$ complexes, with cluster demolition.[182] Rhodium homologues have been reported,[183] which can be obtained by "carbyne coupling",[184] that is the opposite of the C≡C bond breaking

$$2M_3(CO)_6(CD_3)(\text{arene}) \xrightarrow{110\ ^\circ\text{C}} M_4(CO)_{10}[C_2(CD_3)_2] + 2\ M + 2CO + 2\ \text{arene}$$

Isomers $FeRu_3(CO)_{12}(RC_2R')$[127] showing either "hinge–apex" metal isomerism, and "alkyne" isomerism with respect to the heterometallic hinge were obtained from $H_2FeRu_3(CO)_{13}$. In contrast, only "alkyne isomerism" and no hinge–apex isomerism was detected for the $(Cp)NiRu_3(CO)_8(C_6H_9)$ complexes.[153] These isomers are depicted in Scheme III.

Sometimes an "extreme" situation is found, that is the total flattening of a tetrahedral metal core to give



$Fe_2(CO)_8(C_2Ph_2)$ (ref. 209)

3

$Ru_3(CO)_6(C_2Bu^t)_2(PPh_2)_2(Ph_2PC_2Bu^t)$

(ref.58) 4

$Ir_4(CO)_8[C_2(COOMe)_2]_4$ (ref. 148)

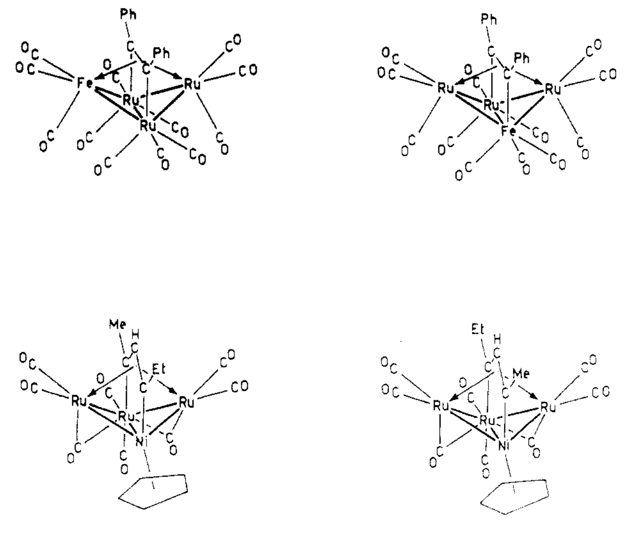
5

$Pt_3(Et_3P)_4(C_2Ph_2)_2$ (ref. 105)

6

Figure 2. Examples of alkyne or alkyne-derived ligands interacting with two metal atoms (bonding modes C, D, E, and F).

Scheme III



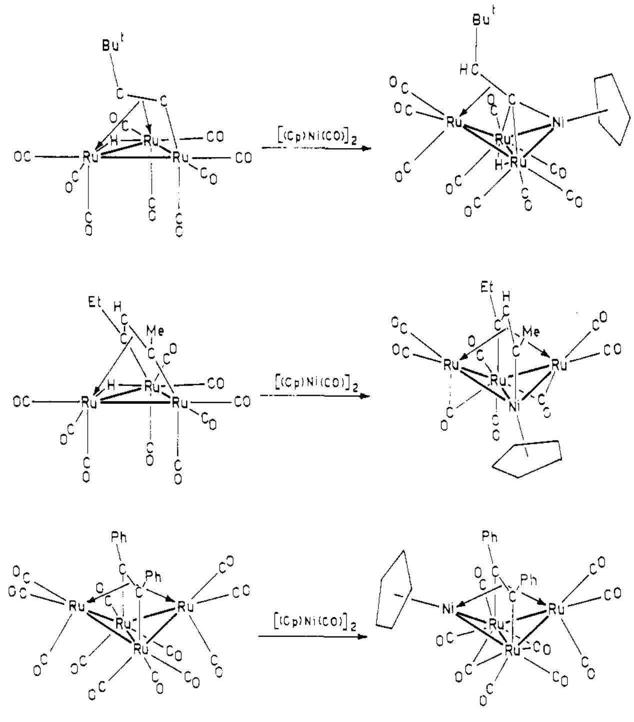
a rectangular ensemble of four metals, as in $Ir_4(CO)_8[C_2(COOMe)_2]_4$ (Figure 2, **5**).[148]

The above way of formation of alkyne-substituted butterfly clusters was considered the only one available;[2] more recently, the butterfly $Ru_4(CO)_{12}(RC_2R)$ was obtained from $Ru_3(CO)_{12}$.[130] Also, the tetrametallic $Fe_4(CO)_{11}(HC_2Et)_2$ (**28**)[125] was obtained from $Fe_3(CO)_{12}$. Two main hypotheses could be formulated for the formation of the above complexes, namely, the presence in solution of tetrametallic species formed upon pyrolysis of the trimetallic carbonyls, or "metal fragments condensation".

Evidence for metal fragment condensation is obtained in the synthesis of heterometallic clusters; thus, the formation of $(Cp)NiRu_3(H)(CO)_9[C_2(H)Bu\text{-}t]$ (**31**) from $HRu_3(CO)_9C_2Bu\text{-}t$ and $[(Cp)Ni(CO)]_2$ is best explained in this manner.[151,152] It has been shown for $NiRu_3$ mixed metal clusters that the "condensation" of nickel fragments with a trimetallic ruthenium core depends upon the structure of the starting ruthenium reactants (which in turn depends upon the nature of the alkyne); thus, in presence of HC_2R-substituted ruthenium clusters, nickel "addition" is observed,[151] whereas for RC_2R' (R, R' = alkyl) substituted ruthenium clusters, nickel "insertion" occurs,[153] and finally, for $Ru_4(CO)_{12}(C_2Ph_2)$ "nickel substitution" is the more probable process.[120] This behavior is summarized in Scheme IV.

Also, several iron–nickel complexes have been obtained by fragment condensation.[62,117,274] In particular, it has been shown that the square-planar complex $(Cp)_2Ni_2Fe_2(CO)_6(C_2Et_2)$ (**25**)[274] cannot be obtained by reaction of the tetrahedral $(Cp)_2Ni_2Fe_2(CO)_7$ with EtC_2Et; hence, once more the metal fragment condensation is the most probable explanation for the formation of the mixed alkyne derivatives. The condensation is probably favored by the alkynes, which could act in

Scheme IV



the same way as the "semibridging CO's",[185] by reducing the differences in electron density between the different metal atom centers.

D. Ligand Exchange between Metals and Metal Exchange on Clusters

In the synthesis of the above ruthenium–nickel and iron–nickel derivatives, we observed that ligand exchange (cyclopentadienyl, CO, and alkyne) also occurs between metals; although in most instances this behavior is not useful as a preparative method, as simpler routes for the products are available, in some cases products are obtained which cannot be synthesized otherwise.

Thus, whereas $Ru_3(CO)_8(HC_2Bu\text{-}t)_3$[55] (Figure 12) can be obtained by treating $Ru_3(CO)_{12}$ or $HRu_3(CO)_9C_2Bu\text{-}t$ with excess $HC_2Bu\text{-}t$, better yields are obtained from the reaction of $Ru_3(CO)_{12}$ with $(Cp)_2Ni_2(HC_2Bu\text{-}t)$. Nickel has been shown to be a good catalyst for alkyne cyclotrimerization, and indeed, in the product the alkynes are linked in the same way as is usually found in nickel-assisted oligomerization. In this reaction obviously alkyne migration occurs.

The product $(Cp)Ni(Cp)Ru_2(CO)_3(\mu_3\text{-}CO)(C_2Ph_2)$ (**15**)[123] is obtained by reacting $Ru_3(CO)_{12}$ with $(Cp)_2Ni_2(C_2Ph_2)$; since it bears a cyclopentadienyl ligand on one ruthenium, ligand migration must have occurred. No alternative preparation for this complex is known at present.

The synthetic application of metal exchange in clusters has been reported very recently; $(Cp)MCo_2(CPh)$ (M = Cr, Mo, W) (**12**) complexes have been obtained under mild conditions from Co_3C clusters "via" $Co_3(CO)_8CR\text{-}AsMe_2M(CO)_3(Cp)$ intermediates;[122] some related Fe–Co–M clusters are obtained via the same procedure.[186]

In the above discussed synthesis of $(Cp)NiRu_3(CO)_9(C_2Ph_2)$ (see Scheme IV) a nickel atom substitutes for a ruthenium in a butterly cluster.

Finally, "metal extrusion" from a heterometallic cluster has been reported to give a lower nuclearity molecule. This process occurs, for example, in the presence of phosphine, which complexes one of the nickel atoms eliminated from a Fe_2Ni_2 core.[119] Proton-induced fragmentation of $[Co_3Ru(CO)_{12}(C_2Ph_2)]^-$ into $Co_2Ru(CO)_{10}(C_2Ph_2)$ has recently been evidenced.[338]

E. Oxidative Addition of C–H and H_2 to Metal Clusters and M–H Addition to Unsaturated Ligands

These reactions lead to hydrido clusters and are widespread in the ruthenium and osmium alkyne and alkene chemistry.[4] The synthesis of $HRu_3(CO)_9(C_2Bu\text{-}t)$[33] and of the $HRu_3(CO)_9(C_6H_9)$ isomers[37,39] are examples of oxidative addition of C–H bonds. Inter- and intramolecular hydrogen shifts involving the organic moieties are found, respectively, in the synthesis of $Fe_3(CO)_8(HC_2Me)_4$ (**10**),[26] $(Cp)NiFe_2(CO)_6C_2Me$, and $(Cp)NiFe_2(CO)_7CCH_2Me$.[62]

Oxidative addition of hydrogen is usually reversible: a remarkable example is the synthesis of $H_3Ru_3(CO)_9C\text{-}CH_2Bu\text{-}t$ from $HRu_3(CO)_9C_2Bu\text{-}t$ and H_2, as a part of a catalytic cycle.[47] In other cases, addition of hydrogen induces the loss of the alkyne ligand, as with $Ru_4(CO)_{12}(C_2Ph_2)$ that gives high yields of $H_4Ru_4(CO)_{12}$ and *trans*-stilbene.[130,131]

The M–H addition to unsaturated ligands is a general process. A very useful starting material is the unsaturated cluster $H_2Os_3(CO)_{10}$ that reacts with alkynes[74,75] as well as with cyclic dienes.[78]

Sometimes, however, hydrogen loss is observed as already discussed for the reactions of $H_2FeRu_3(CO)_{13}$ with alkynes and in the synthesis of $(Cp)NiRu_3(CO)_8(C_6H_9)$ isomers.[153]

F. Protonation Reactions

These reactions afford cationic derivatives; the procedure is not general because often the strong protonating agents used induce cluster demolition; the few derivatives obtained with this technique are listed in Table III. Cationic cobalt reactants have been shown to be useful intermediates in the synthesis of neutral cobalt clusters.[187-189] We believe that the protonation reactions will be used to a larger extent, in view of the interest in the protonation–reduction of CO ligands. A comparative study of the ease of protonation of the metal framework vs. the ligands (alkynes or CO) would be very informative and useful.

G. Reactions of Carbonyl Anions

Only few examples of such syntheses involving alkynes have been reported. The anions are formed in water–alcohol solutions in the presence of strong bases; the final products, usually hydrides, are obtained upon acidification.

$H_2Ru_3(CO)_9(C_2Ph_2)$ was obtained in this way[46] as were structurally related chalcogen complexes.[190]

Cobalt derivatives $HCo_3(CO)_9$ and $Co_3(CO)_9COH$, obtained from cobalt anions, react with alkynes to give $Co_3(CO)_9CR$ derivatives.[191,192]

An interesting reaction sequence starting from iron carbonyl anions and CH_3CN and leading to the re-

TABLE III

reaction					ref
$Co_3(CO)_9CCOOEt$	$\xrightarrow{H_2SO_4}$	$Co_3(CO)_9CCOOH$	$\xrightarrow[H_3O^+]{H_2SO_4}$	$[Co_3(CO)_9CCO]^+$	187
$Co_2(CO)_8 + CF_3COOR$, $R = H$	$\longrightarrow$	$Co_3(CO)_9CCOOR$	$\xrightarrow{(EtCO)_2O}$	$[Co_3(CO)_9CCO]^+$	187
$Co_3(CO)_9C\,C(O)R + Et_3SiH$, $R = H, CH_3, Ph$	$\longrightarrow$	$Co_3(CO)_9CC(R)HOSiEt_3$	$\xrightarrow{H_2SO_4}$	$[Co_3(CO)_9CC(H)R]^+$	187
$Ru_3(CO)_{12} + RC{\equiv}CR'$, $R = R' = Ph$; $R = Ph$, $R' = CH_3$	$\longrightarrow$	$Ru_4(CO)_{12}(C_2RR')$	$\xrightarrow[SO_2]{HSO_3F}$	$[HRu_4(CO)_{12}(RC_2R')]^+$	130
$Ru_3(CO)_{12} + (CH_3)_3C{-}C{\equiv}CH$	$\longrightarrow$	$HRu_3(CO)_9C_2C(CH_3)_3$	$\xrightarrow[H_2SO_4]{ClSO_3H}$	$[H_2Ru_3(CO)_9(HC_2Bu\text{-}t)]^{2+}$	60
$M_3(CO)_{12} + C_8H_{14}$, $M = Ru, Os$	$\longrightarrow$	$H_2M_3(CO)_9C_8H_{12}$	$\xrightarrow[CH_3COOD]{CF_3COOH}$	$[H_2RM_3(CO)_9C_8H_{12}]^+$, $R = H, D$	188
$Os_3(CO)_{12} + C_2H_4$	$\longrightarrow$	$H_2Os_3(CO)_9(C{=}CH_2)$	$\xrightarrow[CF_3COOD]{CF_3COOH}$	$[H_2ROs_3(CO)_9(C{=}CH_2)]^+$, $R = H, D$	188
$H_2Os_3(CO)_9CCH_2$	$\xrightarrow{+H_2}$	$H_3Os_3(CO)_9CMe$	$\xrightarrow[\text{in } SO_2]{Ph_3C^+BF_4^-}$	$[H_3Os_3(CO)_9(C{=}CH_2)]^+$	188
$Os_4(CO)_{12} + R'CH{=}CHR^2$, $R^2 = H$, $R' = H, Ph, CMe_3$; $R' = R^2 = Ph$	$\longrightarrow$	$H_3Os_4(CO)_{11}(R'C{=}CHR^2)$	$\xrightarrow[H_2O]{H^+}$	$[H_4Os_4(CO)_4(R'C{=}CHR^2)]^+$	142
	$\xrightarrow{-H_2}$	$H_2Os_4(CO)_{11}(R'C{=}CR^2)$, $R' = R^2 = Ph)$	$\xrightarrow[H_2O]{H^+}$	$[H_3Os_4(CO)_{11}(R'C{=}CR^2)]^+$	142

duction of acetonitrile has been reported.[163]

Bis(carbyne) "apical" clusters of general formula $(Cp)_3Co_3(\mu_3\text{-}CR')(\mu_3\text{-}CR'')$ are formed in yields up to 27% in the synthesis of organic molecules via alkyne cooligomerization in the presence of $(Cp)Co(CO)_2$.[311,321]

H. Other Reactions

Variations to the above methods, or new reactions of nongeneral application at present are:

Cluster formation from $Ni(CO)_4$ and hexafluorobut-2-yne in sealed vessels, periodically displacing the equilibrium in solution by cooling at −196 °C and pumping off CO. The product is $Ni_4(CO)_4[C_2(CF_3)_2]_3$.[109]

Pyrolysis of a cyclohexadienone–osmium complex obtained from alkynes, with activation of a C–H bond, followed by insertion of a CO molecule between the organic moiety and the cluster metals.[193]

Reaction of metal acetylides with mono- or bimetallic carbonyls to give heterometallic acetylide clusters, of either open or closed structure.[108,159,194]

To our knowledge no reaction of metal vapors in the presence of alkyne and CO has been reported so far; this could be a very promising synthetic method for unusual derivatives.

Also, no redox condensations were attempted in the presence of alkynes; these reactions would be particularly suitable for volatile alkynes. However, there is a great probability that instead of cluster formation, bimetallic derivatives would be obtained as main products.

I. Purification Techniques

The usual purification procedures, crystallization, sublimation, and solvent extraction can be used when few complexes are present in the reaction mixtures, or when these show volatility or solubility properties very different from each other. This is not the common case, especially for the iron derivatives.

Indeed, few examples of high-yield synthesis and very simple purification procedures have been reported.[33,37,39]

Chromatographic techniques are the most widespread purification methods; HPLC has been reported as a useful system for separating mixed-metal clusters.[2] Column chromatography, either under air or under nitrogen, is used for separating mixtures of relative complexity.

Preparative thin layer chromatography has been very useful for complex mixtures (in some reactions of iron carbonyls with HC_2R alkynes, up to 30 products are obtained). Negative aspects of this technique are that air-sensitive products (in particular cobalt and nickel derivatives) are lost; high costs and small quantities of products obtainable are other limiting factors. Sometimes, also, some side reactions occur on the TLC plates, thus, care is required when discussing the reactions leading to oxygenated ligands when this purification technique is employed. On the other hand, the separation of isomeric products that would cocrystallize is often easily achieved by TLC.

III. *Structural Data in the Solid State*

Since 1966 considerable structural work has been performed on the alkyne cluster complexes and a great variety of structures has been encountered.

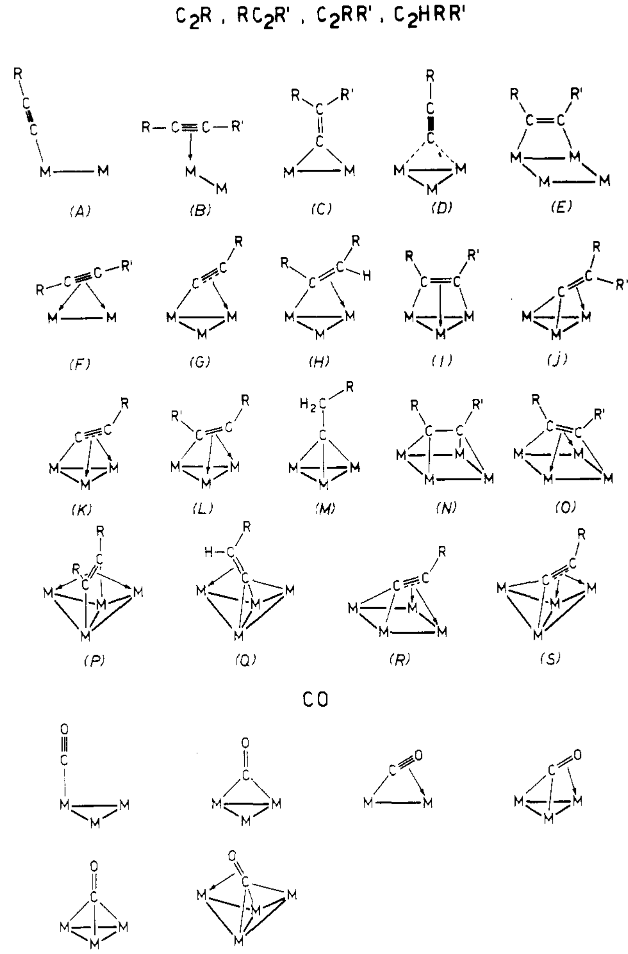
In the following discussion, two main aspects will be separately considered: the coordination and interaction of a *single* alkyne molecule (or of a single alkyne-derived ligand) with more than one metal center and the oligomerization of alkynes on clusters.

