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HIGH-NUCLEARITY CARBONYL CLUSTERS: THEIR SYNTHESIS AND REACTIVITY

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I. Introduction

Over 20 years ago, the structure of the first high-nuclearity carbonyl cluster (HNCC), $Rh_6(CO)_{16}$, was elucidated (*164*). Since that time, the field has grown to a state where there is now an enormous number of such species. We have chosen to define HNCC as homo- or heteronuclear carbonyl clusters of transition and main group metals containing five or more metal atoms, each of which is linked to the metal core by at least one M—M bond.

A review of the area of HNCC by Chini *et al.* in 1976 (*196*) reflected the emphasis of the earlier studies. Efforts were concentrated on establishing new structural forms and rationalizing the bonding patterns rather than understanding the reactivity of these compounds. To some extent this has been corrected over the past few years. With the development of more efficient synthetic routes, a large number of HNCC have become available in reasonable amounts and more effort has been devoted to the investigation of their chemistry.

Several reviews have included aspects of the synthesis and reactivity of HNCC (*77*, 456–469), but the vast amount of information now accumulated in this area justifies a separate discussion of these topics. There is often no clear dividing line between synthesis and reactivity. For convenience, under the heading "synthesis" have been gathered all reactions involving the formation of HNCC through a change in nuclearity. We have chosen to discuss the chemistry of the HNCC in terms of reaction type rather than metal by metal. We hope that this approach will provide a better understanding of what may be viewed as a highly complicated subject. We must emphasize that our expertise is as synthetic chemists, and we apologize for any error that might occur within our discussions of the more theoretical aspects of the field.

All the HNCC that have been characterized to date by X-ray crystallography are listed in Table I together with the methods used for their synthesis and references to their spectroscopic data.

COMPENDIUM OF HNCC WHOSE STRUCTURES HAVE BEEN DETERMINED CRYSTALLOGRAPHICALLY[a]

Cluster[b]	References: X-Ray	References: Synthesis[c]	Reagents and conditions	Yield (%)	Spectroscopic and theoretical studies[d]
$Re_6(CO)_{18}(PMe)_3$	*1*	*1*	$Re_4(CO)_{15}MePP(Me)PMeCl_2 + Re_2(CO)_{10}/\Delta$, Ar	—	
$Re_6(CO)_{19}P(PMe)(PMe_2)$	*1*	*1*	$Re_4(CO)_{15}MePP(Me)PMeCl_2 + Re_2(CO)_{10}/\Delta$, Ar	—	
$[Re_6C(CO)_{19}]^{2-}$	*376*	*376*	$[Re_7C(CO)_{21}]^{3-} + I_2$/MeCN, CO	—	IR (*416*)
$[Re_6C(CO)_{18}H_2]^{2-}$	*2*	*2*	$[Re(CO)_4H_2]^-$/*n*-tetradecane, decaline, Δ	35	^{13}C NMR, ^1H NMR
$[Re_7C(CO)_{21}]^{3-}$	*3*	*3*	$[Re(CO)_4H_2]^-$/*n*-tetradecane, Δ	70	^1H NMR, IR (*416*)
$[Re_8C(CO)_{24}]^{2-}$	*4*	*4*	$[Re(CO)_4H_2]^-$/*n*-tetradecane, Δ	30	^1H NMR
$Fe_5(CO)_{13}(CS)S_2$	*5*	*5*	$Fe_3(CO)_{12} + CS_2 + CO$/Ar, hexane	2	
$Fe_5C(CO)_{15}$	*6*	*7*	$[Fe_6C(CO)_{16}]^{2-} + [C_7H_7][BF_4]$/MeOH	100	^{13}C NMR (*8*), IR (*9*), MO calc. (*6*), ^{57}Fe Mössbauer (*10*, *11*), ESCA (*10*)
$[Fe_5C(CO)_{14}]^{2-}$	*13*	*14*	$Fe_5C(CO)_{15}$ + NaOH, $NaBH_4$ or Na/Hg, THF	80	^{57}Fe Mössbauer (*10–12*), ESCA (*10*)
$Fe_5C(CO)_{12}Br_2$	*7*	*7*	$[Fe_6C(CO)_{16}]^{2-} + C_7H_7Br$/MeOH	—	
$[Fe_5N(CO)_{14}]^-$	*13*	*15*	$NOBF_4 + [Fe_2(CO)_8]^{2-} + Fe(CO)_5$/diglyme, Δ	66	^{57}Fe Mössbauer (*11*)
$Fe_5N(CO)_{14}H$	*15*	*15*	$[Fe_5N(CO)_{14}]^- + H_2SO_4$/toluene	—	^1H, ^{13}C NMR (*15*), ^{57}Fe Mössbauer (*11*)
$[Fe_6C(CO)_{16}]^{2-}$	*16*	*16*	$Fe(CO)_5 + [Mn(CO)_5]^-$/diglyme, Δ	—	^{13}C NMR (*8*), ^{57}Fe Mössbauer (*10*, *11*), ESCA (*10*)
$[Fe_6C(CO)_{15}(NO)]^-$	*17*	*17*	$[Fe_6C(CO)_{16}]^{2-} + NOBF_4/CH_2Cl_2$	50	
$Fe_6C(CO)_{11}(NO)_4$	*17*	*17*	$[Fe_6C(CO)_{15}(NO)]^- + NOBF_4/CH_2Cl_2$	10	
$Ru_5(CO)_{14}(CNBu^t)_2$	*18*	*18*	$Ru_3(CO)_{11}(CNBu^t)/\Delta$, N_2	—	MS, ^1H, ^{13}C NMR
$Ru_5(CO)_{13}H(CCHPPh_2)(PPh_2)$	*19*	*19*	$Ru_5(CO)_{13}(CCPPh_2)(PPh_2) + H_2$/cyclohexane, Δ	—	^1H NMR
$Ru_5(CO)_{13}(CCPh)(PPh_2)$	*20*	*20*	$Ru_3(CO)_{11}(Ph_2PCCPh)$/heptane,	30	^{31}P NMR
$Ru_5(CO)_{14}(CCPh)(PPh_2)$	*20*	*20*	$Ru_5(CO)_{13}(CCPh)(PPh_2) + CO$	100	^{31}P NMR
$Ru_5(CO)_{13}(CCPPh_2)(PPh_2)$	*21*	*21*	$Ru_3(CO)_{12}$ + (i) $Na(Ph_2CO) + C_2(PPh_2)_2$ + (ii) toluene, Δ	62	