This scheme will also be followed when considering the structural data in solution, and when discussing the reactivity of the coordinated alkynes.

The first aspect, namely the activation–reduction of triple bonds upon coordination to several metal centers either in clusters and on surfaces, has been extensively considered by Muetterties.[4,6,7] However, only a limited number of examples was quoted, whereas, several new complexes containing unusually bound alkynes have been recently reported.

In this "model" study of the activation–reduction of small molecules on clusters, isonitriles, CO,[11] and alk-

Scheme V



ynes were considered, together with hydrogen. The alkynes show several advantages with respect to CO, namely that the different substituents on the alkyne triple bond can modify both the "basicity" and the polarity of these molecules to a considerable extent. Thus, terminal (HC_2R), internal (RC_2R', R or R' = alkyl), and symmetrical alkynes (RC_2R, R = alkyl, phenyl, functionalized organic group) often give rise to different reaction patterns, and to a great number of bonding situations. Furthermore, the alkynes can act as formal donors of different numbers of electrons in a more complex and versatile way than CO.

In Scheme V the bonding interactions of alkynes and alkyne-derived ligands with one or more metal centers are reported. Only eight bonding modes (namely B, E, F, I, L, N, O, and P) refer to "true" alkyne ligands, whereas all the others refer to acetylides or to other alkyne-derived ligands. Bonding mode C was found neither for alkyne nor for alkyne-derived clusters: it has been included, nevertheless, because—at least in principle—this feature could be found in the near future for alkyne-derived complexes.

By comparison, the interactions of CO with one or more metal centers are also shown in the scheme. One can observe that the alkynes give a greater variety of bonding interactions; these can be divided in the following way: interaction with a single metal atom (bonding modes A, B); interaction with two metal atoms (bonding modes C, D, E, F, G); interaction with three metal atoms (bonding modes I, J, K, L, M); and interaction with four metal atoms (bonding modes N, O, P, Q, R, S).

For the bonding discussion we have used the old σ and π notation, when possible, and the μ_n–η^m notation, even if this latter, in some cases, may generate confusion.[150]

The second main aspect of the discussion of the structural data concerns the alkyne oligomerization on clusters, and is of importance in view of some stoichiometric or catalytic applications. These complexes can be divided into complexes in which the alkynes form organic rings (cyclopentadienyls, cyclopentadienones, benzenes, quinones, tropones) with or without CO insertion in the organic moiety, complexes containing metallacyclic rings (sometimes these are open clusters), or complexes containing "open chain" ligands interacting with closed or open clusters.

A recent systematization of the structural data for the alkyne-substituted clusters (among others) considering the carbon atoms of the triple bond as part of the cluster skeleton has been proposed by Wade[195] and is useful for explaining some structural particulars and the electron counting in these molecules.

Few studies have been performed on hydridic clusters in which the hydrogen is located on the basis of direct evidence.[196]

For cyclopentadienyl-substituted complexes, it has been hypothesized that the η^5-C_5H_5 ligand has steric requirements approximately equal to that of 2.5 carbonyls, which also agrees with the effective atomic number (E.A.N.) rule.[197]

A. Interaction of a Single Alkyne (or Alkyne-Derived Ligand) with Clusters. Structures and Triple Bond Activation

1. Complexes in Which the Alkyne (or Acetylide) Interacts with One Metal Atom

Examples of "pure" acetylides on clusters (*bonding mode A*) are not known and there is low probability for obtaining this structural feature, which is, on the contrary, very common with CO and CNR ligands. This is probably due to the ease with which the C≡C bond can interact with the other metals present in the cluster; thus, in some metal acetylides, mainly those of the coinage metals,[198] polymeric structures were found in which the acetylide is σ bonded to one metal and interacts in a π manner with another one.

An example of linear acetylide substitution on a bimetallic complex has been found in $Pt_2(C_2Ph)_2(SiMe_2)(PR_3)_2$ (1);[179] this is probably achieved because of the number and steric hindrance of the other substituents in the complex.

The simple π interaction of one alkyne molecule with one metal atom (*bonding mode B*), which is quite common for monometallic platinum complexes,[199] and is rare in bimetallic platinum complexes,[313] is not found in clusters; however, in $HOs_3(CO)_9(C_2H_4)(SMe)$ (2)[79] one ethylene is coordinated to one osmium atom in this way.

The structures of the complexes 1 and 2 are depicted in Figure 1.

2. Complexes in Which the Alkyne (or Alkyne-Derived Ligand) Interacts with Two Metal Atoms

Two different *bonding modes* (*C and D*) can be found with the ligand perpendicular to the M–M bond axis. An example of the first mode (alkenylidene ligand) is

TABLE IV. Bonding Parameters for Alkynes Interacting with One or Two Metal Atoms

complex	bonding mode[a]	bond lengths, Å				ref
		C-C	M-C(σ)	M-C(π)	M-M	
free alkyne		1.204 (2)				
$Pt_2(C_2Ph)_2(SiMe_2)(PPh_3)_2$	A	1.20 (2)	2.01 (1)			179
$Cu_6(C_6H_4NMe_2)_4(C_2C_6H_4Me)_2$	D	1.18 1.17	2.025, 2.015 2.028, 2.054		2.466 2.474	208
$Fe_2(CO)_8(C_2Ph_2)$	C	1.37	1.96, 1.97		2.64	209
$Ru_3(CO)_6(C_2Bu\text{-}t)_2(PPh_2)_2\cdot(Ph_2PC_2Bu\text{-}t)$	D	1.19 (1)	2.185 (9) 2.22 (1)		2.863 (1)	58
$Ir_4(CO)_8[C_2(COOMe)_2]_4$	E	1.278 (11)	2.127 (9), 2.095 (7)		2.715 (1)	148
$Pt(PhC_2Ph)_2$	B	1.280 (6)		2.025[b]		313
$Pt_2(PMe_3)_2(PhC_2Ph)_2$	B	1.26 (5)		2.01 (3)[b]		313
$Fe_2(CO)_6(Ph_2PC_2Ph)_2$	B	1.260 (11)[c] 1.273 (11)[c]		2.046 (8),[c] 2.076 (8) 2.064 (8),[c] 2.068 (8)		206
$(Cp)NiFe(CO)_3(Ph_3PC_2H)$	F	1.37 (3)		1.94 (2), 1.98 (2) (Fe) 1.93 (2), 1.93 (2) (Ni)	2.420 (4)	211
$Pt_2(PMe_3)_2(PhC_2Ph)_2$	F	1.36 (5)	2.10 (3)[b]		2.890 (2)	313
$Ni_2(CO)_2(Ph_2PC_2Bu\text{-}t)_2$	B	1.269 (15)[c] 1.291 (13)[c]		1.898 (10), 1.933 (10) 1.919 (11), 1.916 (9)		206
$Co_2(CO)_6(PhC_2Ph)$	F	1.46		1.89, 1.93 2.01, 2.02	2.47	314
$(Cp)_2Ni_2(PhC_2Ph)$	F	1.35 (3)		1.89 (2), 1.90 (2) 1.89 (2), 1.87 (2)	2.329 (4)	315
$Fe_2(CO)_6(t\text{-}BuC_2Bu\text{-}t)$	F	1.311 (10)		2.060 (7), 2.130 (7) 2.094 (7), 2.044 (7)	2.316 (1)	205
$Co_2(CO)_6(t\text{-}BuC_2Bu\text{-}t)$	F	1.335 (6)		1.994 (4), 2.003 (4) 1.992 (4), 1.995 (4)	2.463 (1)	205
$Fe_2(CO)_4(t\text{-}BuC_2Bu\text{-}t)_2$	F	1.283		2.048, 2.113 2.049, 2.116	2.215	205
$Pt_3(PEt_3)_4(PhC_2Ph)_2$	F	1.34 (3)		2.07 (2)[b]	2.905 (1)	105
$HOs_3(CO)_9(C_2H_4)(SMe)$	B	1.42		2.23 (4) 2.23 (4)		79
$Fe_2(CO)_6(C_2Ph)(PPh_2)$	G	1.232 (10)	1.891 (6)	2.125 (8), 2.304 (7)	2.597 (2)	316
$Fe_2(CO)_5(C_2Ph)(PPh_2)(PPh_3)$	G	1.225 (6)	1.890 (4)	2.116 (4), 2.284 (5)	2.648 (1)	212
$Pt_2(C_2Ph)_2(SiMe_2)(PR_3)_2$	G	1.26 (1)	1.96 (1)	2.14 (1), 2.47 (1)	2.703 (1)	179
$RhAg_2(PPh_3)_3(C_2C_6F_5)_5$	G	1.19-1.22[d]	2.01-2.04[d,i]	2.34-3.13[d,e]	3.086-3.102[f]	124
$Ir_2Cu_4(PPh_3)_2(C_2Ph)_8$	G	1.226[b]	2.044[c,g]	1.989, 2.186[b,h]		158
$HOs_3(CO)_{10}(CH{=}CH_2)$	H	1.396 (3)	2.107 (3)	2.273 (3), 2.362 (3)	2.845 (2)	68
$HOs_3(CO)_{10}(CH{=}CHEt)$	H	1.40 (3)	2.15 (2)	2.28 (2), 2.46 (3)	2.834 (1)	317
$HOs_3(CO)_{10}(CPh{=}CHPh)$	H	1.40 (5)[c] 1.31 (5)	2.11 (4)[c] 2.18 (4)	2.34 (4), 2.44 (4)[c] 2.21 (4), 2.45 (4)	2.820 (3)[c] 2.821 (3)	326
$HOs_3(CO)_{10}(CF_3C{=}CHCF_3)$	H	1.41 (4)	2.16 (3)	2.20 (3), 2.24 (3)	2.848 (2)	72
$FeCo_3(CO)_9(C_2Ph_2)(CPh{=}CHPh)$	H	1.41 (2)	1.981 (11)[j]	1.996 (10), 2.127 (11)[j]	2.369 (4)	298
$Ru_3(CO)_6(C_2Bu\text{-}t)_2(PPh_2)_2\cdot(Ph_2PC_2Bu\text{-}t)$	G	1.24 (3)			3.139 (1)	58

[a] See also Scheme V. [b] Mean values. [c] Values in two independent molecules. [d] Minimum and maximum values. [e] Ag-C distances. [f] Rh-Ag distances. [g] Ir-C distances. [h] Cu-C distances. [i] Rh-C distances. [j] Co-C distances.

$Fe_2(CO)_8(C_2Ph_2)$ (**3**),[209] nevertheless obtained by irradiating a solution of diphenylketene and iron pentacarbonyl in benzene; examples of the second mode (μ-bonded acetylide) are $Ru_3(CO)_6(C_2Bu\text{-}t)_2(PPh_2)_2(Ph_2PC_2Bu\text{-}t)$ (**4**),[58] directly obtained from the corresponding alkyne and $Cu_6R_4(C_2R')_2$.[208]

The bonding with the ligand perpendicular to the M–M axis is quite common for CO, when involved as a bridge between two metal atoms either in a symmetrical or in an unsymmetrical way. Also some =COR ligands[202] and $=CNMe_2$[167,168] or =CNBu-*t*[171] may be bonded to metals in this way.

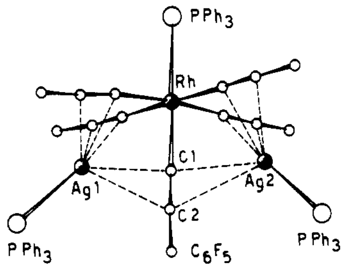
Examples of alkynes disposed parallel to the M–M bond (2σ-bonded alkyne, *bonding mode E*) are relatively rare; one example is $Ir_4(CO)_8[C_2(COOMe)_2]_4$ (**5**).[148]

Alkynes, bonded only via 2π bonds (*bonding mode F*) are very common in bimetallic complexes of cobalt,[314] iron,[205] and nickel.[206] In cluster complexes, on the contrary, this bonding is rarely found; only in the open cluster $Pt_3(PEt_3)_4(C_2Ph_2)_2$ (**6**)[105] has such a behavior been found.

Some examples of the bonding modes C, D, E, and F are represented in Figure 2.

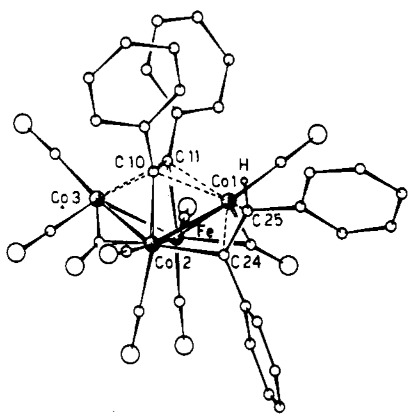
Both acetylide and alkenyl ligands can form a σ bond and a π bond with two metal atoms bridging an edge of the cluster (σ,π- or μ–η^2-bonded ligand, *bonding modes G and H*). Bonding mode G of the acetylides has been proposed for several osmium complexes and found in the trinuclear $Ru_3(CO)_6(C_2Bu\text{-}t)_2(PPh_2)_2(Ph_2PC_2Bu\text{-}t)$ (**4**, Figure 2),[58] in which the two acetylide groups behave in a different way (bonding modes D and G). Also in some mixed-metal acetylide derivatives, such as $RhAg_2(PPh_3)_3(C_2C_6F_5)_5$ (**7**)[124] and $Ir_2Cu_4(PPh_3)_2(C_2Ph)_8$[158] all the acetylides interact in this way with two different metals. Bonding mode H of the alkenyl (vinyl and stilbenyl) ligands, derived from alkynes, has been found in $HOs_3(CO)_{10}(CH{=}CH_2)$,[68] $HOs_3(CO)_{10}(CH{=}CHEt)$,[317] $HOs_3(CO)_{10}(CPh{=}CHPh)$ (**9**, in the solid state both enantiomers are present),[326] and in the tetranuclear mixed cluster $FeCo_3(CO)_9(C_2Ph_2)(CPh{=}CHPh)$ (**8**).[298] Some examples of the bonding modes G and H are shown in Figure 3. Again for comparison with the CO ligand, few examples have been reported, in which the C–O bond is involved in a π interaction with metals.[207]

In Table IV the structural parameters for complexes with alkynes interacting with one or two metal atoms



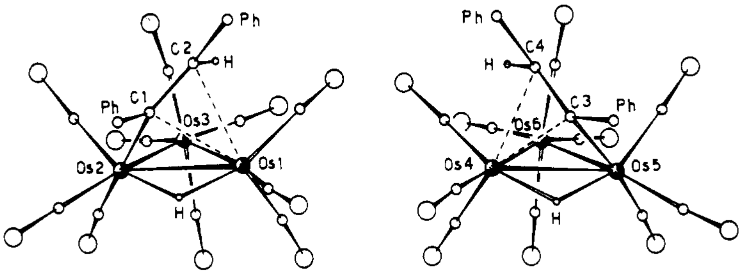
$RhAg_2(PPh_3)_3(C_2C_6F_5)_5$ (ref. 124)

7



$FeCo_3(CO)_9(C_2Ph_2)(CPh{=}CHPh)$ (ref. 298)

8



$HOs_3(CO)_{10}(CPh{=}CHPh)$ (two enantiomers) (ref. 326)

9

Figure 3. Examples of acetylide or alkenyl ligands interacting with two metals (bonding modes G and H).

are reported.

3. Complexes in Which the Alkyne (or Alkyne-Derived Ligand) Interacts with Three Metal Atoms

A large number of clusters containing a tetrahedral or pseudotetrahedral M_3C core is known, in particular for cobalt; in these complexes the "apical" or "capping" CR group (R = alkyl, aryl, halogen) can be derived or not from alkynes (bonding mode M, μ_3-alkylidyne ligand). A large number of cobalt complexes is known at present[5] and the chemistry of these derivatives has been extensively studied (see the section "reactivity" and the Scheme XII). Complexes in which metals other than cobalt occupy the place of the CR group have also been reported.[213]

The above cobalt complexes are obtained by various reactions; among these is the acidic degradation of the $Co_2(CO)_6(RC_2R')$ complexes.[214]

Carbyne complexes have been shown to be precursors for the synthesis of these clusters[215]

$$M{\equiv}C{-}R + Co_2(CO)_8 \xrightarrow{-20\ ^\circ C} Co_3(CO)_9CR + Co_2(CO)_6(C_2R_2)$$

$$M{\equiv}C{-}R + (Cp)_2Ni \xrightarrow{-20\ ^\circ C} (Cp)_2Ni_3CR + (Cp)_2Ni_2(C_2R_2)$$

Another synthetic path for $Co_3(CO)_9CR$ complexes uses bimetallic cobalt carbonyl lactone derivatives.[322]

C≡C bond cleavage also affords M_3C derivatives,[98,216] finally, hydrogenation of $HRu_3(CO)_9C_2Bu$-*t* either with molecular H_2 or hydrogen-releasing ligands affords "apical" derivatives.[47,62]

Nickel derivatives like those above have also been obtained from $(Cp)_2Ni$ and $(C_6H_5CH_2)MgCl$.[103]

Finally the reaction of $Fe_3(CO)_{12}$ with HC_2R alkynes affords complexes $Fe_3(CO)_8(HC_2R)_4$ (**10**), which, upon internal hydrogen shift within the alkyne, are characterized by CR apical ligands.[26] Also, the reactions of $(Cp)_2Ni_2(HC_2R)$ with iron carbonyls gave complexes with apical ligands, upon intermolecular hydrogen transfer.[62]

A comparable situation on a large metal cluster has been reported[157] with $Os_6(CO)_{16}(CMe)_2$, obtained from ethylene.

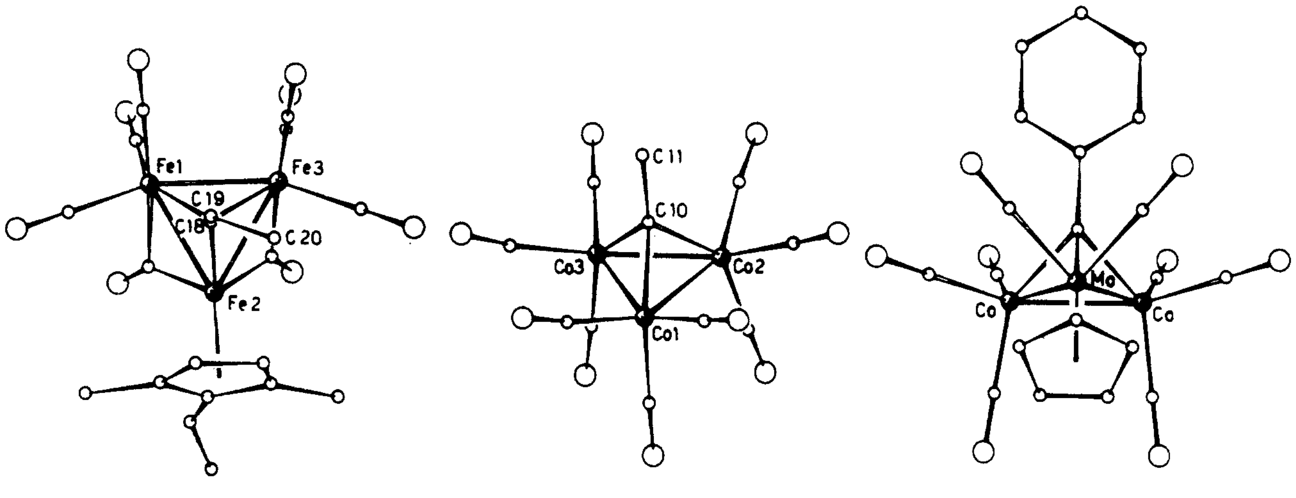
Finally, it is noteworthy that, whereas at the beginning of the study on the alkyne complexes, only apical cobalt derivatives were known, this structural type is now widespread also for nickel and the iron triad.

The structure of some significant complexes with CR apical ligands are reported in Figure 4.

Thus, sufficient evidence for the derivation of these clusters from alkynes in different reactions is obtained (see also the section "reactivity").

When considering the structures of the complexes, the main feature is the "tetrahedral core" with the apical carbon atom. The M–C–M angles are close to 80° and thus considerably different from the ones expected for sp^3 hybridization of the carbon atom.[217]

This situation is also typical for the triply bridging CO's, which have been shown in the past years to be a relatively common feature in metal atom clusters.

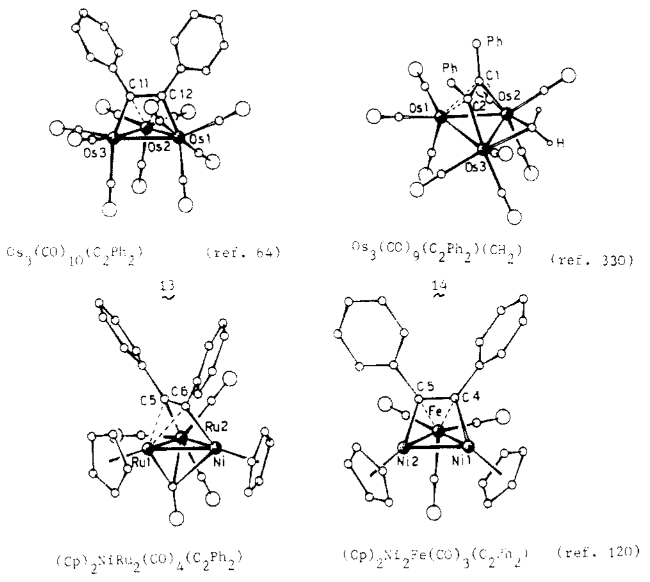


$Fe_3(CO)_8(HC_2Me)_4$ (ref. 26) **10**

$Co_3(CO)_9(CMe)$ (ref. 221) **11**

$Co_2Mo(CO)_8(Cp)(CPh)$ (ref. 122) **12**

Figure 4. Complexes with CR apical ligands (bonding mode M).



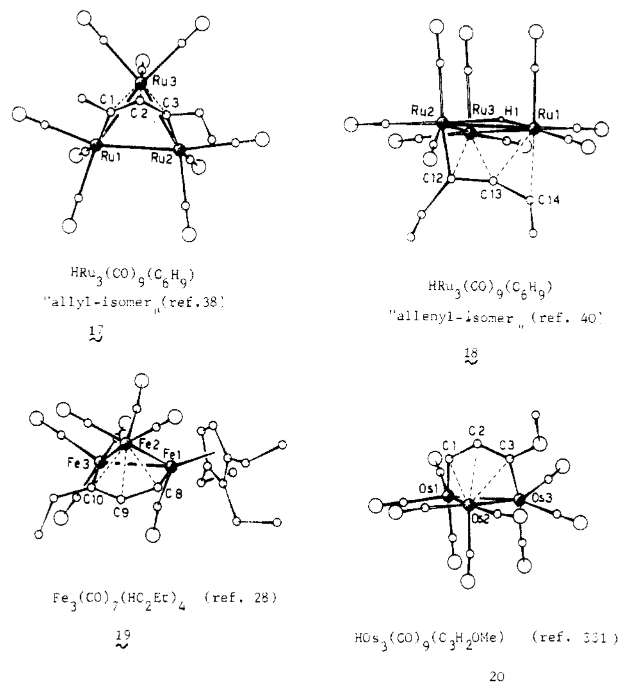
$Os_3(CO)_{10}(C_2Ph_2)$ (ref. 64) **13**

$Os_3(CO)_9(C_2Ph_2)(CH_2)$ (ref. 330) **14**

$(Cp)_2NiRu_2(CO)_4(C_2Ph_2)$ (ref. 123) **15**

$(Cp)_2Ni_2Fe(CO)_3(C_2Ph_2)$ (ref. 120) **16**

Figure 5. Complexes with alkyne ($2\sigma + \pi$) interacting with three metal atoms (bonding mode I).



$HRu_3(CO)_9(C_6H_9)$ "allyl-isomer" (ref. 38) **17**

$HRu_3(CO)_9(C_6H_9)$ "allenyl-isomer" (ref. 40) **18**

$Fe_3(CO)_7(HC_2Et)_4$ (ref. 28) **19**

$HOs_3(CO)_9(C_3H_2OMe)$ (ref. 331) **20**

Figure 6. Complexes with "allyl" and "allenyl" ligands.

In Table V the bonding parameters for complexes with "apical" CR are reported.

Alkyne and alkenylidene ligands can be bonded to three metal atoms via two σ and one π bonds ($2\sigma + \pi$ or μ_3-η^2). When the alkyne is bonded, the two σ bonds involve two different carbon atoms belonging to the alkyne (*bonding mode I*). When the alkenylidene ligand is bonded, the two σ bonds interact with the same carbon atom, whereas the second carbon interacts only in a π manner (*bonding mode J*).

Bonding mode I is commonly found in homo- and heterometallic alkyne clusters and is also common for isonitriles (see Table II). Some significant complexes of this type are represented in Figure 5 and their relevant structural parameters are reported in Table VI. From the structural data, one can see that this class of complexes is one of the most common and represents the one for which the greater number of structural studies has been achieved. It is noteworthy that this bonding brings the alkynic C–C bond nearly parallel to one edge of the cluster (from which the notation μ_3-(η^2-||) is derived for this bonding).

The bonding mode J is less well encountered, at least from the structural point of view. It has been suggested mainly for osmium derivatives, on the basis of NMR evidence[4] and found for $H_2Os_3(CO)_9(CCH_2)$.[80]

A bonding situation with a system of carbon atoms acting as a delocalized η-donor ligand and the terminal carbon atoms σ-bonded to the metals has been also found. The system of carbon atoms often is an "allylic" ligand, obtained by isomerization of the alkyne,[38] by condensation of a CR fragment (from C≡C bond cleavage) with another alkyne,[28] and from the reaction of alkynes with osmium derivatives containing ligands with nitrogen and oxygen atoms.[331] Examples of this type of bonding are shown in Figure 6.

TABLE V. Structural Parameters for Complexes Containing "Apical" CR Ligands

	bonding distances, Å				
complex	M-M	M-C	C-C	M-C-M angles	ref
$Co_3(CO)_9CMe$	2.466 (7)	1.86 (2)	1.53 (3)	81.2 (7)	221
	2.475 (7)	1.93 (2)		80.5 (7)	
	2.462 (7)	1.90 (2)		81.7 (7)	
$Co_3(CO)_8(PPh_3)CMe$	2.510 (6)	1.90 (1)	1.50 (2)	83.1 (5)	222
	2.495 (5)	1.89 (2)		81.3 (5)	
	2.490 (6)	1.93 (1)		81.3 (5)	
$(Cp)_2Co_3(CO)_4CMe$	2.368 (3)	1.88 (2)	1.55 (3)		320
	2.477 (4)	1.82 (2)			
	2.480 (2)	1.84 (2)			
$(C_5Me_5)_2Co_3(CO)_4CMe$	2.405 (1)	1.857 (6)	1.497 (9)	81.9 (2)	97
	2.484 (1)	1.866 (6)		82.4 (2)	
	2.501 (1)	1.932 (6)		80.5 (2)	
$Co_3(CO)_6[P(OMe)_3]_3CMe$	2.491 (2)	1.92 (1)	1.50 (2)	81.7 (5)	95
	2.475 (2)	1.89 (1)		80.8 (5)	
	2.485 (2)	1.90 (1)		81.8 (5)	
$Co_3(CO)_7(As_2Me_4C_4F_4)CMe$	2.440 (1)	1.907 (7)	1.50 (1)	78.9 (3)	223
	2.479 (2)	1.895 (7)		81.1 (3)	
	2.470 (2)	1.907 (7)		81.0 (3)	
$Co_3(CO)_6(C_6H_3Me_3)CPh$	2.441 (2)	1.87 (2)	1.37 (3)	80.7 (5)	225
	2.477 (3)	1.90 (1)		81.5 (6)	
$Co_3(CO)_9CC(=O)Ph$	2.476 (1)	1.891 (6)	1.473 (8)	80.66 (22)	226
	2.467 (2)	1.893 (6)		81.74 (23)	
	2.467 (1)	1.921 (6)		80.59 (21)	
$(Cp)_3Co_3(CSiMe_3)(C_3SiMe_3)$	2.383 (2)[b]	1.873 (9)[b]	1.412 (14)		98
$Co_3(CO)_7(C_7H_8)CEt$	2.483 (3)	1.86 (1)	1.52 (2)	83.0 (6)	227
	2.475 (3)	1.88 (2)		82.2 (6)	
	2.470 (3)	1.90 (2)		81.4 (6)	
$Co_5(CO)_{15}C_3H$	2.462 (5)	1.89 (1)	1.46 (2)	80.4 (6)	228
	2.470 (6)	1.93 (1)		80.6 (6)	
	2.485 (4)	1.93 (2)		80.2 (5)	
$[Co_3(CO)_9C_2]_2$	2.465 (5)	1.91 (1)	1.37 (1)	80.2 (4)	229
	2.485 (4)	1.92 (1)		80.6 (3)	
	2.462 (4)	1.93 (1)		79.5 (3)	
$[(Cp)_3(CO)_9C]_2CO$	2.46, 2.48[a]	1.93, 1.92[a]	1.60, 1.42[a]	82.4, 81.0[a]	230
	2.45, 2.48	1.87, 1.92		83.9, 78.9	
	2.46, 2.45	1.81, 1.94		81.0, 80.2	
$Co_8(CO)_{24}C_6$	2.447 (7)	1.95 (4)	1.44 (3)	79 (1)	231
	2.453 (7)	1.89 (3)		79 (1)	
	2.462 (7)	1.91 (3)		81 (1)	
	2.490 (7)	1.90 (3)	1.36 (3)	83 (1)	
	2.466 (7)	1.87 (3)		80 (1)	
	2.468 (7)	1.95 (3)		80 (1)	
$[Co_3(CO)_9C]_2$	2.457 (2)	1.95 (1)	1.37 (1)	77.6 (2)	233
	2.456 (2)	1.97 (1)		77.6 (2)	
	2.457 (1)	1.97 (1)		77.3 (2)	
$Co_8(CO)_{24}C_6.1/2C_6H_6$	2.467 (6)	1.944 (27)	1.370 (39)	79.4 (1.1)	234
	2.460 (6)	1.918 (27)		79.9 (1.1)	
	2.477 (6)	1.912 (28)		79.9 (1.1)	
	2.482 (6)	1.906 (32)	1.361 (44)	80.5 (1.2)	
	2.471 (6)	1.935 (32)		79.2 (1.2)	
	2.472 (6)	1.970 (32)		78.5 (1.2)	
$Co_2Mo(CO)_8(Cp)CPh$	2.483 (1)	1.933 (5)		79.9 (3)	
	2.677 (1)[c]	2.104 (7)[c]		83.0 (2)[c]	122
$Fe_3(CO)_8[C_5H_2Me_2(C_2H_3)]CEt$	2.525 (3)	1.974 (5)	1.509 (5)	82.0 (2)	26
	2.583 (2)	1.910 (4)		82.6 (2)	
	2.515 (3)	1.938 (4)		80.7 (2)	
$H_3Ru_3(CO)_9CMe$	2.841 (6)	2.086 (10)	1.511 (20)	86.0 (4)	51
	2.844 (6)	2.078 (12)			
$H_3Ru_3(CO)_9C.CH_2Bu$-*t*	2.832 (1)	2.091 (5)	1.525 (9)	84.5 (2)	47
	2.836 (1)	2.098 (5)		84.8 (2)	
	2.820 (1)	2.116 (5)		84.6 (2)	
$Os_6(CO)_{16}(CMe)_2$	2.730 (6)	2.10 (7)			157
	2.672 (6)	2.14 (7)			
	2.722 (6)	1.95 (7)			

[a] Values in two independent molecules. [b] Averaged values. [c] Co-Mo and Mo-C distances and Mo-C-Co angles.

Both alkyne and acetylide ligand can be bonded to three metal atoms via one σ and two π bonds ($\sigma + 2\pi$, μ_3-η^2). This bonding is more common for acetylide ligands, in closed and open clusters (*bonding mode K*). Some of these clusters, such as $HRu_3(CO)_9C_2Bu$-*t* (**22**),[36] are considerably stable and have been studied in detail. With this type of bonding the multiple C-C bond is disposed nearly perpendicular to one side of the metal cluster (so this bonding is indicated by the notation μ_3-(η^2-$\perp$)).

Examples of this bonding involving alkynes (*bonding mode L*) are rather rare; it has been found first in $Fe_3(CO)_9(C_2Ph_2)$ (**24**).[15] Also, some tetrahedral nickel clusters show, on the triangular faces, this alkyne ar-

TABLE VI. Structural Parameters for $(2\sigma + \pi)$ Alkyne Clusters

complex	bond distances, Å[a] M–M	M–C(σ)	M–C(π)	C–C	ref
		Bonding Mode I			
Os$_3$(CO)$_7$(C$_2$Ph$_2$)$_3$	2.680 (2), 2.814 (2) 2.744 (2)	2.08 (2), 2.16 (2)	2.22 (2), 2.28 (2)	1.33 (3)	90
(Cp)$_2$Ni$_2$Fe(CO)$_3$(C$_2$Ph$_2$)	2.404 (4), 2.388 (4)[b] 2.381 (5)[b]	1.85 (2),[e] 1.86 (2)[e]	2.00 (2),[d] 2.04 (2)[d]	1.34 (2)	120
Ru$_3$(CO)$_7$(C$_2$Bu-*t*)[PhC$_2$(H)Ph](C$_2$Ph$_2$)	2.839 (5), 2.812 (3) 2.682 (7)	2.07 (2), 2.33 (2)	2.10 (2), 2.21 (2)	1.37 (2)	59
FeCo$_2$(CO)$_9$(C$_2$Et$_2$)	2.576 (1), 2.479 (1)[b] 2.489 (1)[b]	1.961 (6),[c] 1.957 (6)[c]	2.047 (6)[d] 2.035 (7)[d]	1.37 (1)	113
Os$_3$(CO)$_9$(C$_2$Ph$_2$)(CH$_2$)	2.765 (1), 2.738 (1) 2.763 (1)	2.14 (1), 2.13 (2)	2.27 (2), 2.28 (2)	1.37 (3)	330
(Cp)NiCoFe(CO)$_6$(PhC$_2$Pr-*i*-COO)	2.442,[b] 2.423[b] 2.487[b]	1.947,[c] 1.890[e]	2.021[d] 2.029[d]	1.376	115
Os$_6$(CO)$_{16}$(C$_2$Me$_2$)C	2.745 (4), 2.769 (4) 2.806 (4)	2.13 (2), 2.13 (2)	2.18 (2) 2.20 (2)	1.36 (2)	157
(C$_8$H$_8$)Ni$_3$(CO)$_3$[C$_2$(CF$_3$)$_2$]	2.7017 (13), 2.4560 (12) 2.4583 (12)	1.889 (6), 1.898 (5)	1.989 (6) 2.013 (6)	1.381 (9)	109
(Cp)$_2$NiRu$_2$(CO)$_4$(C$_2$Ph$_2$)	2.712 (3), 2.553 (2)[b] 2.550 (3)[b]	1.926 (5),[e] 2.075 (5)[f]	2.091 (7)[f] 2.148 (6)[f]	1.383 (7)	123
[(Cp)NiFe$_2$(CO)$_6$(C$_2$Ph$_2$)]$^-$	2.453 (1),[b] 2.474 (1)[b] 2.506 (1)	1.918 (5),[e] 1.970 (5)[d]	2.104 (6)[d] 2.014 (5)[d]	1.383 (7)	119
Fe$_3$(CO)$_8$(C$_2$Ph$_2$)$_2$, violet isomer	2.592 (5), 2.469 (6) 2.457 (5)	1.995 (22), 2.057 (24) 2.036 (22), 2.049 (20)	1.980 (22), 1.980 (21) 2.975 (20), 1.954 (22)	1.395 (30) 1.375 (30)	19
(Cp)$_3$Rh$_3$(CO)(C$_2$Ph$_2$)	2.674 (1), 2.655 (1) 2.638 (1)	2.022 (8), 2.040 (7)	2.110 (7) 2.154 (8)	1.385 (10)	106
OsPt$_2$(CO)$_5$(PPh$_3$)$_2$(C$_2$Me$_2$)	2.664 (2),[g] 2.669 (2)[g] 3.033 (2)	2.060 (8),[h] 2.055 (7)[h]	2.22 (1), 2.23 (1)[i]	1.40 (1)	329
(Cp)$_2$Ni$_2$Ru(CO)$_3$(C$_2$Ph$_2$)	2.418 (4), 2.493 (3)[b] 2.496 (3)[b]	1.91 (2),[e] 1.92 (2)[e]	2.15 (2),[f] 2.21 (2)[f]	1.40 (3)	120
(Cp)$_3$Rh$_3$(CO)[C$_2$(C$_6$F$_5$)$_2$]	2.672 (1), 2.599 (2) 2.588 (1)	2.02 (1), 2.03 (1)	2.09 (1), 2.09 (1)	1.41 (2)	106
Os$_3$(CO)$_{10}$(C$_2$Ph$_2$)	2.883 (1), 2.844 (1) 2.711 (1)	2.182 (8), 2.070 (9)	2.188 (8), 2.293 (9)	1.439 (10)	64
(Cp)$_2$W$_2$Os(CO)$_7$[C$_2$(C$_6$H$_4$Me)$_2$],[j] two isomers	2.857 (1),[l] 2.836 (2)[l] 3.158 (1)	2.187 (18),[m] 2.180 (20)[m]	2.229 (19),[i] 2.268 (19)[i]	1.463 (28)	328
	2.987 (1),[l] 2.871 (1)[l] 3.016 (1)	2.202 (18),[m] 2.090 (21)[i]	2.284 (21),[m] 2.365 (19)[m]	1.424 (29)	
(Cp)$_2$W$_2$Os(CO)$_7$[C$_2$(C$_6$H$_4$Me)$_2$],[j] two isomers	2.863 (2),[l] 2.839 (2)[l] 3.159 (2)	2.117 (19),[m] 2.111 (24)[m]	2.320 (20),[i] 2.306 (21)[i]	1.47 (3)	327
	2.981 (2),[l] 2.876 (2)[l] 3.017 (2)	2.193 (18),[m] 2.052 (20)[i]	2.208 (21),[i] 2.304 (18)[i]	1.43 (3)	
HOs$_3$(CO)$_9$(AsMe$_2$)(C$_6$H$_4$)[k]	2.946 (4), 2.839 (4)	2.198 (13), 2.138 (19)	2.296 (15), 2.388 (14)	1.436 (22)	325
		Bonding Mode J			
H$_2$Os$_3$(CO)$_9$(CCH$_2$)	2.89, 2.92 2.80	2.04, 2.05	2.19, 2.29	1.33	80

[a] The complexes are disposed in order of increasing C–C distances (excepting the last ones). [b] Heterometallic M–M′ distances. [c] Co–C distances. [d] Fe–C distances. [e] Ni–C distances. [f] Ru–C distances. [g] Pt–Os distances. [h] Pt–C distances. [i] Os–C distances. [j] Two independent structural studies. [k] Complex with benzyne ligand, only for comparison. [l] W–Os distances. [m] W–C distances.