$Ru_5(CO_{15}(CCPPh_2)(PPh_2)$ (two isomers)	*22*	*22*	$Ru_5(CO)_{13}(CCPPh_2)(PPh_2)$ + CO/cyclohexane (isomer I) + CO/cyclohexane, Δ (isomer II)	80–85 35	
$Ru_5(CO)_{15}(PR)$ (R = Ph, Et)	*23*	*23*	$Ru_3(CO)_{12}$ + $[Mn(CO)_2CpPRCl_2]$/toluene, Δ	5	MS, ^{31}P NMR
$[Ru_5N(CO)_{14}]^-$	*24*	*24*	$Ru_3(CO)_{12}$ + $[N(PPh_3)_2][N_3]$/THF, Δ → $[Ru_6N(CO)_{16}]^-$, $[Ru_6N(CO)_{16}]^-$ + CO/THF overall yield	78	^{15}N NMR
$Ru_5C(CO)_{15}$	*25*	*25*	$Ru_6C(CO)_{17}$ + CO	97	IR (*9*)
$Ru_5C(CO)_{13}H(PPh_3)(SEt)$	*26*	*26*	$Ru_5C(CO)_{14}H(SEt)$ + PPh_3	66	MS, ^1H NMR
$Ru_5C(CO)_{12}H(PPh_3)(SEt)$	*26*	*26*	$Ru_5C(CO)_{13}H(PPh_3)(SEt)$/cyclohexane, Δ	71	MS, ^1H NMR
$Ru_5C(CO)_{14}H(SEt)$	*26*	*26*	$Ru_5C(CO)_{15}$ + EtSH	90	MS, ^1H NMR
$Ru_5C(CO)_{12}H_2\{Ph_2P(CH_2)_2PPh_2\}$	*25*	*25*	$Ru_5C(CO)_{15}$ + (i) $Ph_2P(CH_2)_2PPh_2$ + (ii) H_2	70	^1H NMR
$Ru_5C(CO)_{11}H_3(PPh_2)(PMePh_2)$	*19*	*19*	$Ru_5(CO)_{13}(CCPPh_2)(PPh_2)$ + H_2/cyclohexane, Δ	—	^1H NMR
$Ru_5C(CO)_{15}(MeCN)$	*25*	*25*	$Ru_5C(CO)_{15}$ + MeCN	—	IR (*27*)
$Ru_5C(CO)_{14}(PPh_3)$	*25*	*25*	$Ru_5C(CO)_{15}$ + PPh_3	—	
$Ru_5C(CO)_{13}(PPh_3)_2$	*25*	*25*	$Ru_5C(CO)_{14}(PPh_3)$ + PPh_3	100	
$Ru_5C(CO)_{13}\{Ph_2P(CH_2)_4PPh_2\}$	*28*	*28*	$Ru_5C(CO)_{15}$ + $Ph_2P(CH_2)_4PPh_2$/hexane	—	^{31}P NMR
$Ru_5P(CO)_{16}(PPh_2)$	*29*	*29*	$Ru_3(CO)_9H(PPh_2)$/heptane, Δ	20	^{31}P NMR
$[Ru_6(CO)_{18}]^{2-}$	*30*	*31*	$Ru_3(CO)_{12}$ + KOH/H_2O	80	
$[Ru_6(CO)_{18}H]^-$	*31*	*31*	$[Ru_3(CO)_{11}H]^-$ + H_2SO_4/THF	50	^1H, ^{13}C NMR, IR (*33*), neutron analysis (*32*)
$Ru_6(CO)_{18}H(OCNMe_2)_2$	*34*	*34*	$Ru_3(CO)_{10}H(OCNMe_2)$ + KOH/THF	45	No IR reported
$Ru_6(CO)_{18}H_2$	*35*	*31*	$[Ru_6(CO)_{18}]^{2-}$ + H_2SO_4/CH_2Cl_2	90	MS (*36*), IR (*37*)
$Ru_6C(CO)_{17}$	*38*	*39*	$Ru_3(CO)_{12}$ + CH_2Cl_2/Δ	70	MS (*40*)
$[Ru_6C(CO)_{16}]^{2-}$	*39, 42*	*43*	$Ru_3(CO)_{12}$ + $NaMn(CO)_5$/diglyme, Δ	60	^{13}C NMR (*42*)
$Ru_6C(CO)_{15}H(NO)$	*44*	*44*	$Ru_6C(CO)_{17}$ + (i) $[N(PPh_3)_2]NO_2/CH_2Cl_2$ + (ii) H_2SO_4	—	^1H NMR
$Ru_6C(CO)_{15}H(SEt)_3$	*45*	*45*	$Ru_6C(CO)_{17}$ + EtSH	—	No IR reported
$Ru_6C(CO)_{16}(CNBu^t)$	*46*	*46*	$Ru_5C(CO)_{14}(CNBu^t)_2$/nonane, Δ	13	MS, ^{13}C-labeling experiments
$Ru_6C(CO)_{15}(MeHC(CH)_2CHMe)$	*47*	*47*	$Ru_3(CO)_{12}/CH_2CH_2$, Δ	—	^1H NMR, MS, no IR reported
$Ru_6C(CO)_{14}(C_6H_3Me_3)$	*48*	*139*	$Ru_3(CO)_{12}/C_6H_3Me_3$, Δ	—	^1H NMR, MS (*139*)

(*continued*)

TABLE I (*continued*)

Cluster[b]	References: X-Ray	References: Synthesis[c]	Reagents and conditions	Yield (%)	Spectroscopic and theoretical studies[d]
$Ru_6C(CO)_{11}(C_6H_6)_2$	*49*	*49*	$[Ru_5C(CO)_{14}]^{2-}$ + (i) $[Ru(C_6H_6)(PhCN)_3][ClO_4]_2/CH_2Cl_2$, Δ + (ii) Na_2CO_3/MeOH + (iii) $[Ru(C_6H_6)(PhCN)_3][ClO_4]_2/CH_2Cl_2$	—	^{1}H NMR
$Ru_6C(CO)_{14}(C_{14}H_{14})$	*50*	*43*	$[Ru_6C(CO)_{16}]^{2-}$ + $[C_7H_7]Br$	—	No IR reported
$Ru_6C(CO)_{14}(NO)_2$	*51*	*51*	$Ru_6C(CO)_{17}$ + (i) $[N(PPh_3)_2]NO_2$ + (ii) $NOBF_4$	—	
$Ru_6C(CO)_{16}(PPh_2Et)$	*52*	*52*	$Ru_6C(CO)_{17}$ + PPh_2Et	85	^{13}C NMR
$[Ru_{10}C_2(CO)_{24}]^{2-}$	*53*	*53*	$[Ru_6C(CO)_{16}]^{2-}$/tetraglyme, Δ	35	FABMS, ^{13}C NMR
$Os_5(CO)_{16}$	*54*	*41*	Vacuum pyrolysis $Os_3(CO)_{12}$	7	MS, ΔH M–M, M–L (*55*)
$Os_5(CO)_{19}$	*56*	*56*	$Os_6(CO)_{18}$ + CO (90 atm), heptane, Δ	80	MS
$[Os_5(CO)_{15}H]^-$	*57*	*58*	$[Os_5(CO)_{15}]^{2-}$ + H_2SO_4/MeCN	—	^{13}C and ^{1}H NMR (*57*)
$Os_5(CO)_{13}H(PhNC_6H_5N)$	*59*	*59*	$Os_3(CO)_{10}H_2$ + azobenzene, Δ	20–30	^{1}H NMR, MS
$Os_5(CO)_{13}H(PhNC_6H_4N)(PEt_3)$	*60*	*60*	$Os_5(CO)_{13}H(PhNC_6H_4N)$ + PEt_3	60	^{1}H NMR, MS
$Os_5(CO)_{16}H_2$	*61*	*62*	$Os_5(CO)_{15}H_2$ + CO	40	^{1}H NMR, MS (*63*)
$Os_5(CO)_{15}H_2(CCPh)$	*64*	*64*	$Os_5(CO)_{15}H_2$ + HCCPh/Δ	—	^{1}H NMR, MS
$Os_5(CO)_{14}H_2(C_5H_4N)$	*177*	*177*	$Os_5(CO)_{15}H_2$ + C_5H_5N/octane, Δ	23	
$Os_5(CO)_{15}H_2\{P(OMe)_3\}$	*65*	*65*	$Os_5(CO)_{15}H_2$ + PR_3 (R = OMe, Et, Ph)	60	^{1}H NMR, MS
$Os_5(CO)_{14}H_2(PEt_3)$	*66*	*66*	$Os_5(CO)_{15}H_2(PR_3)/\Delta$ (R = OMe, Et, Ph)	—	MS
$Os_5(CO)_{13}H_2(PEt_3)\{P(OMe)_3\}$	*66*	*66*	$Os_5(CO)_{14}H_2(PEt_3)$ + $P(OMe)_3/\Delta$	—	MS
$Os_5(CO)_{14}H_2S_2$	*67*	*67*	$Os_5(CO)_{15}S$ + H_2S/Δ	7	
$[Os_5(CO)_{15}H_2I]^-$	*65*	*65*	$Os_5(CO)_{15}H_2$ + Bu_4NI	80	^{1}H NMR
$Os_5(CO)_{14}H_3(C_5H_4N)$	*177*	*177*	$Os_5(CO)_{15}H_2$ + C_5H_5N/octane, Δ	9	
$Os_5(CO)_{17}(HCCH)$	*68*	*68*	$Os_5(CO)_{19}$ + HCCH	15	MS
$Os_5(CO)_{14}(PhCCPh)$	*69*	*69*	$Os_5(CO)_{15}(MeCN)$ + RCCR/CH_2Cl_2 (R = Ph, Et, Me)	—	MS
$Os_5(CO)_{15}(HCCPh)$	*70*	*70*	$Os_6(CO)_{20}$(HCCPh)/CH_2Cl_2, Δ	—	^{1}H NMR, MS
$Os_5(CO)_{13}(HCCPh)(PPh_3)$	*377*	*377*	$Os_5(CO)_{15}$(HCCPh) + PPh_3/toluene, Δ	25	^{1}H NMR, MS
$Os_5(CO)_{13}(PhCCPh)_2$	*64*	*64*	$Os_5(CO)_{15}H_2$ + PhCCPh/Δ	—	

$Os_5(CO)_{15}(POMe)$	*71*	*72*	Vacuum pyrolysis $Os_3(CO)_{11}P(OMe)_3$	—	^1H NMR, MS (*72*)
$Os_5(CO)_{16}\{P(OMe)_3\}_3$	*56*	*56*	$Os_5(CO)_{19} + P(OMe)_3$	80	MS
$Os_5(CO)_{15}S$	*73*	*73*	$Os_3(CO)_{10}(MeCN)_2 + Os_3(CO)_{10}S/\Delta$	18	
$Os_5(CO)_{14}S(PPh_3)$	*377*	*377*	$Os_6(CO)_{19}(PPh_3)_2 + S_8$/toluene, Δ	65	^1H NMR, MS
$[Os_5(CO)_{15}I]^-$	*74*	*75*	$Os_5(CO)_{16} + Bu_4NI$	—	No IR quoted
$Os_5C(CO)_{15}$	*76*	*54, 77*	Vacuum pyrolysis $Os_3(CO)_{12}$	5	MS, IR (*9*)
$Os_5C(CO)_{16}$	*78*	*78*	$Os_5C(CO)_{15} + CO$ (50 atm), Δ	80	
$[Os_5C(CO)_{14}]^{2-}$	*78*	*78*	$Os_5C(CO)_{15} + NaCO_3$/MeOH	75	
$Os_5C(CO)_{14}H(CO_2Et)$	*79*	*79*	$Os_5C(CO)_{15} + ROH/\Delta$ (R = Me, Et, Bu^i)	60–80	^1H NMR, MS
$Os_5C(CO)_{14}H(C_5H_4N)$	*80*	*80*	Vacuum pyrolysis $Os_3(CO)_{11}(C_5H_4N)$	4	^1H NMR, MS
$Os_5C(CO)_{14}H\{OP(OMe)_2\}$	*81*	*72*	Vacuum pyrolysis $Os_3(CO)_{11}P(OMe)_3$	—	^1H NMR, MS (*81*)
$Os_5C(CO)_{13}H\{OP(OMe)OP(OMe)_2\}$	*82*	*72*	Vacuum pyrolysis $Os_3(CO)_{11}P(OMe)_3$	—	^1H NMR, MS (*82*)
$Os_5C(CO)_{13}H\{OP(OMe)_2\}\{P(OMe)_3\}$	*72*	*72*	Vacuum pyrolysis $Os_3(CO)_{11}P(OMe)_3$	—	^1H NMR, MS
$Os_5C(CO)_{15}\{Ph_2P(CH_2)_2PPh_2\}$	*83*	*83*	$Os_5C(CO)_{15} + Ph_2P(CH_2)_2PPh_2/CH_2Cl_2$	95	MS, ^{31}P NMR
$Os_5C(CO)_{14}(CO_2Me)I$	*79*	*79*	$Os_5(CO)_{15}I_2 + MeOH$	80–90	^1H NMR, MS (*67*)
$[Os_5C(CO)_{15}I]^-$	*76*	*76*	$Os_5C(CO)_{15} + Bu_4NI/CH_2Cl_2$	—	
$Os_6(CO)_{18}$	*84*	*41*	Vacuum pyrolysis $Os_3(CO)_{12}$	80	^{13}C NMR (VT) (*85*), MS (*41*), ΔH M–M, M—L (*55*), XAFS (*86*)
$[Os_6(CO)_{18}]^{2-}$	*87*	*88*	$Os_6(CO)_{18} + Bu_4NI/CH_2Cl_2$	—	^{13}C NMR (VT) (*88*)
$[Os_6(CO)_{18}H]^-$	*87*	*88*	$Os_6(CO)_{18} + NaBH_4$THF	—	^1H, ^{13}C NMR (*88*), IR (*37*)
$Os_6(CO)_{17}H(CCEt)$	*89*	*89*	$Os_6(CO)_{17}(MeCN) + RCCH$/toluene, 70°C (R = Et, Ph, Me)	—	MS, ^1H NMR
$Os_6(CO)_{16}H(C_5H_4N)$	*177*	*177*	$Os_6(CO)_{18} + C_5H_5N$/octane, Δ	40	
$Os_6(CO)_{16}H\{C_5H_3(Me)N\}$	*177*	*177*	$Os_6(CO)_{18} + C_5H_4(Me)N$/octane, Δ	—	
$Os_6(CO)_{19}H(SEt)$	*90*	*90*	$Os_6(CO)_{19}(MeCN)_2$ + (i) HSEt + NEt_3/CH_2Cl_2 + (ii) HBF_4/CH_2Cl_2	—	^1H NMR, MS
$Os_6(CO)_{18}H_2$	*87, 91*	*88*	$[Os_6(CO)_{18}]^{2-} + H_2SO_4$/MeCN	100	^1H, ^{13}C NMR (*88*), MS (*63*)
$Os_6(CO)_{19}H_2$	*92*	*92*	$Os_5(CO)_{16}$ + (i) Me_3NO + $MeCN/CH_2Cl_2$ + (ii) H_2OsCO_4/CH_2Cl_2	52	^1H NMR, MS
$Os_6(CO)_{18}H_2(PPh)$	*93*	*93*	$Os_6(CO)_{20}(MeCN)$ + (i) $PPhH_2/CH_2Cl_2$ + (ii) toluene, Δ	80	^1H NMR

(*continued*)

TABLE I (*continued*)