TABLE VII. Structural Parameters for $(\sigma + 2\pi)[\mu_3\text{-}(\eta^2\text{-}\perp)]$ Alkyne Clusters

complex	bond distances, Å[a] M–M	M–C(σ)	M–C(π)	C–C	ref
	Bonding Mode K				
$HRu_3(CO)_9[C_2C(=CH_2)Ph]$	2.791 (2), 2.810 (2) 2.812 (2)	1.904 (14)	2.178 (15), 2.188 (14) 2.190 (15), 2.276 (14)	1.272 (22)[a]	45
$(PPh_2)Ru_3(CO)_9(C_2Pr\text{-}i)$	2.839			1.284 (8)	29
$(PPh_2)Os_3(CO)_9(C_2Pr\text{-}i)$	2.879			1.28 (1)	29
$(PPh_2)Ru_3(CO)_8(C_2Bu\text{-}t)$	2.8257 (4), 2.8151 (4) 2.7084 (4)				29
$(Cp)NiFe_2(CO)_6(C_2Bu\text{-}t)$	2.378 (3),[c] 2.564 (3)[c] 2.610 (3)	1.813 (10)[d]	1.929 (10),[e] 2.034 (10)[e] 2.010 (10),[d] 2.060 (10)[d]	1.284 (14)	118
$(Cp)Fe_3(CO)_7(C_2Ph)$	2.524 (1), 2.632 (1) 2.639 (1)	1.829 (6)	2.040 (4), 2.081 (5) 2.006 (5), 2.031 (5)	1.299 (9)	17
$HRu_3(CO)_7(C_6H_{10})(C_2Bu\text{-}t)$	2.864 (2), 2.826 (2) 2.841 (2)	1.944 (21)	2.165 (13), 2.243 (20) 2.209 (13), 2.252 (14)	1.303 (27)	235
$HRu_3(CO)_9(C_2Bu\text{-}t)$	2.792 (3), 2.795 (3) 2.799 (3)	1.947 (3)	2.207 (3), 2.268 (3) 2.214 (3), 2.271 (3)	1.315 (3)	36
$HRu_3(CO)_8(Ph_2POEt)(C_2Bu\text{-}t)$	2.7988 (5), 2.8212 (4) 2.8407 (5)	1.946 (4)	2.209 (4), 2.194 (4) 2.243 (4), 2.252 (4)	1.321 (6)	67
$[Ru_3(CO)_9(C_2Bu\text{-}t)(HgBr)]_2$	2.900 (3), 2.813 (3) 2.806 (2)	1.96 (2)	2.19 (2), 2.25 (2) 2.20 (2), 2.26 (2)	1.31 (3)	121
	Bonding Mode L				
$Ni_4(CO)_4[C_2(CF_3)_2]_3$	2.377 (7), 2.670 (6) 2.385 (7), 2.670 (10)	1.99 (3) 2.01 (4)	2.17 (3), 2.16 (3) 1.93 (3), 1.97 (3) 2.22 (3), 1.96 (3)	1.27 (4) 1.29 (6)	109
$Ni_4(CNBu\text{-}t)_4(C_2Ph_2)_3$	2.374 (2), 2.686 (6)	1.972 (8) 1.977 (8)[f]	2.203 (8)	1.344 (10)	150
$Fe_3(CO)_9(C_2Ph_2)$	2.480 (10), 2.501 (9) 2.579 (11)	2.048 (16)	2.098 (15), 1.947 (16) 2.048 (16), 1.945 (15)	1.409 (22)	15
$(Cp)_2W_2Fe(CO)_6[C_2(C_6H_4Me)_2]$	2.745 (1),[g] 2.731 (1)[g] 2.747 (1)	2.264 (7)[h]	2.040 (6),[h] 2.289 (5)[h] 2.052 (5),[d] 2.011 (5)[d]	1.399 (9)	327

[a] The complexes are in order of increasing "alkyne activation". [b] Open clusters, mean value of two bonding distances. [c] Heterometallic M–M′ distances. [d] Fe–C distances. [e] Ni–C distances. [f] Averaged values. [g] W–Fe distances. [h] W–C distances.

rangement.[109,149,150] This particular bonding mode (L) of the alkyne to the clusters has been discussed by Dahl and co-workers in detail.[15]

Some examples of the bonding mode K (complexes 21, 22, and 23) and one example of the bonding mode L (complex 24) are represented in Figure 7. The structural parameters of the complexes presenting these bonding modes are given in Table VII.

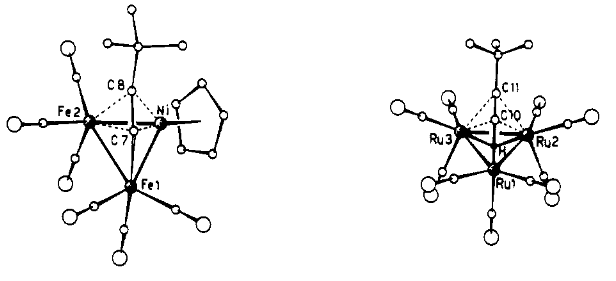
4. Complexes in Which the Alkyne (or Alkyne-Derived Ligand) Interacts with Four Metal Atoms

This is the maximum number of metal atoms with which an alkyne has been found to interact, at the present state of the knowledge. This interaction cannot occur, for obvious reasons, in tetrahedral clusters; whereas it has been found in butterfly, square-pyramidal, or square-planar clusters and in more complex arrangements.

Planar clusters are rare, and within the tetrametallic ones one example is $Ir_4(CO)_8[C_2(COOMe)_2]_4$ (5, Figure 2, where the alkynes behave in two different ways),[148] in which two alkyne units interact with four metals apparently only via σ bonds (*bonding mode N*).

Other examples of planar clusters are the heterometallic $(Cp)_2Ni_2Fe_2(CO)_6(RC_2R')$ (25) (R = R′ = Et, Ph;[274] R = Ph, R′ = COOR)[115] in which the alkyne interacts with all the metals; these are alternatively disposed, and, as both the iron atoms interact π and the nickel atoms interact σ with the organic moiety, a σ–π–σ–π bonding situation results (*bonding mode O*).

A square-planar face bearing an acetylide is also found in $Ru_5(CO)_{13}(PPh_2)(C_2Ph)$(26);[155] in this structure, however, two adjacent metal atoms are interested in σ bonds with the acetylide, whereas the other two adjacent atoms interact π (*bonding mode R*). The resulting situation is a two-by-two σ–σ–π–π interaction.

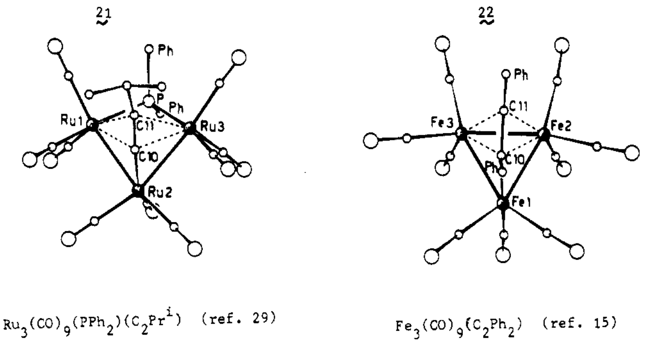


$(Cp)NiFe_2(CO)_6(C_2Bu^t)$ (ref. 235)

21

$HRu_3(CO)_9(C_2Bu^t)$ (ref. 36)

22



$Ru_3(CO)_9(PPh_2)(C_2Pr^i)$ (ref. 29)

23

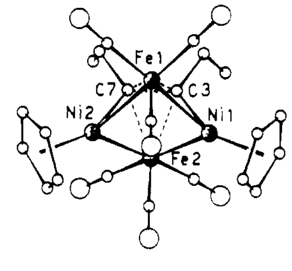
$Fe_3(CO)_9(C_2Ph_2)$ (ref. 15)

24

Figure 7. Complexes with alkyne or acetylide ligands (σ + 2π) interacting with three metal atoms (bonding modes K and L).

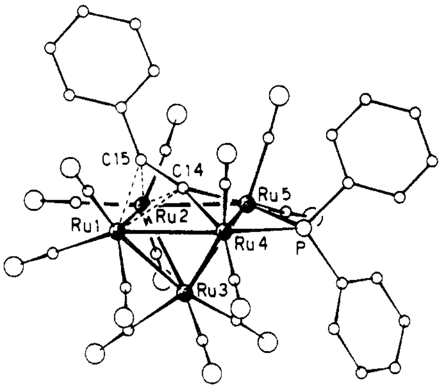
These three bonding situations on a square-planar metal arrangement are depicted in Figure 8 and in Figure 2 for the iridium complex.

On the other hand, alkyne-substituted butterfly clusters, either homo- or heterometallic, are relatively common; the bonding of the alkyne is usually μ_4–η^2



$(Cp)_2Ni_2Fe_2(CO)_6(C_2Et_2)$ (ref. 274)

25



$Ru_5(CO)_{13}(PPh_2)(C_2Ph)$ (ref. 155)

26

Figure 8. Examples of alkyne or alkyne-derived ligands interacting with four metal atoms (bonding modes O and R).

(σ–π–σ–π) (*bonding mode P*), e.g., $Ru_4(CO)_{12}(C_2Ph_2)$ (**27**).[131] These structures can be formally considered as derived from σ–π–σ, μ_3–η^2 complexes upon addition of a $M(CO)_n$ fragment on one side of the cluster. Conversely, this fragment can be removed from the tetrametallic cluster, as shown with $[Co_3Ru(CO)_{10}(C_2Ph_2)]^-$.[338] The already discussed "substitution" of a $Ru(CO)_3$ with a Ni(Cp) fragment on $Ru_4(CO)_{12}(C_2Ph_2)$[120] indicates that this interpretation is probably correct. The isomerism of the $FeRu_3(CO)_{12}(RC_2R')$ butterfly complexes showing this type of structure has already been discussed (see Scheme 3).[127]

Further substitution with alkyne of the above structures leads to flattened butterflies, or nearly square-planar structures with two independent alkynes, e.g., $Ru_4(CO)_{11}(RC_2R)(R'C_2R'')$.[130] The structure of these complexes has been hypotheszied; whereas an iron homologue, $Fe_4(CO)_{11}(HC_2Et)_2$ (**28**), has been studied by X-ray diffraction.[125] Also in this complex a μ_4–η^2 (σ–π–σ–π) bonding mode is observed for each alkyne unit.

Alkyl-substituted alkynes on ruthenium clusters isomerize to allenic, then to allylic ligands.[37,39] These allylic ligands are also found to coordinate to butterfly clusters. In particular it was found for the $(Cp)NiRu_3(CO)_8(C_6H_9)$ isomers[153] that there is no significant modification of this organic moiety when passing from the starting trinuclear complex to the tetranuclear product (see Scheme III).

Another structural arrangement is found in some butterfly derivatives, like $(Cp)NiRu_3(H)(CO)_9[C_2(H)Bu\text{-}t]$ (**31**),[151,152] where the vinylidene interacts σ with three metal atoms and π with the fourth (*bonding mode Q*). A comparable situation in a homometallic cluster is found in $(HO)Ru_4(CO)_{10}(PPh_2)[C_2(H)Pr\text{-}i]$ (**29**).[135] Finally, the situation with an acetylide interacting σ and π with two (wingtip and hinge) metals has been found in the heterometallic complex $NiRu_4(CO)_9(PPh_2)_2(C_2Pr\text{-}i)_2$ (**30**)[156] (*bonding mode S*). The structures of the complexes **27**–**31** are represented in Figure 9.

A similar coordination for CO and for methyne has been found respectively in $HFe_4(CO)_{13}^-$ [236] and $HFe_4(CO)_{12}(CH)$;[237] a related structure is that of the $HFe_4(CO)_{12}(COMe)$ cluster.[318] All these have been shown to be of importance in the general picture of the homogeneously catalyzed Fischer–Tropsch reactions. Indeed, from the methyne clusters,[237] carbido clusters can be obtained by reversible hydrogenation–dehydrogenation; on the other hand, it was shown that reactions of coordinated CO with acetyl chloride afford carbido clusters[238] (and release CO_2). This type of carbido clusters is expected to present carbocationic reactivity.[239,240]

The structures of these formally analogous complexes are represented in Figure 10.

At present, no similar reactions were attempted or found for alkyne derivatives. Further investigations in this field would be highly desirable.

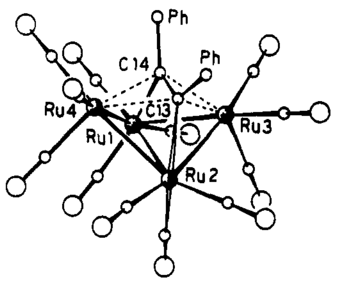
In Table VIII the main structural features of the above complexes are reported.

B. "Activation" of the Alkyne upon Coordination to the Metals

Following a criterion introduced by Muetterties,[6] either for CO, isonitriles, or alkyne triple bonds, the elongation of this bond after coordination to more than one metal center is taken as a parameter of "activation" upon coordination, and used for comparison with the behavior of these molecules on surfaces. (When discussing the C–C bond activation, and the bonding parameters in general, in mixed-metal clusters, the different metal radii should be taken into account and the distances should be corrected in this sense.) This means that the structural parameters in the solid state play a very important role in discussing the effects of the coordination to several metal centers. It should also be noted that the concept of "activation" is obviously related to chemical reactivity and may often involve specific features of the solution chemistry (such as lability, dynamic behavior...) that are not directly accessible through solid-state structural data.

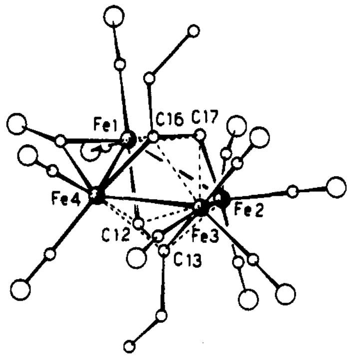
A gap still exists between metal surfaces and clusters; indeed relatively few very high-nuclearity clusters have been obtained, which could be compared to crystallites.[3] The other clusters still are "small" metal fragments, in which the ligands play a major role; thus, there is a difference in the M–M distances in the bulk metals and in small clusters, as pointed out by Muetterties; the metal–metal distances in clusters are usually longer than in the bulk metal. On the other hand, the bridging ligands (hydrogen, CO, isonitriles, alkynes) can shorten or lengthen the M–M distances with respect to nonbridged situations.

Thus, a delicate balance of effects determines the cluster size, and hence, in part, the "activation" of small molecules on clusters. This has been discussed, in particular, for the $2\sigma + \pi$ clusters;[120] electronic and



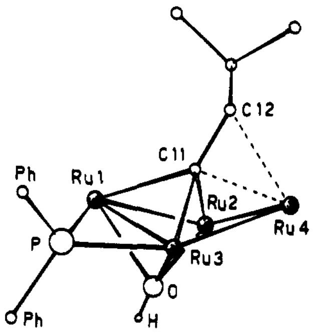
$Ru_4(CO)_{12}(C_2Ph_2)$ (ref. 131)

27



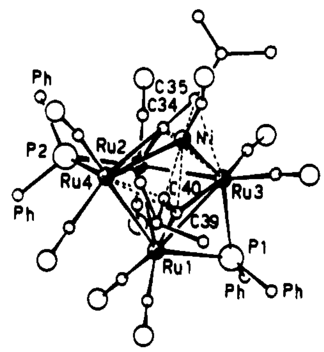
$Fe_4(CO)_{11}(HC_2Et)_2$ (ref. 125)

28



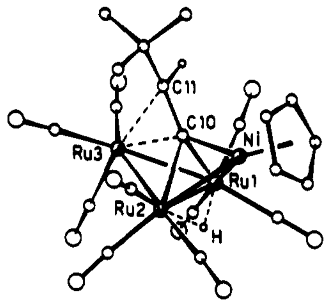
$(HO)Ru_4(CO)_{10}(PPh_2)[C_2(H)Pr^i]$(ref.135)

29



$NiRu_4(CO)_9(PPh_2)_2(C_2Pr^i)_2$ (ref. 156)

30



$(Cp)NiRu_3(H)(CO)_9[C_2(H)Bu^t]$ (ref. 151)

31

Figure 9. Examples of alkyne or alkyne-derived ligands interacting with four metal atoms (bonding modes O, P, Q, and S).

steric factors also play a role in determining the degree of "activation", and sometimes clusters of comparable size interact with alkynes in different ways.

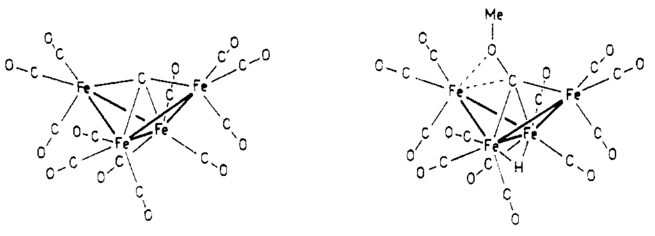
However, the considerable number of structures now available, for carbonyl clusters as well as for alkyne-substituted clusters, allows at least some *statistical* considerations. For the alkyne clusters, in particular, these agree to a considerable extent with the hypothesis of Muetterties.

Thus, the stronger is the interaction with the cluster, either for only σ-bound or for σ–π-bound alkynes, the greater is the probability of finding long C–C distances, sometimes close to the single C–C bond. Perhaps, the main "irregularity" is found for the $2\sigma + \pi$ and $\sigma + 2\pi$ derivatives; in the former a slightly greater activation is found. This may be explained when considering the relationships between the different structures (see reactivity section).

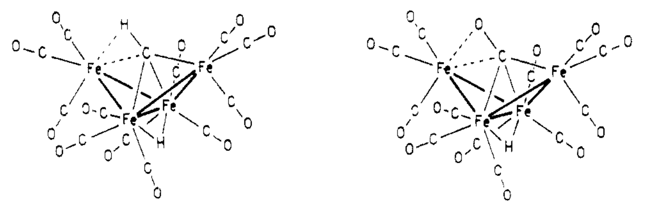
C. Complexes Containing Organic Rings or Chains Formed upon Interaction of Alkynes Held in Proximity

Often, after the coordination of one (or two) alkynes on clusters, interaction between the ligands occurs, which leads to still coordinated oligomers. This process is usually accompanied by hydrogen shift; sometimes cluster opening is also observed. For the iron clusters, easy demolition to products of lower nuclearity is also observed in the presence of excess alkyne.

Few examples are known in which the alkynes oligomerize to give an organic cyclic ligand coordinated to the metals; thus in $Fe_3(CO)_8(HC_2Me)_4$ (**10**)[26] and $Fe_3(CO)_7(HC_2Et)_4$ (**19**)[28] substituted cyclopentadienyls are formed from alkynes. Complexes containing metallacyclic rings are more common. Metallacyclobutenes have been reported,[241] as well as metallacyclo-

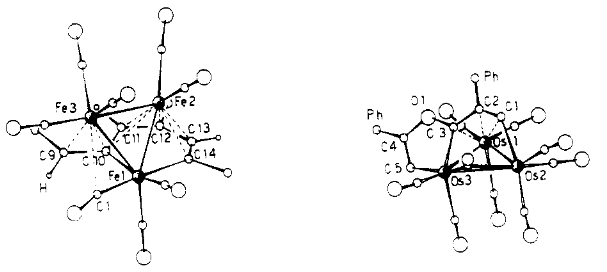


$[Fe_4(CO)_{12}C]^{2-}$ $HFe_4(CO)_{12}(COMe)$



$HFe_4(CO)_{12}(CH)$ $[HFe_4(CO)_{13}]^-$

Figure 10. Butterfly clusters in which CO, CH, COMe, and C interact with four iron atoms (see related **29** and **31**).