Cluster[b]	References: X-Ray	References: Synthesis[c]	Reagents and conditions	Yield (%)	Spectroscopic and theoretical studies[d]
$Os_6(CO)_{20}H_2(PH)$	*94*	*94*	$Os_3(CO)_{10}H(PH_2) + Os_3(CO)_{10}(MeCN)_2$	90	^1H NMR
$Os_6(CO)_{17}H_2\{P(OMe)_3\}$	*313*	*313*	$Os_6(CO)_{18}$ + (i) Me_3NO/CH_2Cl_2, + (ii) HBF_4/CH_2Cl_2, + (iii) $POMe_3$	72	^1H NMR
$Os_6(CO)_{18}H_2S_2$	*95*	*95*	$Os_3(CO)_{10}H(SCH_2C_6H_5)$, $h\nu/N_2$/hexane	8	^1H NMR
$Os_6(CO)_{17}H_2S_2$ (two isomers)	*95*	*95*	$Os_3(CO)_{10}H(SCH_2C_6H_5)$/nonane, Δ isomer I	2.5	^1H NMR
	95	*95*	isomer II	10	^1H NMR
$Os_6(CO)_{15}H_4S_2(HCNC_6H_5)_2$ and	*96*	*96*	$Os_3(CO)_9HS(HCNC_6H_5) + H_2$/octane, Δ	47	^1H NMR
$Os_6(CO)_{14}H_6S_2(HCNC_6H_5)_2$	*96*	*96*		12	^1H NMR
$Os_6(CO)_{17}(PPh_3)$	*97*	*97*	$Os_6(CO)_{17}(MeCN) + PR_3/CH_2Cl_2$ (R = Ph, OMe)	69	^1H NMR, MS
$Os_6(CO)_{16}(PPh_3)_2$	*97*	*97*	$Os_6(CO)_{16}(MeCN)_2 + PPh_3$/MeCN, CH_2Cl_2	25	
$Os_6(CO)_{20}\{P(OMe)_3\}$	*98*	*99*	$Os_3(CO)_{10}(CH_3CN)_2 + PdCl_2/CH_2Cl_2 \rightarrow$		
			Os_6CO_{20}(MeCN) (two isomers)	46	
			+ $Os_6CO_{19}(MeCN)_2$ (two isomers)	30	
			$Os_6CO_{20}(MeCN) + P(OMe)_3/CH_2Cl_2$	70	^1H NMR, MS
$Os_6(CO)_{19}\{P(OMe)_3\}_2$	*98*	*99*	$Os_6(CO)_{19}(MeCN)_2 + P(OMe)_3/CH_2Cl_2$	80	^1H, $^{31}P\{^1H\}$ NMR
$Os_6(CO)_{17}\{P(OMe)_3\}_4$	*100*	*100*	$Os_6(CO)_{21} + P(OMe)_3$ (excess)/benzene, Δ	—	
$Os_6(CO)_{17}P(OMe)_3(MeCN)_2$	*101*	*101*	$Os_6(CO)_{17}\{P(OMe)_3\} + MeCN$	—	
$Os_6(CO)_{18}(PPh_3)O$	*102*	*102*	$Os_6(CO)_{20}(PPh_3) + O_2$/toluene, Δ	80	^1H NMR, MS
$Os_6(CO)_{20}(PhCCH)$	*70*	*70*	$Os_6(CO)_{20}(MeCN) + RCCH$, (R = Ph, Me)/$CH_2Cl_2$	90	^1H NMR, MS
$Os_6(CO)_{17}(EtCCH)$	*89*	*89*	$Os_6(CO)_{17}(MeCN) + RCCH$/toluene, 45°C (R = Et, Ph)	—	MS, ^1H NMR
$Os_6(CO)_{16}(CMe)_2$	*103*	*103*	$Os_6(CO)_{18} + CH_2CH_2$/decane, Δ	10	^1H NMR, MS
$Os_6(CO)_{16}(MeCCEt)$	*89*	*89*	$Os_6(CO)_{17}MeCN + RCCR'$/toluene, Δ (R = R′ = Me, Et, Ph; R = Me, R′ = Et)	50-60	MS, ^1H NMR
$Os_6(CO)_{16}(CPh)_2$	*104*	*104*	$Os_6(CO)_{18} + PhCCPh$, $h\nu$	—	No spectral data reported
$Os_6(CO)_{16}(CMe)(CEt)$	*89*	*89*	$Os_6(CO)_{16}RCCR'$/octane, Δ (R = R′ = Me, Ph; R = Me, R′ = Et)	40-50	MS, ^1H NMR

$Os_6(CO)_{15}(MeCCMe)_2$ (isomer I)	*106*	*106*	$Os_6(CO)_{16}(MeCCMe)$ + (i) Me_3NO + $MeCN/CH_2Cl_2$ + (ii) MeCCMe/toluene, Δ	45	MS, ^1H NMR
(isomer II)	*106*	*106*	Isomer I/toluene, 45°C	100	MS, ^1H NMR
$Os_6(CO)_{16}(C_4H_6)$	*105*	*105*	$Os_6(CO)_{16}(MeCN)_2 + C_4H_6$/toluene, Δ	50	MS, ^1H NMR
$Os_6(CO)_{16}(CNCMe_3)_2$	*107*	*108*	Pyrolysis of $Os_3(CO)_{11}(CNCMe_3)$	—	MS, ^1H NMR
$Os_6(CO)_{18}(CNC_6H_4\text{-}p\text{-}Me)_2$	*109*	*110*	$Os_6(CO)_{18} + CNC_6H_4\text{-}p\text{-}Me$	—	^1H NMR (*110*)
$Os_6(CO)_{15}S_2(HCNC_6H_5)_2$	*111*	*111*	$Os_3(CO)_9HS(HCNC_6H_5)_2$/octane, Δ	1	^1H NMR
$Os_6(CO)_{17}(NC_5H_5)_2$	*112*	*112*	$Os_6(CO)_{18} + C_5H_5N/CH_2Cl_2$	10	^1H NMR
$Os_6(CO)_{19}O$	*113*	*113*	$Os_6(CO)_{21} + O_2$/toluene, Δ	—	MS
$Os_6(CO)_{19}S$	*114*	*114*	$Os_3(CO)_{10}(MeCN)_2 + Os_3(CO)_{10}S$/benzene, Δ	31	
$Os_6(CO)_{17}S$	*114*	*114*	$Os_6(CO)_{19}S$/toluene, Δ	23	
$Os_6(CO)_{17}S_2$	*115*	*115*	$Os_3(CO)_{10}(MeCN)_2 + Os_3(CO)_9S_2$/hexane, Δ	27	
$Os_6(CO)_{16}S_2$	*115*	*115*	$Os_6(CO)_{17}S_2$/octane, Δ	100	
$Os_6(CO)_{16}S_4$	*116*	*116*	$Os_3(CO)_9S_2/N_2/h\nu$	34	
$Os_6C(CO)_{16}(MeCCMe)$	*103*	*103*	$Os_6(CO)_{18} + CH_2CH_2$/decane, Δ	5	^1H NMR, MS
$Os_7(CO)_{21}$	*117*	*41*	Vacuum pyrolysis $Os_3(CO)_{12}$	max. 20	^{13}C NMR (*117*), MS (*41*)
$Os_7(CO)_{20}H_2$	*118*	*119*	$Os_6(CO)_{16}(MeCN)_2 + Os(CO)_4H_2$	64	^1H NMR (*118*), MS (*118*)
$Os_7(CO)_{21}H_2$	*119*	*119*	$Os_6(CO)_{18} + Os(CO)_4H_2 + 1.5Me_3NO/CH_2Cl_2$	41	MS, ^1H NMR
$Os_7(CO)_{22}H_2$	*119*	*119*	$Os_6(CO)_{18} + Os(CO)_4H_2 + 1.5Me_3NO/CH_2Cl_2$	13	MS, ^1H NMR
$Os_7(CO)_{19}S$	*120*	*120*	$Os_4(CO)_{12}S + Os_3(CO)_{10}(MeCN)_2$/octane, Δ	23	
$Os_7(CO)_{20}S_2$	*121*	*121*	$Os_4(CO)_{12}S_2 + Os_3(CO)_{10}(MeCN)_2$/octane, Δ	16	
$Os_8(CO)_{23}$	*122*	*41*	Vacuum pyrolysis $Os_3(CO)_{12}$	max. 5	MS (*41*)
$[Os_8(CO)_{22}]^{2-}$	*122*	*123*	$Os_8(CO)_{23}$ + Bu_4NI/THF	—	
$[Os_8(CO)_{22}H]^-$	*124*	*124*	$Os_6(CO)_{18}/Bu^iOH$, Δ	30	^1H NMR, MS
$Os_8(CO)_{22}HI$	*124*	*124*	$[Os_8(CO)_{22}H]^- + I_2/CH_2Cl_2$	95	^1H NMR, MS
$[Os_9(CO)_{21}\{CHC(R)CH\}]^-$ (R = Me, Et)	*125*	*125*	$Os_3(CO)_{12}/Bu^iOH$, Δ	—	^1H NMR, FABMS
$[Os_3(CO)_{10}HO_2COs_6(CO)_{17}]^-$	*126*	*127*	$[Os_3(CO)_{11}H]^- + Os_6(CO)_{18}$	79	^{13}C NMR (VT) (*127*)
$[Os_{10}(CO)_{24}H_4]^{2-}$	*128*	*128*	$Os_3(CO)_{12}/Bu^iOH$, Δ	—	^1H NMR (VT)
$Os_{10}(CO)_{23}S_2$	*129*	*129*	Vacuum pyrolysis $Os_3(CO)_{12}/S_8$	—	FABMS
$[Os_{10}C(CO)_{24}]^{2-}$	*80*	*80*	Vacuum pyrolysis $Os_3(CO)_{11}(C_5H_5N)$	65	XAFS (*86*), IR (*424*)
$[Os_{10}C(CO)_{24}H]^-$	*130*	*130*	$[Os_{10}C(CO)_{24}]^{2-} + H_2SO_4/CH_2Cl_2$	95	^1H NMR (*130*, *131*), ^{13}C NMR (*131*)
$[Os_{10}C(CO)_{24}(NO)]^-$	*132*	*132*	$[Os_{10}C(CO)_{24}]^{2-} + NOBF_4/MeCN$	85	
$[Os_{10}C(CO)_{23}(NO)]^-$	*132*	*132*	$[Os_{10}C(CO)_{24}(NO)]^-/CH_2Cl_2$	—	