$Fe_3(CO)_8(HC_2Me)_3$ (ref. 22) $Os_3(CO)_9[(HC_2Ph)_2CO]$ (ref. 83)

32 **33**

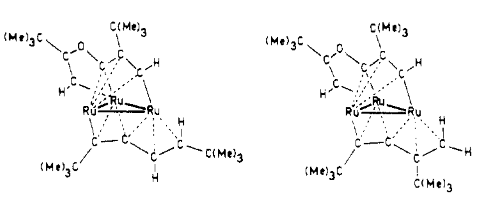
Figure 11. Complexes containing metallacycles obtained from alkynes.

pentadienes either on closo osmium clusters[86,88,90] or on the central atom of an open iron[19] or ruthenium cluster.[53,55] In some instances one of the terminal metals of an open cluster can be incorporated into a 5-membered ring.[57] Isomers of these derivatives can be obtained, depending upon the alkyne substitution. A unique metallacyclohexatrienic ring has been found in $Fe_3(CO)_8(HC_2Me)_3$ (**32**).[22]

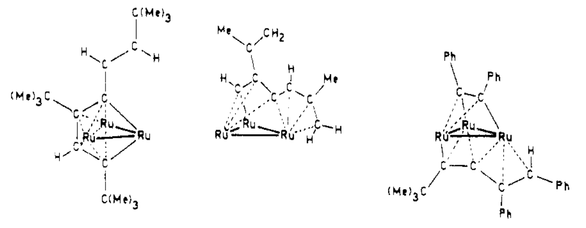
Unusual metallacyclic rings with insertion of one CO, which is probably a former terminal CO of the cluster, have been found for $Os_3(CO)_9[(HC_2Ph)_2CO]$ (**33**)[83] and for the isomers $Ru_3(CO)_6(C_{12}H_{20})(C_{13}H_{20}O)$, these latter also containing an "open chain" alkyne dimer[60] (see the next section). The structures of the complexes **32** and **33** are represented in Figure 11 and those of the isomers in Figure 12.

D. Complexes Containing "Open Chain" Oligomers

Alkyne di- and trimerization can result in "open chain" substituents linked to metal clusters; thus, in the above $Ru_3(CO)_6(C_{12}H_{20})(C_{13}H_{20})$[60] one of the substituents is a dimer formed upon insertion or nucleophilic attack to the coordinated acetylide in the starting $HRu_3(CO)_9C_2Bu$-*t*; the same process occurs for $Ru_3(CO)_7(C_2Ph_2)[(C_2Bu\text{-}t)(HC_2Ph_2)]$[59] and results in a comparable organic moiety.



$Ru_3(CO)_6(C_{12}H_{20})(C_{12}H_{20}O)$ (two isomers, ref. 60)



$Ru_3(CO)_8(HC_2Bu^t)_3$ (ref. 57) $Ru_3(CO)_8(C_{10}H_{12})$ (ref. 53) $Ru_3(CO)_7\{(C_2Ph_2)(C_2Bu^t)[PhC_2(H)Ph]\}$ (ref. 59)

Figure 12. Complexes containing "open chain" oligomers obtained from alkynes.

Also, insertion of two *tert*-butylacetylene molecules in the Ru–C σ bond of the above hydride accounts for the formation of the open chain chelating the central metal atom of the open triangle in $Ru_3(CO)_8(HC_2Bu\text{-}t)_3$.[57] Dimerization of isopropenylacetylene on $Ru_3(CO)_{12}$ also affords an open chain in $Ru_3(CO)_8(C_{10}H_{12})$.[53]

The structures of the above complexes, in which the carbonyl groups are omitted for clarity, are schematically represented in Figure 12.

The "open" chains discussed above always contain one carbon atom involved in a complex bonding with the metals, which is characterized by "irregular" bonding angles, not consistent with the known hybridizations of the carbon atoms. At present the reasons for this rather common behavior are not clearly understood.

On the other hand, the dienes simply substitute CO ligands without affecting the main characteristics of the clusters, either substituted[235] or not.[242]

IV. Spectroscopic Data in Solution

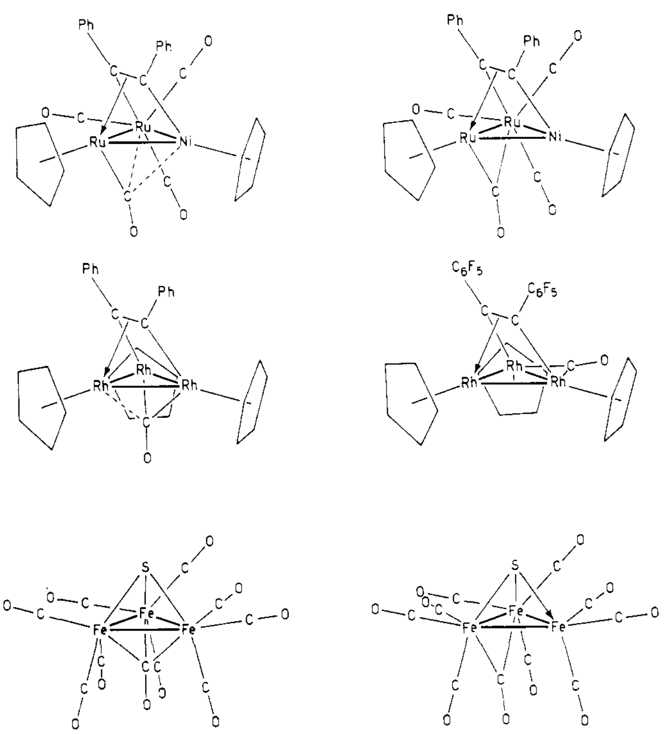
A. Infrared Studies

At present no studies on frequency assignments or force constant calculations have been performed, mainly because of the complexity of these molecules. Also, whereas it is very easy to detect the different types of coordinated CO's, the detection of the C–C vibration is very difficult.

On the other hand, routine use of IR has been shown to be useful for the detection of some functional groups, as well as for indications on the bonding of the CO substituents.

In particular, the observation in solution of one more absorption than expected for the bridging carbonyls of $(Cp)_2NiRu_2(CO)_3(\mu_3\text{-}CO)(C_2Ph_2)$[123] has shown the presence of an isomer with a double CO bridge, whereas in the solid state an asymmetrical triple bridge has been found. A similar isomerism has been found for $Fe_3(CO)_9(\mu_3\text{-}CO)S$[143] in solution, and for rhodium com-

Scheme VI



plexes with different alkynes, in the solid state.[106]

These isomers are represented in Scheme VI.

B. ^{1}H NMR Studies

The best known application of this technique is the detection of the hydrido ligands, which are frequently found in the alkyne–carbonyl cluster chemistry.

The hydrido clusters have been recently reviewed,[4] thus only few comments will be added here.

Although some differences can be observed between the chemical shifts in different complexes, these data are not sufficient for unequivocal structural assignments. Indeed there are only limited correlations between the substituent type and the hydridic signals; also it is difficult to find suitable parameters for describing the influence of the alkyne ligands on the cluster, and hence on the hydrido ligand chemical shift.

Alkyne fluxionality has been detected by means of NMR for $\sigma + 2\pi$ and $2\sigma + \pi$ bonded ligands;[244] these findings agree with the structural relationships found for these complexes (see reactivity section).

Examples of hydride fluxionality, and H/D exchange processes have been observed;[4,245] also, protonation studies have been performed.[60] These are of interest in order to detect the nucleophilic centers in these clusters.

Two other potentialities of the NMR technique deserve attention, namely:

The identification of substitution isomers either in homo- or in heterometallic clusters,[153] which could be detected, but not fully characterized by IR. However, the knowledge of their molecular structure by X-ray diffraction remains fundamental for a complete identification.

The detection of hydrogen atoms bound to carbons interacting either σ or π with the metals. This allows structural predictions with remarkable accuracy, as, either in bimetallic derivatives or in clusters it has been found that these hydrogens give rise to lowfield signals with respect to their expected normal shifts.

These data are collected in Table IX.

One can observe that these signals fall usually between −1 and +1.5 τ and hence they constitute a good diagnostic mean. The very deep reason for this behavior has not been clearly explained; it is interesting to observe that carbon atoms σ–π-bonded to metals also give lowfield signals in the ^{13}C NMR probably because of their pseudocarbenic situation (see Table XI).

C. ^{13}C NMR Studies

Of the many structural studies using this technique, relatively few concern alkyne clusters. Common features in alkyne–carbonyl clusters are multistep processes.[257] Thus, in the spectra of $Fe_3(CO)_8(C_2Ph_2)_2$, "black" and "violet" isomers,[18] and of $Fe_3(CO)_8(HC_2Me)_3$ (**32**)[22] it was found that the CO's on the iron atoms σ-bonded to the organic moiety did not participate to the exchange processes. In the spectrum of $Fe_3(CO)_8(HC_2Et)_4$ (**10**)[26] a two-step exchange process was found: equivalence of terminal CO's (via axial–equatorial or pairwise bridge–terminal CO exchange), then delocalized scrambling involving bridging carbonyls.

Rigidity up to 100 °C has been reported for the $H_3M_3(CO)_9CMe$ (M = Ru, Os) species.[258] In the $HM_3(CO)_9C_2Bu$-*t* (M = Ru, Os) hydrides[34] first stereochemical nonrigidity at M–C(σ), then delocalized scrambling for Ru (for Os only up to 173 °C) were observed. In several $HRu_3(CO)_9(RCCHCR')$ derivatives[259] only localized scrambling has been observed and the exchange processes at each metal have different activation energies depending upon the nature of the M–C bonding, the substituents of the organic moiety and the presence or not of hydrido bridges. The nature of the M–C bonding may also influence the regiospecific substitution of phosphines for CO's.

In these complexes no fluxionality was found for the organic moiety with respect to the cluster; in these, as well as in other examples, the fluxionality of the alkyne would require intermediates with different metal–carbon bonds, hence high activation energies.

Indeed, Hoffmann's recent work on bimetallic perpendicular and parallel acetylene complexes has shown that the two alternative geometries have different electronic requirements;[323] each mode of acetylene coordination requires a different coordination geometry at the metals and the interconversions hence require a relatively high activation energy.[324]

However, some examples of alkyne fluxionality have been discussed, on similar structures.[244] Also, in the $HOs_3(CO)_{10}(CH{=}CHR)$ derivatives[260] results consistent with ligand fluxionality were reported. One of the forms of $H_2M_3(CO)_9(C_2RR')$ (M = Ru, Os) shows CO rigidity up to 100 °C, then localized exchange and hydrogen migration, whereas the other one shows three processes, namely, hydride exchange, then localized exchange of CO's at M–C(σ), then fluxionality of the organic moiety.[261]

Rapid intramolecular rotation of the benzyne ligand in $HOs_3(CO)_9(AsMe_2)(C_6H_4)$, via the formation of CO-bridged intermediates has been recently proposed.[325]

Also, the different orientation of the alkenyl ligands with respect to the hydridic clusters in the complexes

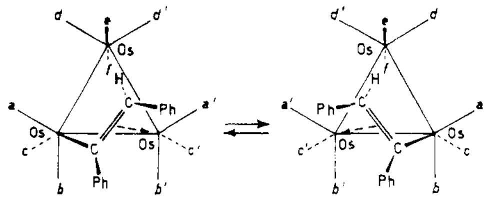
TABLE VIII. Structural Parameters for Alkynes Coordinated to Four Metal Atoms

complex	bonding mode	bonding distances, Å M-M	M-C(σ)	M-C(π)	C-C	ref
$Os_6(CO)_{16}(CMe)_2$	N		2.13 (7), 2.19 (7) 2.17 (7), 2.24 (7)			157
$Ir_4(CO)_8[C_2(COOMe)_2]_4$	N	2.715 (1), 2.715 (1) 2.810 (1), 2.810 (1)	2.120 (7), 2.136 (7) 2.117 (8), 2.161 (7)		1.446 (9)	148
$(Cp)_2Ni_2Fe_2(CO)_6(C_2Et_2)_2$	O	2.426 (3),[a] 2.417 (3)[a] 2.422 (3),[a] 2.414 (3)[a]	1.918 (17),[b] 1.955 (15)[b]	2.043 (16),[c] 2.054 (17)[c] 2.091 (16),[c] 2.081 (16)[c]	1.431 (23)	274
$Ru_4(CO)_{12}(C_2Ph_2)$	P	2.85 (1),[i] 2.74 (1) 2.71 (1), 2.71 (1) 2.74 (1)	2.16 (1), 2.16 (1)	2.24 (1), 2.24 (1) 2.25 (1), 2.26 (1)	1.46 (2)	131
$Os_4(CO)_{12}(C_2H_2)$	P	2.847 (2),[i] 2.791 (2) 2.792 (2), 2.799 (2) 2.791 (2)	2.19 (3), 2.11 (3)	2.22 (3), 2.22 (3) 2.16 (3), 2.24 (3)	1.55 (4)	140
$Os_4(CO)_{12}(HC_2Et)$	P	2.849 (2),[i] 2.760 (2) 2.760 (2), 2.740 (2) 2.764 (2)	2.17 (3), 2.11 (3)	2.23 (3), 2.21 (3) 2.21 (3), 2.26 (3)	1.54 (3)	140
$Ru_4(CO)_9(C_6H_6)(C_6H_8)$	P	2.809 (3),[i] 2.702 (3) 2.643 (3), 2.700 (4) 2.655 (3)	2.078 (12), 2.153 (12)	2.222 (14), 2.229 (13) 2.221 (12), 2.276 (12)	1.400 (17)	137
$Ir_4(CO)_5(C_8H_{12})_2(C_8H_{10})$	P	2.695 (1), 2.710 (1) 2.731 (1), 2.787 (1)[i] 2.741 (1)	2.10 (1), 2.12 (1)	2.16 (1), 2.24 (1) 2.21 (1), 2.24 (1)	1.49 (2)	147
$Co_4(CO)_{10}(C_2Et_2)$	P	2.450 (5), 2.433 (5) 2.438 (5), 2.416 (5) 2.552 (5)[i]	2.01 (1)[f]	2.03 (1), 2.18 (1) 2.03 (1), 2.15 (1)	1.44 (2)	143
$Fe_4(CO)_{11}(HC_2Et)_2$	O	2.608 (4), 2.633 (4) 2.515 (5), 2.644 (4)	1.998 (9), 2.013 (11) 1.997 (12), 1.991 (10)	2.145 (13), 2.187 (11) 2.113 (12), 2.229 (9) 2.152 (12), 2.173 (13) 2.133 (10), 2.209 (9)	1.374 (15) 1.397 (16)	125
$Ru_4(CO)_{10}(C_{12}H_{16})$	allyl	2.850 (6), 2.811 (8) 2.776 (6), 2.775 (5) 2.775 (6)	2.14 (4), 2.14 (5)	2.19 (6), 2.17 (5) 2.19 (4), 2.09 (6) 2.28 (5), 2.20 (9) 2.40 (7), 2.17 (11) 2.34 (4)		133
$Ru_4(CO)_{11}(C_8H_{10})$	P	2.823,[i] 2.728 2.735, 2.749 2.739	2.15, 2.18	2.21, 2.25 2.20, 2.20	1.43	136
$(Cp)NiRu_3(CO)_8(C_6H_9)$	allyl	2.664 (3),[a,i] 2.611 (5)[a] 2.595 (5),[a] 2.708 (3) 2.693 (3)	1.877 (18),[b] 2.169 (16)[d]	2.313 (18),[d] 2.330 (18)[d] 2.261 (15),[d] 2.338 (17)[d] 2.304 (18),[d] 2.260 (15)[d]		153
$Ru_5(CO)_{13}(PPh_2)(C_2Ph)$	S	2.696 (1), 2.855[e]	2.114 (8), 2.095 (8)	2.190 (8), 2.216 (8) 2.234 (8), 2.163 (9)	1.342 (11)	155
$(HO)Ru_4(CO)_{10}(PPh_2)[C_2(H)Pr\text{-}i]$	Q	2.7584 (6), 2.8004 (6) 2.7027 (5), 2.8027 (5) 3.4559 (6)	2.183 (5), 2.178 (5) 2.236 (5)	2.105 (5), 2.267 (6)	1.415 (7)	135

$NiRu_4(CO)_9(PPh_2)_2(C_2Pr\text{-}i)_2$	S	2.813 (5),[i] 2.771 (5) 2.789 (6), 2.831 (5) 2.770 (4), 2.662 (6)[a] 2.668 (6)[a]	2.04 (3),[d] 2.27 (4)[d] 2.06 (2),[d] 2.31 (2)[d]	2.25 (2),[d] 1.99 (3)[b] 2.44 (3),[d] 1.89 (3)[b] 2.28 (3),[d] 2.02 (2)[b] 2.50 (3),[d] 2.08 (4)[b]	1.34 (3) 1.38 (4)	156
$(Cp)NiRu_3(H)(CO)_9[C_2(H)Bu\text{-}t]$	Q	2.825 (2),[i] 2.788 (3) 2.833 (2), 2.572 (3)[a] 2.555 (3)[a]	1.834 (8),[b] 2.156 (8)[d] 2.176 (9)[d]	2.159 (8), 2.227 (10)	1.436 (13)	151
$FeCo_3(CO)_9(C_2Ph_2)(CPh{=}CHPh)$	P	2.437 (4),[a] 2.452 (4)[a] 2.369 (4), 2.468 (4) 2.670 (4)[a,i]	1.974 (10),[g] 2.092 (10)[c]	2.143 (10), 2.051 (11) 2.063 (10), 2.059 (11)	1.41 (2)	298
$FeRu_3(CO)_{12}(C_2Ph_2)$, two isomers, Fe on the wing	P	2.681 (1),[a] 2.649 (1)[a] 2.700 (1),[a] 2.681 (1)[a] 2.849 (1)[i]	2.166 (3),[d] 2.188 (3)[d]	2.160 (3),[h] 2.163 (3)[h] 2.204 (3),[h] 2.185 (3)[h]	1.458 (4)	127
Fe in the hinge	P	2.712 (1),[a] 2.646 (1)[a] 2.680 (1),[a] 2.688 (1)[a] 2.780 (1)[i]	2.136 (2),[h] 2.105 (3)[h]	2.235 (1),[d] 2.234 (2)[d] 2.259 (3),[d] 2.237 (2)[d]	1.460 (3)	127
$Os_4(CO)_{12}(C_2H_2)$	P	2.791 (2), 2.792 (2) 2.799 (2), 2.791 (2) 2.847 (2)[i]	2.19 (3), 2.11 (3)	2.22 (3), 2.16 (3) 2.22 (3), 2.24 (3)	1.55 (4)	140
$Os_4(CO)_{12}(C_2HEt)$	P	2.760 (2), 2.760 (2) 2.740 (2), 2.764 (2) 2.849 (2)[i]	2.17 (3), 2.11 (3)	2.23 (3), 2.21 (3) 2.21 (3), 2.26 (3)	1.54 (3)	140

[a] Heterometallic distances. [b] Ni–C distances. [c] Fe–C distances. [d] Ru–C distances. [e] Mean of seven values. [f] Averaged values. [g] Co–C distances. [h] Distances involving C and Ru or Fe, as disordered in two positions. [i] Distances refer to the "hinge" side of the "butterfly" cluster.

Scheme VII



$HOs_3(CO)_{10}(RC{=}CHR')$ in the solid state has been considered; thus the vinyl groups —HC═CHR (R = H, Et) behave differently from the stilbenyl ligand — PhC═CHPh.[326] The fluxional behavior of this latter has been reported[326] and the proposed fluxional mechanism is shown in the Scheme VII.

The ^1H and ^{13}C NMR techniques have also allowed several reactions of the alkynes on clusters to be easily followed. Thus, thermal decarbonylation of $Os_3(CO)_{11}(AsMe_2CHCH_2)$ in refluxing hydrocarbons gives successively $Os_3(CO)_{10}(AsMe_2)(CHCH_2)$, $HOs_3(CO)_9(AsMe_2)(C.CH_2)$ and $HOs_3(CO)_9(AsMe_2)(CHCH)$; this is the first known example of isomerization of μ_3-vinylidene to μ_3-acetylene on clusters.[256]

Also, the reactivity of hydroxyalkynes and aminoalkynes has been followed by this technique (see, for example, ref 45).

Also, temperature-dependent "flipping" of an organic moiety has been found, in the binuclear $Fe_2(CO)_6[(COO)(C_2Et_2)]$ complex, and in related systems.[262] As a personal opinion of the authors, we consider that these NMR experiments should be more often followed by a complete and stoichiometric recharacterization of the products after variable temperature runs.

Among the tetranuclear derivatives, $Co_4(CO)_{10}(C_2Ph_2)$ has been studied;[18] the limiting spectrum was not obtained because of the poor solubility of the compound. Interchange of bridging and terminal CO's on the four metals was reported.

From the above results, and with the expressed reservations, one can see that CO fluxionality is obviously dependent upon the structure of the complexes; and that alkyne fluxionality is not infrequent, despite the predicted high-activation energies. The significance of these behaviors for the study of the adsorption phenomena of small molecules onto surfaces are clearly understandable.

From ^{13}C NMR spectroscopy other interesting data can be obtained, such as chemical shifts of the alkyne carbons involved in the bonding with the metals. This is of considerable value, either when considering the lack of IR results available on these ligands, or when discussing the electron donor–acceptor properties of these carbons.

Unfortunately, only few attempts of rationalization of these data have been performed, one being addressed to the $Co_3(CO)_9CR$ complexes.[92] In Table X the data for these complexes and for "apical" CO's are compared; also, some complexes for which structural work has not been possible are considered.

Also the chemical shifts of carbons involved in σ–π-bonding with the metals can be of interest, and usually low-field chemical shifts are found. Experimental problems, as well as several steric and electronic factors superimposed with the primary interaction, limit the utility of these data. Nevertheless a rough correlation

Table IX. Low-Field ^{1}H Chemical Shifts in Binuclear and Cluster-Alkyne Complexes Containing σ-π-Bonded Carbon Atoms (and Related Compounds)

complex	^{1}H chem. shift, τ	ref
$(Cp)Fe(CO)_2(RCOCH{=}CH)$ R = Me	1.23	246
R = Ph	0.79	246
$(Cp)Fe_2(CO)_5(RCOCH{=}CH)$ R = Me	−1.34	246
R = Ph	−1.60	246
$(Cp)Fe_2(CO)_6(X')(XCH{=}CH)$ X = X′ = I	0.83	247
X = Br, X′ = I	1.09	247
X = X′ = Br	1.35	247
X = X′ = Cl	1.76	247
X = F, X′ = Br	2.10	247
$Fe_2(CO)_6(SR)(CH{=}CH_2)$	1.85	247
$Fe_2(CO)_6[(R'C_2R)(CO)(HC_2R)]$ R = Ph, R′ = H	0.50	248
R = R′ = Ph	0.64	248
R = R′ = Bu-*t*	1.30	248
R = R′ = Pr-*n*	1.35	248
R = R′ = Me	1.42	248
R = Pr-*n*, R′ = H	1.50	248
R = Me, R′ = H	1.54	248
R = Bu-*t*, R′ = H	1.76	248
$Fe_2(CO)_5(HC_2R)_3(CO)$ R = Ph	−1.80	249
R = Et	−0.15	250
R = Bu-*t*	0.01	249

complex	solvent	temp, K	chem. shift, τ	ref
$Os_3(CO)_{10}(HC_2C_6H_5)$	$(CD_3)_2CO$		−0.06	63
$Os_3(CO)_{10}(HC_2C_6H_5)_2$	CCl_4		1.20	63
$HOs_3(CO)_9(C_4H_5)$, form B	$CDCl_3$	300	1.94 (d)	74
$HOs_3(CO)_9(C_6H_4)(PMe_2)$	$CDCl_3$	213	1.45, 0.99	251
$HOs_3(CO)_9(C_6H_4)(AsMe_2)$	$CDCl_3$	223	1.35, 0.88	251
	$CDCl_3$	365	1.16	251
$HOs_3(CO)_8(C_6H_4)(PMe_2)(PMe_2Ph)$	$CDCl_3$	333	1.32 (m)	309
$HOs_3(CO)_9(HC_2H)$	$(CD_3)_2CO$	153	1.64, −0.14	244
$HOs_3(CO)_9(HC_2Ph)$	$CDCl_3$	300	1.55	74
$HOs_3(CO)_9(C_3H_4)$	$CDCl_3$	308	1.05	81
$H_2Os_3(CO)_9(C_8H_{14})$	$CDCl_3$	313	1.82	81
$H_3Os_3(CO)_{10}(CH)$	$CDCl_3$		0.64 (q)	254
$HRu_3(CO)_9(C_4H_5)$	CCl_4		1.38	39
$HRu_3(CO)_9(C_5H_7)$	CCl_4		1.45	39
$HRu_3(CO)_9(HC{=}NBu$-$t)$			0.55	255
$Os_4(CO)_{12}(HC_2H)$	CD_2Cl_2		−0.28	140
$Os_4(CO)_{12}(HC_2Et)$	CD_2Cl_2		−1.0	140
$H_2Os_4(CO)_{11}(CHCHCHMe)$			−0.37 (ddd)	253
$H_2Os_4(CO)_{11}(CHCPhCHMe)$			−0.25 (dd)	253
$H_3Os_4(CO)_{11}(HC_2HR)$	$CDCl_3$	308	1.32, 1.17, 0.94	252
$H_2Os_4(CO)_{11}(HC_2R)$ R = H	$CDCl_3$	308	0.20	252
R = Ph	$CDCl_3$	308	0.07	252
R = Bu-*t*	$CDCl_3$	308	0.10	252

with the reactivity of the involved carbons can be evidenced.[319]

The chemical shifts for "pseudo-carbenic" carbons, by comparison with terminal and doubly bridging CO's are in Table XI.

Provided that the NMR data are somewhat indicative of the electronic density on the involved carbons, and that much more systematic work is made, this could become in the future an even more important method for predicting the reactivity of the complexes.

V. Mass Spectra

Mass spectrometry is a quick and useful tool for identification—and some structural predictions–on volatile complexes, which is usually the case for trimetallic alkyne derivatives of the iron triad.

Nature of the metal cluster (particularly important in case of heterometallic clusters), number of carbonyls and other ligands, molecular weight, and hydrogen loss are the main information obtainable on small samples.

Instruments working with electron impact ionization systems have been reported[2] as the most useful; other ionization techniques (chemical ionization, field ionization or desorption, negative ionization) have been applied in very limited extent until now. Field desorption and fast atom bombardment (FAB) seem particularly useful for detecting the parent ions in complexes that would otherwise fragment.[269,270]

Limiting factors are essentially:

Volatility of the samples: it is drastically reduced in the case of phosphidoalkynes, phosphine derivatives, anionic clusters and large polymetallic derivatives.

Rearrangements in the instrument; this has been reported in particular for Co–Rh derivatives.[2]

Dependence of the results from the characteristics of the instrument[271] or from the experimental conditions.[47,272]

Finally, in the working conditions, especially when the temperature increase in the introduction systems is not rigorously controlled, deposition of metal in the instrument can occur, resulting in gradual loss of sensitivity and reduced machine lifetime, and frequent maintenance operations. In particular, instruments with sealed-glass connections must be avoided for these analyses.

For these reasons a low number of studies has been performed on alkyne clusters, whereas it would be

TABLE X. ^{13}C NMR Chemical Shifts for Apical Carbons, Triply Bridging CO's and Apical-COR Groups

complex	solvent	temp, K	chem. shift[a]	ref
A. Triply Bridging CO's				
$Rh_6(CO)_{15}I^-$	*e*	204	245.3, 239.2, 232.9	263
$Fe_3(CO)_{10}(COCH_3)^-$	*f*	153	264	265
$Fe_3(CO)_{10}[COC(=O)CH_3]^-$	*f*	173	281.6	265
B. Apical COR				
$Fe_3(CO)_{10}(COCH_3)^-$	*f*	153	336.8	265
$Fe_3(CO)_{10}[COC(=O)CH_3]^-$	*f*	173	292.9	265
$HFe_3(CO)_{10}(COCH_3)$	*f*	153	356.5	265
$HFe_3(CO)_{10}(COH)$	*f*	173	358.8	265
$[HFe_3(CO)_{11}]^-$	*f*	166	301.3	266
$[HFe_3(CO)_{11}]^-$ [b]	*f*	153	285.7	266
$[HFe_3(CO)_{11}]^-$ [b,d]	*f*	186	355.1	266
$HRu_3(CO)_{10}(COCH_3)$	*f*	173	366.5	267
$H_3Os_3(CO)_9(COCH_3)$			205.2	264
$Fe_4(CO)_{12}(COCH_3)^-$	*e*	183	361.2	268
C. Apical CR				
$Co_3(CO)_9CH$	*g*		263	92
$Co_3(CO)_9CCH_3$	*g*		296	92
$Co_3(CO)_9CPh$	*g*		286	92
$Co_3(CO)_9CCF_3$	*g*		255	92
$Co_3(CO)_9CCOOCH_3$	*g*		268	92
$Co_3(CO)_9CX$, X = F	*g*		309	92
X = Cl	*g*		276	92
X = Br	*g*		269	92
X = I	*g*		234	92
$Fe_3(CO)_8(HC_2Me)_4$	*g*		345.6[c]	26
$Fe_3(CO)_8(HC_2Et)_4$	*g*		342.3[c]	250
$H_3Ru_3(CO)_9CCH_2Bu$-*t*	*g*		205.2	47, 60

[a] δ, downfield positive with respect to TMS. [b] Different counterions. [c] "Isomer 1" (of known structure). [d] With $BF_3 \cdot Et_2O$. [e] CD_2Cl_2. [f] $CHFCl_2/CD_2Cl_2$. [g] $CDCl_3$.

highly desirable that more systematic information was available, especially when considering the accessibility of this technique.

Mass spectrometric "irregularities" were useful for a more complete study of the structure of $(Cp)NiFe_2(CO)_6(C_2Bu\text{-}t)$,[117,118] which effectively was found different from the predictions based on the E.A.N. rule. Some work on bimetallic derivatives has also shown that the fragmentation patterns usually are in good agreement with the structural ^1H and ^{13}C NMR findings, especially for σ–π-bound carbons.[273]

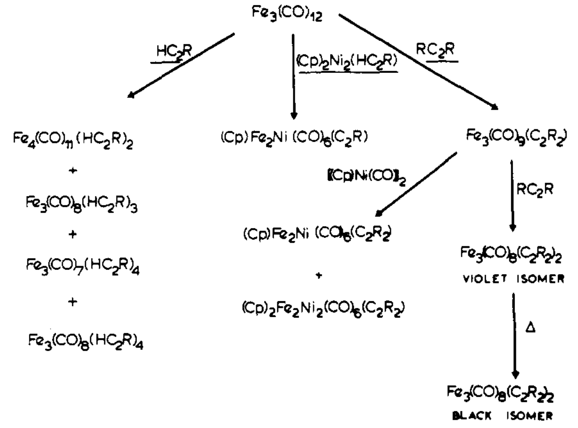
Some heterometallic alkyne clusters have been studied by means of electron impact and metastable ions kinetic energy (MIKE) techniques;[129] the fragmentation patterns can be described as "retrosynthetic patterns" for these clusters. Also "metal extrusion" from the ionized species, comparable to that reported in solution[119] has been found.

In general, the substitution of CO's with ligands stabilizes the clusters and more fragments of high nuclearity are detected. In case of mixed-metal clusters, ligand exchange and metal exchange processes can be evidenced by the nature of the fragments; some apparent irregularities for tetrametallic mixed clusters are under investigation.[129]

VI. Reactivity

The main aspect of the reactivity of the alkyne–carbonyl clusters to be considered is the "modellistic approach", i.e., the triple bond activation. This has already been discussed in the structural section. Two other related aspects must, however, be taken into account: the behavior of alkynes showing different polarity of the triple bond (HC_2R, RC_2R', and RC_2R) toward the same metal cluster and "vice versa" the behavior of metal clusters of the same triad toward a given alkyne; the reactivity of differently coordinated alkynes or acetylides toward nucleophiles and electrophiles, and the reactivity of the alkyne-substituted clusters at points other than the triple bond.

Scheme VIII



Finally, the reactivity of functionalized alkynes must be also taken into account, because of its implicit potentiality in preparative chemistry as well as its relevance to the study of the relationship between clusters and surfaces.

Last, but not least, is the present and potential use of the alkyne–carbonyl clusters in stoichiometric or catalytic processes and their role as intermediates in some reactions.

A. Reactivity of HC_2R, RC_2R', and RC_2R Alkynes toward the Same Metal Cluster

Better known is the reactivity of the trimetallic carbonyls of the iron triad.

Considerable differences are found in the behavior of the different clusters. Thus, easy cluster opening, followed by demolition to bimetallic products is found for iron in the presence of C_2Ph_2; the same occurs with C_2Et_2 that does not isomerize (this occurs for ruthenium and osmium). No hydridic derivatives, which are common for both ruthenium and osmium, were found for iron. With HC_2R alkynes, complex structures are isolated, in particular, the formation of cyclopentadienylic ligands seems to be characteristic for iron.[26,28] These are derived from alkyne coupling; the other metals give metallacyclic structures more easily. These reactions are summarized in Scheme VIII.

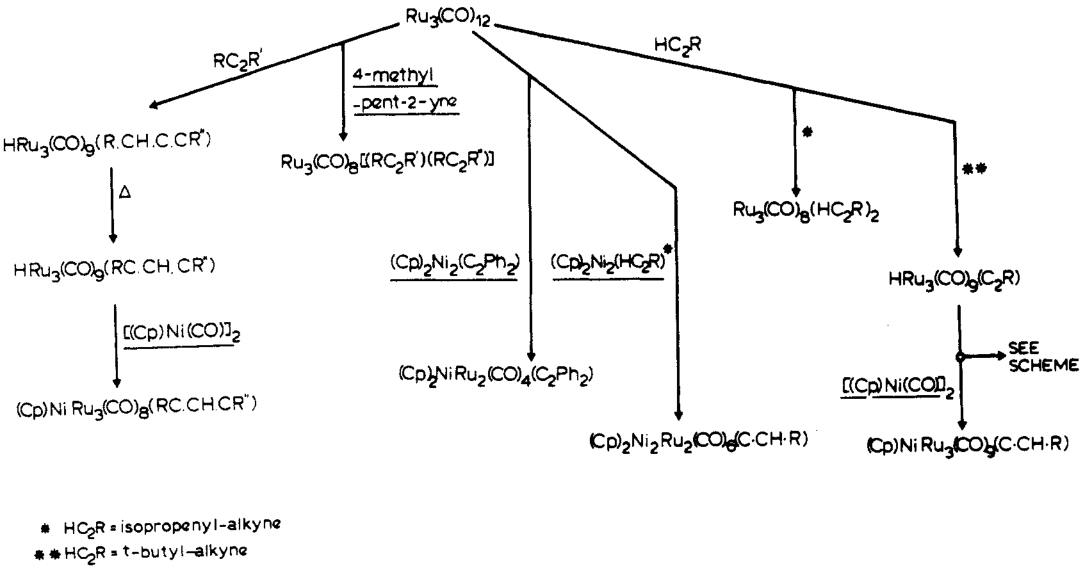
Triruthenium dodecacarbonyl shows more pronounced differences in reactivity; with C_2Ph_2 a monosubstituted butterfly complex is obtained; it undergoes further substitution and, finally, thermal demolition to trimetallic derivatives occurs. C_2Et_2 and the other alkyl-substituted alkynes undergo isomerization to "allenic", then to "allylic" hydrides. HC_2R alkynes give acetylido hydrides, then polysubstituted complexes. Isopropenylacetylene and 4-methylpent-2-yne give linear dimers and dehydrogenated metallacyclic products, respectively. The behavior of the phosphino alkynes

Table XI. Low-Field ^{13}C Signals for "Pseudo-Carbenic" Carbon on Bimetallic and Cluster-Alkyne Complexes, by Comparison with the CO Chemical Shifts

complex	solvent	temp, K	chem. shift[a]	ref
A. Terminal CO's (Selected Values)				
$H_3Ru_3(CO)_9CMe$	C_6D_6	273-298	190.1	49
$HRu_3(CO)_9(C_6H_9)$		273-298	192-199[b]	38
$HRu_3(CO)_9(C_2Bu\text{-}t)$	C_6D_6	211	186-196[b]	34
$HOs_3(CO)_9(C_2Bu\text{-}t)$	C_6D_6	236	163-183[b]	34
$Rh_4(CO)_{12}$	CD_2Cl_2	208	175-183[b]	263
$Co_4(CO)_{12}$	CD_2Cl_2	213	192-196[b]	263
$RhCo_3(CO)_{12}$	CH_2Cl_2	188	183-200[b]	263
B. Doubly Bridging CO's (Selected Values)				
$Rh_4(CO)_{12}$	CD_2Cl_2	208	228.8	263
$Co_4(CO)_{12}$	CD_2Cl_2	213	243.1	263
$RhCo_3(CO)_{12}$	CH_2Cl_2	188	238-251	263
C. Pseudo-Carbenic Binuclear Iron Complexes (Selected Values)				
$Fe_2(CO)_6(RC_2R')_2$	$CDCl_3$		157-197[b,c]	248
$Fe_2(CO)_6[(RC_2R')_2CO]$	$CDCl_3$		172-216[b,d]	248
$Fe_2(CO)_6(C_2Me_2)_3$, deep red	$CDCl_3$		181.8	273
$Fe_2(CO)_6(HC_2Et)_3$, orange	$CDCl_3$		167-184	273
$Fe_2(CO)_5[(RC_2R')_3CO]$	$CDCl_3$		176-213	273
D. "Pseudo-Carbenic" Carbon on Alkyne Clusters				
$Fe_3(CO)_9(C_2Et_2)$	$CDCl_3$		222.3	273
$Fe_3(CO)_8(C_2Ph_2)_2$, black	$CDCl_3$		119-120	257
$Fe_3(CO)_8(C_2Ph_2)_2$, violet	$CDCl_3$		201	257
$(Cp)_3Rh_3(CO)(C_6F_5C_2C_6F_5)$			301.6	106
$(Cp)_3Rh_3(CO)(C_2Ph_2)$			151	106
$HRu_3(CO)_9(C_2Bu\text{-}t)$	$CDCl_3$		164.2	34
$HRu_3(CO)_9(C_6H_9)$, allene	$CDCl_3$		176.7	257
$HRu_3(CO)_9(C_6H_9)$, allylic	$CDCl_3$		161.6-198.2[b,e]	257
$Fe_3(CO)_8(HC_2Me)_3$	$CDCl_3$		205-217	257
E. "Pseudo-Carbenic" CO's in Alkyne Clusters				
$Ru_3(CO)_6(C_{12}H_{20})(C_{13}H_{20}O)$	$CDCl_3$		235.7[f]	60
			234.6	60

[a] δ, downfield positive with respect to TMS. [b] Minimum and maximum of several values. [c] R = R' = H, Me, Ph; R = H, R' = Me, Bu-*t* (lowest value), several isomers. [d] R = R' = Me, Et, Ph; R = H, R' = Me, Bu-*t* (lowest value), several isomers. [e] Several complexes with different ligands. [f] Two isomers, same basic structure.