(*continued*)

TABLE I (*continued*)

Cluster[b]	References: X-Ray	References: Synthesis[c]	Reagents and conditions	Yield (%)	Spectroscopic and theoretical studies[d]
$[Os_{10}C(CO)_{22}(NO)I]^{2-}$	*133*	*133*	$Os_{10}C(CO)_{24}I_2 + [N(PPh_3)_2]NO_2/CH_2Cl_2$	64	
$Os_{10}C(CO)_{23}\{P(OMe)_3\}I_2$	*133*	*133*	$Os_{10}C(CO)_{24}I_2 + P(OMe)_3$/xylene, Δ	—	
$Os_{10}C(CO)_{21}\{P(OMe)_3\}_4$	*133*	*133*	$Os_{10}C(CO)_{24}I_2 + P(OMe)_3$/xylene, Δ	—	
$[Os_{10}C(CO)_{24}I]^-$	*133*	*133*	$[Os_{10}C(CO)_{24}]^{2-} + 2I_2/CH_2Cl_2$	71	
$Os_{10}C(CO)_{24}I_2$	*133*	*133*	$[Os_{10}C(CO)_{24}]^{2-} + 4I_2/CH_2Cl_2$	82	
$[Os_{11}C(CO)_{27}]^{2-}$	*134*	*134*	Vacuum pyrolysis $Os_3(CO)_{12}$	1	FABMS
$Co_5(CO)_{11}(PMe_2)_3$	*135*	*136*	$Co(CO)_3(C_3H_5) + Co(CO)_2(NO)(PMe_2H)$	7	^1H, ^{31}P NMR (*135*)
$Co_6(CO)_{16}$	*137*	*138*	$[Co_6(CO)_{15}]^{2-} + Na_2[HgCl_4]$	8	
$[Co_6(CO)_{15}]^{2-}$	*137*	*140*	$Co_2(CO)_8$ + (i) EtOH, (ii) Δ, vacuum, + (iii) H_2O/KBr	80	^{13}C NMR (*156*)
$[Co_6(CO)_{14}]^{4-}$	*141*	*142*	$Co_4(CO)_{12}$ + Na or Li/THF	46	MO calc. (*143*)
$[Co_6(CO)_{15}(H)]^-$	*144*	*144*	$[Co_6(CO)_{15}]^{2-} + HCl/H_2O$	—	^1H NMR
$[Co_6C(CO)_{15}]^{2-}$	*145*	*145*	$[Co(CO)_4]^-$ + (i) $Co_3(CO)_9CCl$/diisopropyl ether, Δ + (ii) KBr	70-80	^{13}C NMR (*156*), IR (*146*)
$[Co_6C(CO)_{14}]^-$	*147*	*147*	$[Co_6C(CO)_{15}]^{2-} + FeCl_3$/acetone	75-85	ESR (*148*)
$Co_6C(CO)_{12}S_2$	*149*	*150*	$Co_2(CO)_8 + CS_2$/hexane	20-35	IR (*149*)
$Co_6(C_2)(CO)_{14}S$	*151*	*151*	$Co_2(CO)_8 + CS_2$/petroleum ether, Δ	5	IR
$[Co_6N(CO)_{15}]^-$	*152*	*152*	$[Co_6(CO)_{15}]^{2-} + NOBF_4$/THF	40-50	^{13}C, ^{15}N, ^{14}N NMR
		234	$Co_4(CO)_{12} + [N(PPh_3)_2][NO_2]$/THF	40-50	IR (*146*)
$[Co_6P(CO)_{16}]^-$	*153*	*154*	$[Co(CO)_4]^- + PCl_3$/THF	5-10	^{31}P NMR (*154*)
$[Co_8C(CO)_{18}]^{2-}$	*155*	*145*	$[Co(CO)_4]^-$ + (i) $Co_3(CO)_9CCl$ + $Co_4(CO)_{12}$/diisopropyl ether + (ii) KBr	75-85	
$[Co_9Si(CO)_{21}]^{2-}$	*157*	*157*	$Si[Co_2(CO)_7]_2 + [Co(CO)_4]^-/CH_2Cl_2$, Δ	12	
$[Co_{11}(C_2)(CO)_{22}]^{3-}$	*158*	*158*	$[Co_6C(CO)_{15}]^{2-}$/diglyme, Δ	50	
$[Co_{13}(C)_2(CO)_{24}]^{4-}$	*159*	*159*	$[Co_6C(CO)_{15}]^{2-}$/diglyme, Δ	40-50	ESR (*148*)
$[Co_{13}(C)_2(CO)_{24}]^{3-}$	*160*	*160*	$Co_{13}(C)_2(CO)_{24}]^{4-} + \frac{1}{2}I_2$/MeCN	75-85	
$Co_{16}As_4(CO)_{32}(AsPh)_4$	*161*	*161*	$Co_2(CO)_8 + (AsPh)_6$/toluene, Δ	21	
$[Rh_5(CO)_{15}]^-$	*162*	*162*	$Rh_4(CO)_{12} + [Rh(CO)_4]^-$	80	^{13}C NMR
$[Rh_5(CO)_{14}I]^{2-}$	*163*	*163*	$Rh_4(CO)_{12} + Bu^n_4NI$	—	

$Rh_6(CO)_{16}$	*164*	*165*	$RhCl_3 \cdot 3H_2O$ + CO (40 atm)/MeOH, Δ	80–90	MO calc. (*167*)
		166	$Rh_2(O_2CMe)_4$ + HBF_4 + CO/Pr^{i}OH, Δ	87	^{13}C NMR (*168*), MS (*165*)
$[Rh_6(CO)_{14}]^{4-}$	*169*	*170*	$Rh_6(CO)_{16}$ + KOH/H_2O	70–80	
$[Rh_6(CO)_{15}(COEt)]^-$	*171*	*172*	$Rh_4(CO)_{12}$ + C_2H_4 + H_2O	—	
$[Rh_6(CO)_{15}CO(OMe)]^-$	*171*	*173*	$Rh_4(CO)_{12}$ + Na_2CO_3/MeOH	80	
$[Rh_6(CO)_{14}(C_3H_5)]^-$	*174*	*174*	$[Rh_6(CO)_{15}]^{2-}$ + C_3H_5Cl	—	^{1}H NMR
$Rh_6(CO)_{10}(C_7H_8)_3$	*175*	*175*	$Rh_6(CO)_{16}$ + C_7H_8/methylcyclohexane	—	
$Rh_6(CO)_{12}\{P(OPh)_3\}_4$	*176*	*176*	$Rh_6(CO)_{16}$ + $P(OPh)_3/CH_2Cl_2$, Δ	65	
$Rh_6(CO)_{10}\{Ph_2P(CH_2)PPh_2\}_3$	*178*	*179*	$Rh_6(CO)_{16}$ + $Ph_2P(CH_2)PPh_2/CH_2Cl_2$	87	^{13}C, $\{^{103}$Rh$\}$ NMR (*178*), ^{31}P NMR (*179*)
$Rh_6(CO)_9(Bu^t{}_2As)_2(Bu^tAs)$	*180*	*180*	$[Rh(CO)_2Cl]_2$ + $Li(Bu^t)_2As$/THF, −78°C	35	^{1}H NMR
$[Rh_6(CO)_{15}I]^-$	*181*	*173*	$[Rh_6(CO)_{15}]^{2-}$ + I_2	10	^{13}C NMR (*182*)
$[Rh_6C(CO)_{15}]^{2-}$	*183*	*183*	$Rh_4(CO)_{12}$ + (i) NaOH/MeOH + (ii) $CHCl_3$	70	^{13}C NMR (*184*), IR (*146*),
		187	$[RhCl_6]^{3-}$ + KOH + CO + $CHCl_3$/MeOH	70	^{13}C $\{^{103}$Rh$\}$ NMR (*185*), ^{103}Rh NMR (*186*)
$[Rh_6C(CO)_{13}]^{2-}$	*188*	*188*	$K_2[Rh_6C(CO)_{15}] \cdot MeO(CH_2)_4OMe/\Delta$	—	^{13}C $\{^{103}$Rh$\}$, ^{13}C NMR (*185*)
$[Rh_6N(CO)_{15}]^-$	*189*	*234*	$Rh_6(CO)_{16}$ + $[N(PPh_3)_2][NO_2]$/THF	77	^{13}C, ^{15}N NMR (*190*), IR (*146*)
$[Rh_7(CO)_{16}]^{3-}$	*191*	*192*	$Rh_6(CO)_{16}$ + KOH/MeOH	90	^{13}C $\{^{103}$Rh$\}$ (*193*), ^{13}C NMR (*169*)
$[Rh_7(CO)_{16}I]^{2-}$	*194*	*195*	$Rh_6(CO)_{16}$ + R_4NI	80	^{13}C NMR (*196*)
$[Rh_7N(CO)_{15}]^{2-}$	*197*	*197*	$[Rh_6N(CO)_{15}]^{2-}$ + $[Rh(CO)_4]^-$	80	
$Rh_8C(CO)_{19}$	*198*	*199*	$K_2[Rh_6C(CO)_{15}]$ + (i) $Fe[NH_4][SO_4]_2$ + CO/H_2O + (ii) CO/CH_2Cl_2	—	
$[Rh_9(CO)_{19}]^{3-}$	*200*	*200*	$[Rh_5(CO)_{15}]^-$ + $[Rh_4(CO)_{11}]^{2-}$	—	
$[Rh_9P(CO)_{21}]^{2-}$	*201*	*201*	$Rh(CO)_2(acac)$ + CO/H_2 (400 atm) + $Cs[C_6H_5COO]$ + PPh_3/tetraglyme, Δ	80	^{31}P NMR, ^{103}Rh NMR (*186*)
$[Rh_{10}S(CO)_{22}]^{2-}$	*202*	*203*	$Rh_4(CO)_{12}$ + SCN^-	85	^{103}Rh, ^{13}C, ^{13}C $\{^{103}$Rh$\}$ NMR
$[Rh_{10}P(CO)_{22}]^{2-}$	*204*	*204*	$Rh(CO)_2(acac)$ + CO/H_2 (400 atm) + $Cs[C_6H_5COO]$ + $Cs[BH_4]$ + PPh_3/diglyme, Δ	98	^{13}C NMR (*205*)
$[Rh_{10}As(CO)_{22}]^{2-}$	*205*	*205*	$Rh(CO)_2(acac)$ + CO/H_2 (400 atm) + $Cs[C_6H_5COO]$ + $AsPh_3$/diglyme, Δ	98	^{13}C NMR
$[Rh_{11}(CO)_{23}]^{3-}$	*206*	*206*	$[Rh_7(CO)_{16}]^{3-}$ + $FeCl_3$	—	

(*continued*)

TABLE I (*continued*)

Cluster[b]	References: X-Ray	References: Synthesis[c]	Reagents and conditions	Yield (%)	Spectroscopic and theoretical studies[d]
$[Rh_{12}(CO)_{30}]^{2-}$	*207*	*208*	$Rh_4(CO)_{12}$ + (i) Na[MeCOO] + H_2O/acetone + (ii) NaCl/H_2O	85	^{13}C NMR (*209*)
$Rh_{12}(C_2)(CO)_{25}$	*210*	*210*	$[Rh_6C(CO)_{15}]^{2-}$ + (i) $Fe[NH_4][SO_4]_2/H_2O$ + (ii) CH_2Cl_2	79	
$[Rh_{12}(C)_2(CO)_{24}]^{2-}$	*211*	*211*	$[Rh_6C(CO)_{15}]^{2-}$ + H_2SO_4/Pr^{i}OH	90	
$[Rh_{12}(C)_2(CO)_{23}]^{3-}$	*212*	*212*	$[Rh_{12}(C)_2(CO)_{23}]^{2-}$ + NaOH/MeOH	40	ESR (*148*)
$[Rh_{12}(C)_2(CO)_{23}]^{4-}$	*213*	*213*	$[Rh_{12}(C)_2(CO)_{24}]^{2-}$ + KOH/Pr^{i}OH, Δ	65-75	
$[Rh_{13}(CO)_{24}H]^{4-}$	*214*	*214*	$[Rh_{13}(CO)_{24}H_3]^{2-}$ + KOBu^t/THF	—	^1H NMR
$[Rh_{13}(CO)_{24}(H)_2]^{3-}$	*215*	*216*	$Rh(CO)_2(acac)$ + CO/H_2 (12 atm) + $Cs[C_6H_5COO)]/(CH_2OH)_2$, tetraglyme, Δ	91	^1H, ^{13}C, ^1H {^{103}Rh} NMR (*217*)
$[Rh_{13}(CO)_{24}H_3]^{2-}$	*218*	*218*	$[Rh_{12}(CO)_{30}]^{2-}$ + H_2	50	^1H, ^{13}C, ^1H {^{103}Rh} NMR (*217*)
$[Rh_{14}(CO)_{26}]^{2-}$	*219*	*216*	$[Rh_7(CO)_{16}]^{3-}$ + CF_3SO_3H	86	^{13}C NMR (*216*)
$[Rh_{14}(CO)_{25}]^{4-}$	*220*	*221*	$Rh(CO)_2(acac)$ + CO/H_2 (200 atm) + $Cs[C_6H_5COO]$ + $(CH_2OH)_2$ + *n*-methyl morpholine/tetraglyme, Δ	60	
$[Rh_{14}(CO)_{25}H]^{3-}$	*223*	*223*	$[Rh_{14}(CO)_{25}]^{4-}$ + H_3PO_4, MeCN/H_2O	—	^1H NMR (*233*), ^{13}C, ^{103}Rh NMR (*222*)
$[Rh_{14}(C)_2(CO)_{33}]^{2-}$	*224*	*224*	$[Rh_6C(CO)_{15}]^{2-}$ + $[Rh(CO)_2(MeCN)_2]^+$	30	
$[Rh_{15}(CO)_{27}]^{3-}$	*225*	*226*	$Rh(CO)_2(acac)$ + CO/H_2 (19 atm) + $Cs[C_6H_5COO]$ + $(CH_2OH)_2$ + *n*-methylmorpholine/tetraglyme, Δ	87	^{13}C NMR (*226*)
$[Rh_{15}(CO)_{30}]^{2-}$	*227*	*227*	$Rh(CO)_2(acac)$ + (i) CO/H_2 (15 atm) + $Cs[C_6H_5COO]$ + 18-crown-6 + $(CH_2OH)_2$ + *n*-methylmorpholine, Δ + (ii) MeOH + $(CH_2OH)_2$	—	
$[Rh_{15}(C)_2(CO)_{28}]^{-}$	*228*	*199*	$[Rh_6C(CO)_{15}]^{2-}$ + $Fe[NH_4][SO_4]_2/N_2$	—	
$[Rh_{17}(CO)_{30}]^{3-}$	*229*	*229*	$Rh_4(CO)_{12}$ + NaOH/Pr^{i}OH	20	
$[Rh_{17}(S)_2(CO)_{32}]^{3-}$	*230*	*230*	$Rh(CO)_2(acac)$ + CO/H_2 (300 atm) + $Cs[C_6H_5COO]$ + H_2O + H_2S or SO_2/tetraglyme, Δ	73	^1H NMR (*230*), ^{13}C NMR (*231*), ^{103}Rh NMR (*186*)