Scheme IX



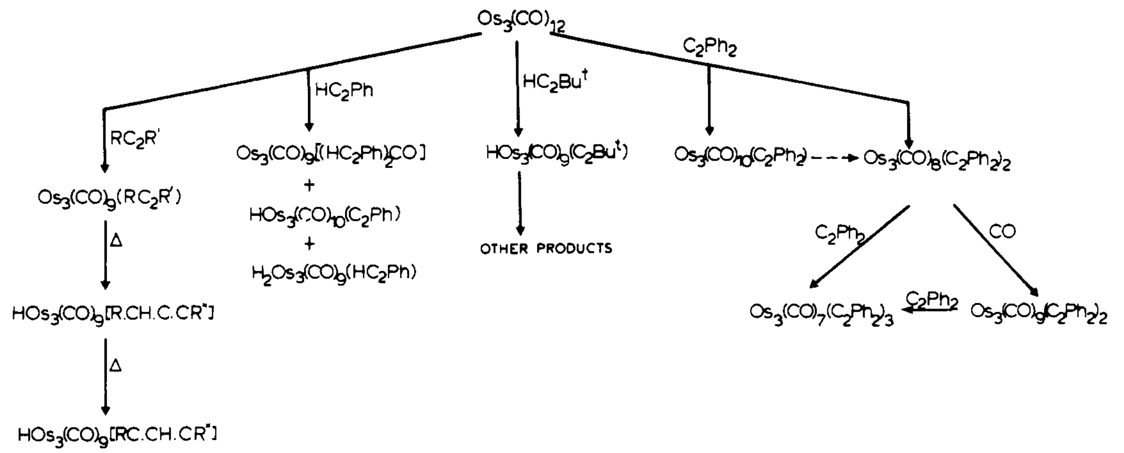
has already been shown in Scheme I. The other reactions are summarized in Scheme IX.

The above clusters of iron and ruthenium have been shown to be valuable "building blocks" for mixed-metal clusters upon reaction with nickel complexes. The influence of the structure of the reactants has been discussed for iron ("metal fragment condensation" is probably the main reaction pattern)[274] and is far more evident for ruthenium (see Scheme IV). Similar reactions are now under investigation for phosphidoruthenium acetylides, the first product being $NiRu_4(CO)_9(PPh_2)_2(C_2Pr\text{-}i)_2$ (**30**)[156] and for alkyne osmium carbonyls.

Cluster demolition is less frequent in the ruthenium cluster–alkyne chemistry.

Finally, the osmium carbonyl, after monosubstitution to $Os_3(CO)_{10}(C_2Ph_2)$ affords metallacyclopentadienyl derivatives, *without* cluster opening (in contrast with

Scheme X



ruthenium and iron). Cluster opening is virtually absent as well as cluster demolition, in this reaction sequence. More recently, cluster shape modifications for tetrahedral osmium derivatives and cluster opening upon alkyne substitution on pentametallic derivatives, have been reported.[336,337] C_2Me_2 affords an osmacyclohexadienone structure (closed cluster).

The chemistry of the interactions between HC_2R and RC_2R' alkynes and $Os_3(CO)_{12}$ is, apparently, similar to that found for $Ru_3(CO)_{12}$. These reactions are summarized in Scheme X.

For hydrogen-releasing alkynes the reaction sequence could be more complex because of the possible formation of $H_2Os_3(CO)_{10}$: this latter reacting further with alkynes to give bridging vinyl and alkylidene derivatives.

Reactions of mixed-metal clusters toward alkynes have been reported; tetrahedral iron–ruthenium clusters have been shown to give $FeRu_3(CO)_{12}(RC_2R)$ butterfly clusters,[127] thus following the reactivity trend observed for ruthenium. Mixed Co–Ru alkyne clusters have been recently described, particularly with Co_2Ru_2[126] and Co_3Ru cores.[145,338] Furthermore, a considerable number of polynuclear tungsten–iron, –ruthenium, and –osmium derivatives, containing alkynes or related ligands have been obtained by Stone and co-workers.[237] These are considered again in the next section.

B. Reactivity of the Alkyne-Substituted Clusters

1. Reactivity of the Clusters

A detailed study on this point is far from being complete; in general only CO substitutions with other ligands have been performed. Nevertheless, the knowledge of the reactivity of the cluster itself, namely cluster opening, metal substitution and extrusion, role of the M–H–M bonds, etc... is in itself important and of interest in view of applications.

Thus, in general PR_3 ligands substitute for the CO groups on the metals capable of σ-bonding with the organic moiety;[67] however, in some instances, the substitution leads to cluster opening.[72,76] Also, in some heterometallic clusters, reversible M–M' bond breaking occurs in the presence of phosphines.[275] Related reactions are the metal-atom exchange in mixed clusters, favored by bridging arsine ligands;[122] also related—at least in part—the behavior of the phosphido bridges, which sometimes afford open clusters.[29]

Metal-fragment condensation has also been shown to be a process leading to mixed-metal clusters; the reverse reaction can also occur, as demonstrated in the nickel extrusion from a tetrametallic mixed cluster[119] or in the cobalt extrusion from the "butterfly" $[Co_3Ru(CO)_{10}(C_2Ph_2)]^-$ cluster.[338]

Finally, cluster opening is a very frequent process when alkyne oligomerization takes place on closed clusters, as discussed above.

To our knowledge, few reactions have been attempted on the M–H–M bridges in this class of clusters, probably because many reactants will interact with the coordinated alkyne rather than with the hydride. However, it has been shown that the hydrido bridge in $HRu_3(CO)_9C_2Bu$-*t* is highly reactive; indeed it is involved in the general reactivity pattern of the cluster either with alkynes or nucleophiles, by shifting onto the organic moiety. In the presence of bases the corresponding anionic cluster $[Ru_3(CO)_9(C_2Bu\text{-}t)]^-$ is obtained[276] and in the presence of mercury halides the hydrido bridge is substituted by a mercury atom without affecting the other part of the cluster.[121] A different route for obtaining the anionic derivative has been recently explored; in the presence of $(PPh_3)AuCl$ the $(PPh_3)AuRu_3(CO)_9(C_2Bu\text{-}t)$ cluster has been obtained.[277]

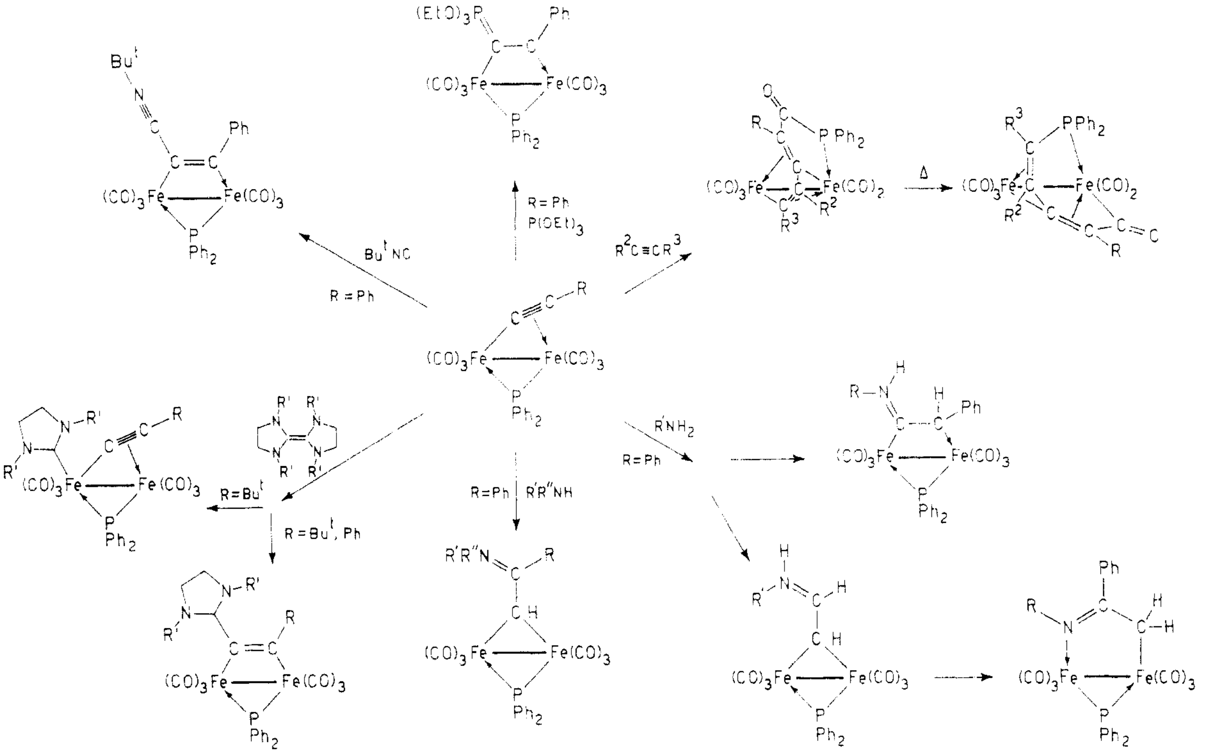
This same M–H–M system reacts with Ph_2PCl to give the open phosphido cluster $(PPh_2)Ru_3(CO)_9C_2R$ in small yields; the reverse reaction occurs in the presence of HCl.[278] In this case, the electronic equivalence of a M–P–M "open" arrangement with a closed M–H–M one, has been evidenced.

2. Reactivity of the Coordinated Alkynes or Acetylides

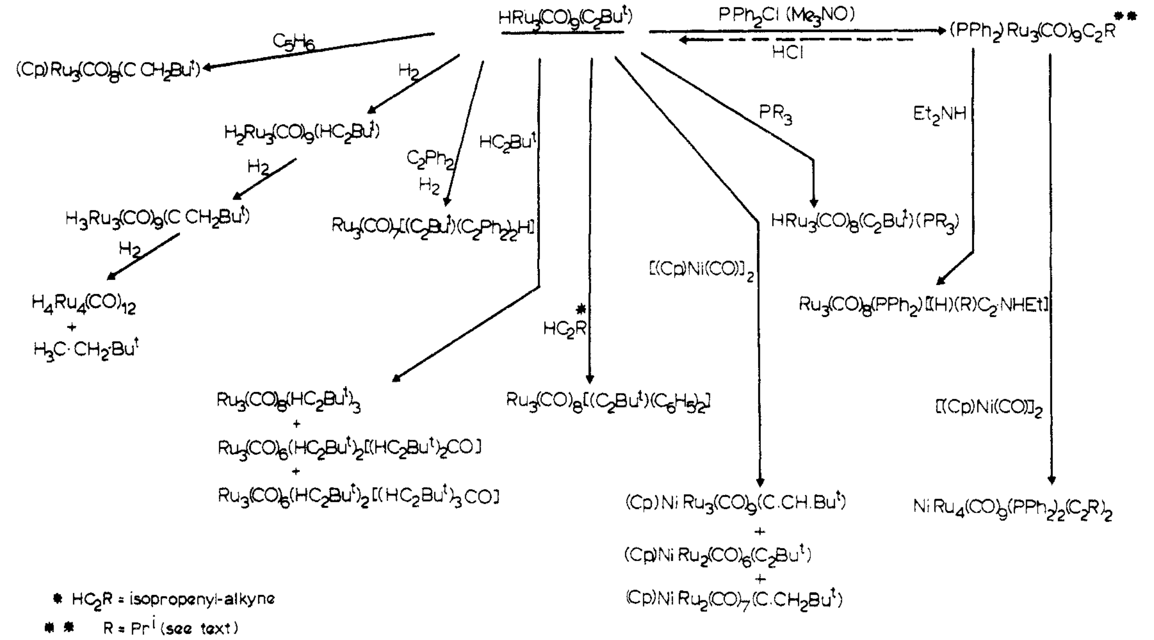
The reactivity of these ligands should be strongly dependent upon their coordination mode to the metals. Some indications of the possible reactivity of the alkyne carbons can be deduced from the NMR data, as sometimes low-field chemical shifts are found (see Tables IX, XI), which indicate deshielding of these carbons, and hence, presumably, reactivity toward nucleophiles. This is, at least in part, confirmed by experimental evidence.

The reactivity of the σ,π acetylide has been extensively studied mainly on bimetallic derivatives[279] because only one example of a cluster containing this ligand is known.[58] (This cluster 4 contains other acetylides with different coordination, and hence it would

Scheme XI



Scheme XII



be difficult to decide on the contribution of a given ligand to the global reactivity). The main results of this work are summarized in Scheme XI.

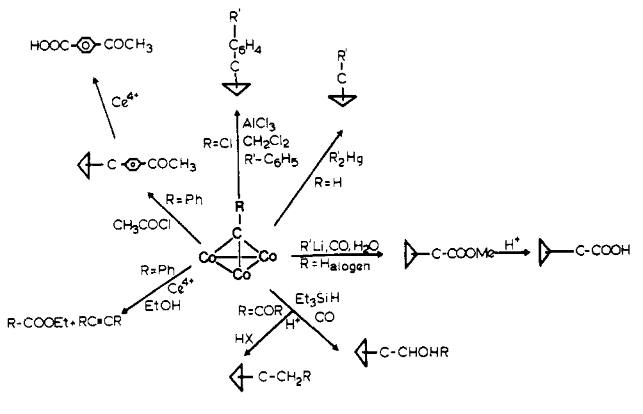
The α-carbon of the acetylide shows carbocationic reactivity; this is of interest either because functionalized ligands can be obtained "via" nucleophilic attack, or because this reactivity bears some resemblance to that of the coordinated CO in the Fischer–Tropsch catalysis. Also, the cationic reactivity could suggest the possibility of a cationic catalysis for alkyne oligomerization, the cluster acting as a promoter and having a template effect.

The above clusters are also characterized by phosphido bridges, which usually stabilize the metal–metal bonds; these bridges are usually far less reactive than the acetylide ones, and show different structural characteristics.

The σ + 2π acetylide is also well-known; it has been studied mainly on $HRu_3(CO)_9(C_2R)$ and on the related $(Ph_2P)Ru_3(CO)_9C_2R$. The results obtained on the above hydride are summarized in the Scheme XII.

It has been shown that, besides the reactivity of the hydrido ligand and of the cluster itself, the α-carbon of the acetylide shows high reactivity, giving nucleophilic additions,[59] insertions in the M–C(σ) bond,[55,57] and addition of "metallic nucleophiles" such as (Cp)Ni.[151] Easy alkyne oligomerization is also observed[55,60] sometimes with cluster opening. These reactions very often occur with shift of the hydrido ligand (deuteration experiments[60]). The possibility of eliminating the hy-

Scheme XIII



dride to give the related $(PPh_2)Ru_3(CO)_9(C_2R)$ systems[278] has already been discussed.

The C(α) atom of the latter complexes is usually more reactive toward "classical" nucleophiles; e.g., an adduct with amines is formed, which is shown in Scheme XII. On the corresponding hydrides, spectroscopic evidence of *initial* attack at the α-carbon has been obtained; whereas the final products are CO-substitution derivatives[280] in the case where nitrogen- and phosphorus-containing bases were used. A preliminary study with $[(Cp)Ni(CO)]_2$ has lead to a mixed-metal product also in case of the phosphido cluster; this complex (**30**, Figure 9), which is probably obtained by partial demolition of the parent ruthenium complex, followed by condensation of fragments, is represented in Scheme XII. Also in this product, interaction of the nickel with the former α-carbon of the acetylides occurs.[156]

In $HRu_3(CO)_9C_2Bu\text{-}t$, the α-carbon of the acetylide is at similar distances from the three metal atoms, so that a "pseudo-tetrahedral" Ru_3–C(α) core is present, comparable with the ones of the $Co_3(CO)_9CR$ complexes. Indeed, it is possible by hydrogenation of $HRu_3(CO)_9(C_2Bu\text{-}t)$ to obtain the "apical" $H_3Ru_3(CO)_9C.CH_2Bu\text{-}t$ derivative.[47]

Thus, in view of this chemical relationship within the $\sigma + 2\pi$ and the "apical" μ_3 complexes, one could expect some nucleophilic reactivity also for the apical carbon in the latter. Indeed, this carbon—on the basis of all the available X-ray and spectroscopic data—is not sp^3 hybridized: for the related cationic $(CO)_9Co_9C.CR_2^+$ the possibility of a "noncentered" structure has also been considered.[281] Finally, some "carbenic" reactivity for the apical carbon has been evidenced.[282]

The main reactions found for the apical carbon are:

Substitution of the R group by electrophilic and nucleophilic agents.

Insertion of a CO group into the C–R bond to give C—C(=O)R species, induced by nucleophiles or electrophiles.

Hydrolysis or reduction of the above esters under conditions typical for sterically hindered esters.

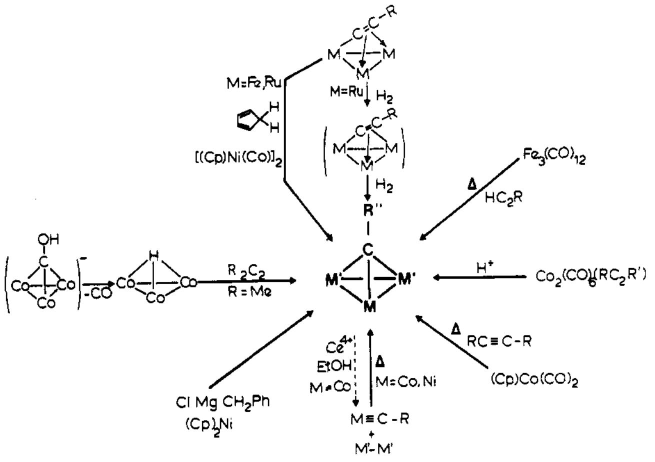
Cleavage of the CR group from the cluster, in the presence of oxidizing agents:

$$(CO)_9Co_3CR \xrightarrow[EtOH]{Ce^{4+}} RCOOEt + RC{\equiv}CR$$

$$R = Ph,\ CH_2Ph$$

Alkynes can also be obtained upon thermal decomposition or carbonylation of the above clusters.

Scheme XIV



These reactions are summarized in Scheme XIII. The relationships between the apical derivatives and the alkynes, or other alkyne-containing structures are presented in Scheme XIV.

Finally, it has been reported that treatment of $Co_3(CO)_9CMe$ with hydrogen, under light, affords ethane.[283] Similarly, it has been found that when $H_3Ru_3(CO)_9C.CH_2Bu\text{-}t$ is treated with hydrogen,[47] neohexane is obtained.