$[Rh_{22}(CO)_{37}]^{4-}$	*232*	*232*	$Rh_4(CO)_{12}$ + NaOH/Pr^{i}OH	1-10	^{13}C, ^1H NMR, MO calc.
$[Rh_{22}(CO)_{35}H_x]^{5-}$ *and* $[Rh_{22}(CO)_{35}H_{(x+1)}]^{4-}$	*233*	*233*	$Rh(CO)_2$(acac) + 18-crown-6 + CO + $Cs[C_6H_5COO]$ + H_2O	25	^1H, ^{13}C NMR
$Ir_6(CO)_{16}$ (red)	*235*	*236*	$[Ir_6(CO)_{15}]^{2-}$ + MeCOOH/CO	87	
$Ir_6(CO)_{16}$ (black)	*235*	*235*	$[Ir_6(CO)_{15}]^{2-}$ + $MeCOOH/CH_2Cl_2$	10	
		234[e]	$[Ir_6(CO)_{15}]^{2-}$ + CF_3SO_3H/CH_2Cl_2	94	
$[Ir_6(CO)_{15}]^{2-}$	*237*	*234*	$Ir_4(CO)_{12}$ + (i) Na sand + CO/THF + (ii) $Ir_4(CO)_{12}$ + CO	84	FABMS (*234*)
$[Ir_6(CO)_{15}(COEt)]^-$	*238*	*238*	$Ir_6(CO)_{16}$ + CO/H_2 + H_2CCH_2 + H_2O/THF	—	^1H NMR
$Ir_6(CO)_{12}\{P(OPh)_3\}_4$	*239*	*239*	$Ir_6(CO)_{16}$ + $P(OPh)_3$/toluene, Δ	—	^{13}C NMR
$Ir_6(CO)_{11}\{P(OMe)_3\}_5$	*240*	*240*	$Ir_6(CO)_{16}$ + $P(OMe)_3$/toluene, Δ	—	
$Ir_7(CO)_{12}(C_8H_{12})(C_8H_{11})(C_8H_{10})$	*241*	*242*	$Ir_4(CO)_{12}$ + 1,5-cyclooctadiene/chlorobenzene, Δ	3	MS, ^1H NMR (*242*)
$[Ir_8(CO)_{22}]^{2-}$	*243*	*244*	$Ir_4(CO)_{12}$ + (i) Na/THF/CO + (ii) Et_4NCl/H_2O	42	
$[Ni_5(CO)_{12}]^{2-}$	*245*	*246*	$Ni(CO)_4$ + Na/THF	—	^{13}C NMR (*247*)
$Ni_5(CO)_6\{(Me_3Si)_2HCPPCH(SiMe_3)_2\}Cl$	*248*	*248*	$[Ni_6(CO)_{12}]^{2-}$ + $P\{CH(SiMe_3)_2\}Cl_2$/ether	15	^{31}P NMR
$[Ni_6(CO)_{12}]^{2-}$	*249*	*250*	$Ni(CO)_4$ + $NaBH_4$/THF	68	^{13}C NMR (*247*)
$[Ni_8(CO)_{18}(PPh)_6]$	*251*	*251*	$[Ni_6(CO)_{12}]^{2-}$ + $PhPCl_2$/THF	20	^1H NMR
$[Ni_8C(CO)_{16}]^{2-}$	*252*	*252*	$[Ni_9C(CO)_{17}]^{2-}$ + CO/THF	69	IR (*416*)
$[Ni_9(CO)_{18}]^{2-}$	*253*	*253*	$Ni(CO)_4$ + $[N(PPh_3)_2][BH_4]/CH_2Cl_2$	80	^{13}C NMR (*247*)
$[Ni_9C(CO)_{17}]^{2-}$	*252*	*252*	$[Ni_6(CO)_{12}]^{2-}$ + CCl_4/THF	80	IR (*416*)
$[Ni_{10}(C_2)(CO)_{16}]^{2-}$	*254*	*254*	$[Ni_6(CO)_{12}]^{2-}$ + CCl_4 or C_2Cl_6/MeCN	60	
$[Ni_{12}(CO)_{21}]^{4-}$	*255*	*255*	$Ni(CO)_4$ + Na/THF	—	
$[Ni_{12}(CO)_{21}H]^{3-}$	*256*	*257*	$Ni(CO)_4$ + (i) NaOH/DMSO/N_2 + (ii) H_2O + NH_4Cl	—	^1H NMR (*257*)
$[Ni_{12}(CO)_{21}H_2]^{2-}$	*256*	*257*	$Ni(CO)_4$ + (i) NaOH/DMSO/N_2 + (*ii*) H_2O + H_3PO_4	—	^1H NMR (*257*)
$[Ni_{16}(C_2)_2(CO)_{23}]^{2-}$	*380*	*380*	$[Ni_{10}(C_2)(CO)_{16}]^{2-}$ + $8PPh_3$/THF	100	
$Pd_7(CO)_7(PMe_3)_7$	*258*	*258*	$Pd(C_8H_{12})(PMe_3)$ + CO/toluene	—	
$Pd_{10}(CO)_{14}(PBu_3)_4$	*259*	*259*	$Pd(OAc)_2$ + PBu^n_3 + CF_3COOH/dioxane/acetone	17	^{31}P NMR (*260*)
$Pd_{10}(CO)_{12}(PBu_3)_6$	*261*	*261*	$Pd(OAc)_2$ + PBu^n_3 + CF_3COOH/dioxane/acetone	—	^{31}P NMR (*260*)
$Pt_5(CO)_6(PPh_3)_4$	*262*	*263*	$Pt(PPh_3)_2Cl_2$ + $[Fe(CO)_3NO]^-$	75	
$Pt_5(CO)_3(PPh_3)_4(SO_2)_3$	*264*	*264*	$Pt_5(CO)_6(PPh_3)_4$ + SO_2	60	^{31}P, ^1H NMR, powder diffraction study

(*continued*)

TABLE I (*continued*)