Two points not directly related to the alkyne reactivity are meanwhile worthy of interest:

In the extensively studied reactivity of the $Co_3(CO)_9CR$ complexes[5] (see also ref 284) it was found that the tetrahedral Co_3C core is very stable to both oxidation and thermal demolition. This behavior is at the basis of the recent tendency of "capping" clusters in order to improve their stability in homogeneously catalyzed reactions.[285]

The well-evidenced alkyne C≡C bond splitting, and the reverse reactions are of interest from another point of view. Indeed, in the formation of some carbides such as $Fe_5(CO)_{15}C$[286] (obtained by refluxing $Fe_3(CO)_{12}$ and pent-1-yne) the origin of the carbido carbon was explained by cleavage of the HC≡CR alkyne, followed by dehydrogenation of the CH moiety. More recently it has been shown via ^{13}C labelling that the origin of the carbido carbon in several carbide–cluster carbonyls is the CO[287] itself. In some other instances the source of C can be CS_2, $CHCl_3$, or CCl_4.[288] However the above hypothesis cannot be ruled out without further investigations. Thus, another relationship can be hypothesized between the carbido-cluster chemistry and the alkyne-cluster chemistry.

Few reactivity experiments have been performed on the most widespread $2\sigma + \pi$ *alkynic* substituents; these have been shown to be intermediates in the reversible hydrogenation of $\sigma + 2\pi$ structures to apical complexes.[47] Moreover, the stability of these clusters in the presence of CO or alkynes is usually not very high; thus, probably, many experiments will be prevented because of the easy reactivity toward hydrogen, and of the easy alkyne oligomerization or CO insertion, in the presence of these reagents.

Another system of interest is the "*allylic*" one; regiospecific substitution of phosphines for the CO's has been reported for these clusters.[67] Protonation experiments and thermal "decomposition" (of butterfly structures) have been performed[289] as well as reaction with excess of alkynes to give metallacyclic open clusters.[290] Formation of butterfly clusters also occurs in presence of $(Cp)_2Ni$.[153]

In the latter reactions it is of interest to consider the possibility of the allylic ensemble to coordinate to three or four metal centers, without important structural modification.

The formation of such metallated units can be achieved by condensation, on clusters, of C–R or CH fragments obtained by C≡C bond cleavage, with another alkyne; this occurs for $Fe_3(CO)_7(HC_2Et)_4$ (**19**)[28] and is indicative of the potentialities of the chemistry of the "methyne" or "carbyne" fragments obtained by acetylene cleavage. (This behavior is in accord with the "olefin metathesis" reactions discussed below (see also ref 292).) Also, functionalized allylic ligands can be obtained on metal clusters by reacting nitrogen-donor substituted clusters with alkynes.[291]

At present no information is available on the reactivity of the μ_4–η^2 coordinated alkynes in bonding mode Q, and also ^{13}C NMR data are not available. The interest in this bonding mode is however considerable, when one thinks of these structures as derived from the butterfly carbido-clusters[236–240] in which carbide–methylene coupling would have occurred. This could be of some importance in the discussion of the mechanisms of the homogeneously catalyzed Fischer–Tropsch reaction. Indeed, one of the most interesting reactions of the carbides (and a class of reactions unique to these complexes) is the carbon–carbon bond formation at the carbido carbon. This has formal analogies with the proposed "carbidic" mechanisms of the Fischer–Tropsch reaction. In the light of the existing structural similarities between the butterfly carbido clusters and related derivatives[236–240] the vinylidene ruthenium and nickel heterometallic derivatives[151] could be considered as formed by reaction between carbide mixed clusters (with carbocationic character) and methylenes or carbenes. At present no ruthenium–nickel carbide derivatives could be obtained; however, the above hypothesis was supported, at least in part by showing that olefin metathesis reaction occurs when the above clusters are treated with hex-3-ene.[292]

3. Other Reactions of Single Alkyne Molecules with Clusters

These are, in particular, the reactions of functionalized alkynes toward metal clusters; this type of studies is at the beginning but shows considerable promises.

Early examples of modification of alkynes through the interaction with clusters are known; thus $C_2(CH_2Cl)_2$ reacts with $Fe_3(CO)_{12}$ with loss of Cl_2 to form the bimetallic, *trans*-butadienic $Fe_2(CO)_6(C_4H_4)$.[293] In the presence of $Ru_3(CO)_{12}$, PhC_2COOH releases CO_2 to give $HRu_3(CO)_9C_2Ph$.[33]

The reactions of alkynols and alkynediols toward the iron triad clusters have been studied. Triiron dodecacarbonyl reacts with HC≡C—C(OH)Me_2 (ligand L) to give, upon water elimination, $Fe_2(CO)_6(L_2 - H_2O)$ and $Fe_3(CO)_8(L_2 - H_2O)$ (open cluster) of known structures.[24] The diol $C_2(C(OH)Me_2)_2$ gives $Fe_2(CO)_6(C_2(CMe_2)_2)$ and smaller amounts of $Fe_2(CO)_6(L_2 - nH_2O)$ (n = 1, 2).

$Ru_3(CO)_{12}$ reacts with the alkynols (L) to give first the hydrides $HRu_3(CO)_9$(L–H), then in the presence of CF_3COOH water elimination occurs, leaving an unsaturated substituent; the hydride is unaffected.[45] With but-2-yne-1,4-diol, the hydrides $HRu_3(CO)_9(HCCHC_2H_2OH)$ and $HRu_3(CO)_9$(HCCHCC(=O)H) are obtained; allylic structures have been proposed, based on spectroscopic data.[44]

The reaction of $Ru_3(CO)_{12}$ with $C_2(C(OH)RR')_2$ (R = Me, R' = Me, Ph) leads to $HRu_3(CO)_9C_2X$ (X = C(OH)RR') and a ketone (for R' = Ph, acetophenone) by cleavage of the C–C single bond that is α to the C≡C bond, and hydrogen transfer from one OH to the metal cluster.[176]

Reactions with the osmium carbonyls are under investigation.[177]

The above water elimination reactions would lead one to think that the same could occur with C–OH and Si–OH groups on surfaces and could be used as a method for anchoring clusters. Similar reactions of hydroxymethylsilyl substituents have been attempted on osmium clusters.[294] However, the possibility of side reactions, such as cluster opening, reduction by hydrogen, etc., is high for these clusters; this could result in unpredictable modification of the anchored species.

4. CO Insertion Reactions

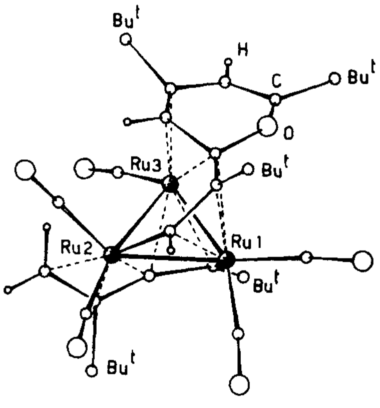
Insertion of CO between the metal and the coordinated alkynes, as well as between coordinated alkynes is well-known in particular for binuclear derivatives. Thus, in $Fe_2(CO)_6$[C(Et)=C(Et)C(=O)O] a chelating diethyl acrylate ligand is obtained, in apolar conditions, the supplementary oxygen atom being probably obtained by the splitting of a CO.[262] In $Fe_2(CO)_6[C_2(OH)Et]_2$ and $Fe(CO)_4[(CO)_2(C_2Et_2)]$ insertion of C–OH (upon CO reduction) and CO groups between the alkyne and the metal is observed.[295] This has also been observed in $Fe_2(CO)_6(C_9H_{14}CO)$ and related complexes.[296]

Quite common, on binuclear derivatives, is the CO insertion between two molecules of coordinated alkyne, as in $Fe_2(CO)_6[(RC_2R')_2CO]$.[13]

The first behavior is, at present, not known for clusters whereas the second one leads to osmacyclohexadienonic complexes.[74] Also, some "carbenoid" complexes are obtained, namely $Os_3(CO)_9[(HC_2Ph)_2CO]$ (**33**)[83] and the isomers (Figure 12) $Ru_3(CO)_6[(C_{12}H_{20})(C_{13}H_{20}O)]$[60] in which probably a former terminal CO is inserted between two alkynes. All these reactions are of interest in view of the potential use of clusters in organic reactions starting from alkynes; indeed, in the above $Ru_3(CO)_6[(C_{12}H_{20})(C_{13}H_{20}O)]$[60] the dimeric chain $C_{12}H_{20}$ shows the same alkyne coupling as in the catalytic reaction of $H_2Ru(CO)(PPh_3)_3$.

Moreover, reaction of this product with excess alkyne leads to a closed cluster complex (**34**), shown in Figure 13, in which three alkynes and one CO are oligomerized, thus forming an organic heterocycle bound to the cluster.[61]

This complex is probably obtained by nucleophilic addition of one alkyne on the "carbenic" carbon of the tetrasubstituted cluster, and represents, to our knowledge, a rare example of direct synthesis of an heterocycle without cluster demolition. Also, in the latter stage of the reaction, a sort of "shifting" of the (L(CO)L) ligand with respect to the metal-cluster-dienic ligand is observed, which could be of interest in connection with the mobility of the coordinated organic



$Ru_3(CO)_5(C_{12}H_{20})(C_{19}H_{30}O)$ (ref. 61)

34

Figure 13. An example of organic heterocycle resulting from alkyne and CO coupling on a cluster.

Scheme XV

$$\begin{tikzcd}
Ru_3(CO)_{12} \arrow[d, "DC_2R"] & \\
DRu_3(CO)_9C_2R \arrow[d, "HC_2R"] & \\
Ru_3(CO)_8[(C_2R)(HRC_2D)] \arrow[d, "HC_2R"] & \\
Ru_3(CO)_7[C_4R_2HD](HC_2R) \arrow[d, "HC_2R"] \arrow[r, "+CO"] & \text{Cluster opening} \\
Ru_3(CO)_6[C_4R_2HD][(HC_2R)(CO)(HC_2R)] \arrow[d, "HC_2R"] & \\
Ru_3(CO)_5[C_4R_2HD][(CO)(HC_2R)_2(HC_2R)] &
\end{tikzcd}$$

species on small metal fragments.

Finally, the intermediate stages of this reaction are, at present, relatively well known, and several intermediates have been studied by X-ray diffraction. The reaction sequence is shown in the Scheme XV.

VII. Applications

The alkyne–carbonyl clusters have found limited applications until now.

The reaction of $Fe_3(CO)_{12}$ with alkynes, affording cyclopentadienones, tropones, and quinones[13], in which well-established alkyne–clusters are intermediates, has no practical use because of its low selectivity and stoichiometric yields.

In the presence of acetylene and water, $Ru_3(CO)_{12}$ catalyzes the formation of hydroquinones.

$Os_3(CO)_{12}$ is active in alkyne cyclotrimerization; this reaction is not convenient, in view of the high cost of the osmium cluster, especially when considering that mononuclear nickel complexes are effective in the same process.[13]

Also $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$ are active in alkyne cyclotrimerization,[299] the rhodium complex being more active and less selective; stoichiometric amounts of alkynes gave the $M_4(CO)_{10}(RC_2R')$ clusters, which are probable intermediates.

Penta-, hexa-, and dodecametallic anionic nickel clusters have been reported as effective catalysts of acetylene polymerization.[300] No hypotheses on the intermediates were made.

Also, the majority of the unsubstituted cluster carbonyls of the iron and cobalt triads have been found active in the water-gas shift reaction (WGSR); in particular, $Ru_3(CO)_{12}$ has been successfully tested in this reaction and in homogeneous Fischer–Tropsch reaction. During these reactions, however, slow decomposition occurs, and "capping" of the cluster with a suitable ligand has been proposed in order to improve the stability.[11,285] The apical CR groups are capping ligands; and indeed, some $Co_3(CO)_9CR$ clusters have been reported effective in the WGSR and hydroformylation reactions. Catalytic activity and 90% recovery of the cluster were claimed.[301] These results, however, should be accurately checked, as other groups found low activity and extensive cluster demolition.[302] Since the presence of unsaturated fragments coming from partial decomposition of the cluster could also be responsible for some catalytic activity, the claim that $Co_3(CO)_9CPh$ is a "cluster" catalyst" for olefin hydroformylation should be considered with care. $Co_3(CO)_9COR$ clusters have also been used as acylating agents on different substrates.[303] Some alkyne-substituted hydrido clusters have been shown to be effective in pent-1-ene isomerization.[304] Finally, the catalytic hydrogenation of *tert*-butylacetylene to neohexane, on ruthenium clusters has been reported; this involves alkyne-substituted intermediates, as shown in Scheme XVI. Also for this reaction, there is not certainty that the true catalyst is the homogeneous system, and not the metal powder obtained when excess hydrogen is used.

The hydrogenation reactions of alkynes bound to *bimetallic* derivatives of molybdenum and nickel were recently studied.[305] Hydrogen reacts with $(Cp)_2Mo_2(CO)_4(RC_2R)$ to form *cis*-RCH=CHR and $(Cp)_2Mo_2(CO)_4$. This reaction is catalytic (and stereospecific as only the cis isomer is obtained) in the presence of excess alkyne but is in competition with the insertion of alkyne, which leads to metallacyclic species. The phosphito-substituted molybdenum–alkyne complex is more active as catalyst precursor. There is evidence that the hydrogenation occurs via dissociation of a CO as the first step.

Also $(COD)_2Ni_2(RC_2R)$ is a selective catalyst for the alkyne hydrogenation in the presence of alkenes; the selectivity is due to the poorer ability of the alkenes to coordinate to the metals (this also explains the absence of alkanes in the reaction products).

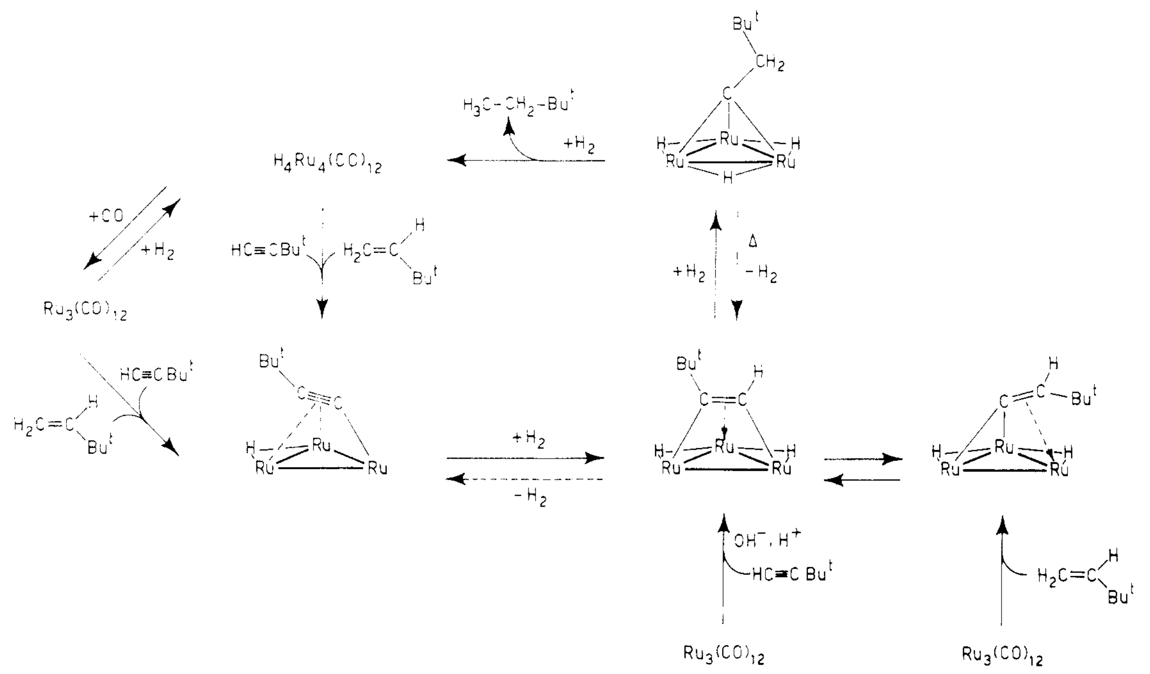
Selective hydrogenation of alkynes in cis olefins is also obtained on *clusters* such as $Ni_4(CNR)_4(RC_2R)_3$ (R = aryl).

Catalytic processes involving isonitrile and alkyne-substituted clusters have also been reported; thus $Ni_4(CNBu\text{-}t)_7$ catalyzes the oligomerization of acetylene to benzene, and of butene to cyclooctadiene, at 25 °C.[306] The same cluster reacts with alkynes following this stoichiometry

$$4Ni_4(CNBu\text{-}t)_7 + 15C_2Ph_2 \rightarrow 12Ni(CNBu\text{-}t)_2(C_2Ph_2) + Ni_4(CNBu\text{-}t)_4(C_2Ph_2)_3$$

At the same temperature, with excess of alkyne and in the presence of hydrogen, catalytic yields of *cis*-styrene are obtained.[307]

Scheme XVI



$Ni_4(CNBu\text{-}t)_7$ is also a precursor of the hydrogenation of alkynes to cis olefins, and of the reduction of CNR to $RNHCH_3$.[308] Other reduction reactions of nitriles on carbonyl clusters can be found in Table II; in particular for iron, these follow the same mechanisms as observed for alkynes.

Finally, alkyne-substituted clusters are detected in the reduction of PhC_2H_3 to ethylbenzene, in the presence of $Ru_3(CO)_{12}$.[309] Also alkyne–clusters are likely to be intermediates in the hydrogenation of PhC_2H to styrene in the presence of $Pt_2Co_2(CO)_8(PPh_3)_2$; this is a catalytic process; indeed, coordinatively unsaturated tetra- and trinuclear mixed clusters, of the type $Pt_2Co_2(CO)_8L_2$ (L = phosphine, arsine) or PtM_2L_2 (L = C_6H_{11}, NC; M = $Co(CO)_4$, $(Cp)Mo(CO)_3$, $Fe(NO)(CO)_3$) show catalytic activity under mild condition in the selective hydrogenation of acetylenes to olefins (50 °C, 50 atm hydrogen pressure).[310]

When considering the alkyne oligomerization reactions, a new and fascinating field has been recently evidenced by Vollhardt.[311,321] Indeed, by using cobalt complexes the catalyzed alkyne trimerization of a wide range of complex organic molecules is obtained, ranging from hormones to polycondensed aromatics of importance in the knowledge of the coal by-products and of their carcinogenicity.

As byproducts of the above syntheses, Co_3C clusters are found; this could suggest that alkyne–clusters could be intermediates in these processes. Also, the first steps of these syntheses are simple oligomerizations leading to cyclobutadienes, pentadienes, etc... as shown in cluster-assisted processes. Finally, the above discussed cluster assisted RC≡CR′ bond cleavage and reactivity of the CR fragments, could also be of considerable importance in these syntheses. Carbon–carbon bond formation can be achieved by treating bi- or trimetallic complexes bearing bridging CR ligands (obtained in a stepwise manner from mononuclear metal carbyne complexes and low-valent compounds of other metals) with alkynes, via intermediate mixed-cluster complexes.[116,327] This preparative method, based on the isolobal analogy of metal fragments with hydrocarbon "fragments",[324] is now one of the most important and promising for the synthesis of a variety of mixed-metal clusters. The interest in these reactions is mainly due to the possibility of "predicting" or, anyway, orienting the syntheses toward some specifically desired products.

From all the above exposed reasons, it is our opinion that the alkyne triple bond chemistry on clusters is only at the start of a long and possibly profitable journey.

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