Cluster[b]	References: X-Ray	References: Synthesis[c]	Reagents and conditions	Yield (%)	Spectroscopic and theoretical studies[d]
$[Pt_6(CO)_{12}]^{2-}$	*265*	*265*	$[PtCl_6]^{2-}$ + CO + NaOH/MeOH	—	^{195}Pt NMR (*266*)
$[Pt_9(CO)_{18}]^{2-}$	*265*	*265*	$[PtCl_6]^{2-}$ + CO + NaOH/MeOH	—	^{195}Pt NMR (*266*)
$[Pt_{15}(CO)_{30}]^{3-}$	*265*	*265*	$[PtCl_6]^{2-}$ + CO + NaOH/MeOH	—	
$[Pt_{19}(CO)_{22}]^{4-}$	*267*	*267*	$[Pt_9(CO)_{18}]^{2-}$/MeCN, Δ	50	^{13}C NMR
$[MoFe_5C(CO)_{17}]^{2-}$	*268*	*269*	$[Fe_5C(CO)_{14}]^{2-}$ + $Mo(CO)_3(THF)$	51	^{13}C NMR (*269*)
$MoRu_3Hg(CCBu^t)(CO)_9(C_5H_5)$	*270*	*270*	$Ru_3(CO)_{12}$ + (i) Bu^tCCH + (ii) KOH/EtOH + (iii) HgI_2 + (iv) $Mo(C_5H_5)(CO)_3$	14	^{1}H NMR, MS
$[Mo_2Ni_3(CO)_{16}]^{2-}$	*271*	*271*	$[Mo_2(CO)_{10}]^{2-}$ + $Ni(CO)_4$/THF, Δ	60	
$[Mo_2Ni_4(CO)_{14}]^{2-}$	*271*	*271*	$[Mo_2(CO)_{10}]^{2-}$ + $Ni(CO)_4$	—	
$WRu_5Au_2C(CO)_{17}(PEt_3)_2$	*272*	*272*	$[Ru_5C(CO)_{14}]^{2-}$ + (i) $W(CO)_3(MeCN)_3$ + (ii) $Au(PEt_3)Cl$		^{31}P, ^{1}H NMR
$W_2Os_3(CO)_{14}(PMe_2Ph)_2(S)_2$	*273*	*273*	$Os_3(CO)_9(S)_2$ + $W(CO)_5(PMe_2Ph)/h\nu \rightarrow$ $WOs_3(CO)_{12}(PMe_2Ph)(S)_2$ + $W_2Os_3(CO)_{14}(PMe_2Ph)(S)_2$ $WOs_3(CO)_{12}(PMe_2Ph)(S)_2$ + $W(CO)_5(PMe_2Ph)/h\nu$	27	
$[W_2Ni_3(CO)_{16}]^{2-}$	*271*	*271*	$[W_2(CO)_{10}]^{2-}$ + $Ni(CO)_4$/THF, Δ	68	
$W_2Pt_3(CO)_4(CR)_2(C_5H_5)_2(COD)_2$	*274*	*274*	$W(CO)_2(CR)(C_5H_5)$ + $Pt(COD)_2$, 2 steps	33	^{13}C{^{1}H}, ^{195}Pt{^{1}H} NMR
$W_3Pt_2(CO)_6(CR)_3(C_5H_5)_3$	*274*	*274*	$W(CO)_2(CR)(C_5H_5)$ + $Pt(COD)_2$, 2 steps	30	^{13}C{^{1}H}, ^{195}Pt{^{1}H} NMR
$Mn_4Hg_4(CO)_8(MeC_5H_4)_4$	*275*	*275*	$[MnGe(CO)_2(H)_3(MeC_5H_4)]^-$ + $HgCl_2/H_2O$	55	
$Re_2Os_3(CO)_{20}H_2$	*276*	*277*	$Os_3(CO)_{10}(C_8H_{14})_2$ + $Re(CO)_5H$/benzene	90	^{1}H, ^{13}C, ^{1}H NMR, MS (*277*)
$Re_8In_4(CO)_{32}$	*278*	*279*	$Re_2(CO)_{10}$ + In/Δ	41	
$FeOs_3Au(CO)_{13}H(PPh_3)$	*378*	*326*	$[FeOs_3CO_{13}H]^-$ + $Au(PPh_3)Cl$ + $TlPF_6$	60–65	
$FeCo_3Au(CO)_{12}(PPh_3)$	*280*	*280*	$[FeCo_3(CO)_{12}]^-$ + $Au(PPh_3)NO_3$	—	
$[FeRh_4(CO)_{15}]^{2-}$	*281*	*281*	$Rh_2(CO)_4Cl_2$ + (i) $[Fe(CO)_4H]^-$, N_2 + (ii) CO	—	^{103}Rh, ^{13}C{^{1}H} NMR
$[FeRh_5(CO)_{16}]^-$	*282*	*281*	$Rh_2(CO)_4Cl_2$ + (i) $[Fe(CO)_4H]^-$, N_2 + (ii) $Rh_2(CO)_4Cl_2$	—	^{103}Rh, ^{13}C{^{103}Rh} NMR (*281*)

		282	$Fe(CO)_5$ + $RhCl_3$ + Na/Hg/diglyme, Δ	—	
$[Fe_2Rh_4(CO)_{16}]^{2-}$	*281*	*281*	$Rh_2(CO)_4Cl_2$ + (i) $[Fe(CO)_4H]^-$, N_2 + (ii) Pr^iOH, N_2	—	^{103}Rh, $^{13}C\{^{103}Rh\}$ NMR
$[Fe_3Pt_3(CO)_{15}]^{2-}$	*283*	*283*	$[Pt_3(CO)_6]^{2-}$ + $Fe(CO)_5$/MeCN, Δ	70	
$[Fe_3Pt_3(CO)_{15}]^-$	*283*	*283*	$[Fe_3Pt_3(CO)_{15}]^{2-}$ + H^+ or I_2	100	ESR (*284*)
$[Fe_3Cu_3(CO)_{12}]^{3-}$	*379*	*379*	$[Fe(CO)_4]^{2-}$ + CuBr/THF	100	^{63}Cu, ^{13}C, ^{17}O NMR (*470*)
$Fe_3Ag_6(CO)_{12}\{(Ph_2P)_3CH\}$	*285*	*285*	$Na_2[Fe(CO)_4](dioxane)_{3/2}$ + $Ag_3Cl_3\{(Ph_2P)_3CH\}$	50	^{31}P NMR
$Fe_3Au_2(CO)_9(PPh_3)_2S$	*286*	*286*	$Fe_3(CO)_9H_2S$ + (i) KH/THF + (ii) $Au(PPh_3)Cl$	47	
$Fe_3Bi_2(CO)_9$	*287*	*287*	$[Fe(CO)_4H]^-$ + (i) $NaBiO_3$ + (ii) H_2SO_4	7	
$[Fe_4CoC(CO)_{14}]^-$	*288*	*288*	$[Fe_4C(CO)_{12}]^{2-}$ + $Co_2(CO)_8$, CH_2Cl_2	65	^{13}C NMR
$Fe_4CoRhC(CO)_{14}$	*381*	*381*	$[Fe_6C(CO)_{16}]^{2-}$ + (i) $CoCl_2$/diglyme, Δ	28	
			+ (ii) $[Rh(CO)_2Cl]_2/CH_2Cl_2$	28	
$[Fe_4RhC(CO)_{14}]^-$	*268*	*269*	$[Fe_4C(CO)_{12}]^{2-}$ + $[Rh(C_8H_{12})Cl]_2$	—	^{13}C NMR (*269*)
$[Fe_4Pd(CO)_{16}]^{2-}$	*289*	*289*	$[Fe_3(CO)_{11}]^{2-}$ + $0.7PdCl_2$/MeCN	70–80	
$[Fe_4Pt(CO)_{16}]^{2-}$	*289*	*289*	$[Fe_3(CO)_{11}]^{2-}$ + $0.7PtCl_2$/MeCN	70–80	
$[Fe_4Pt_6(CO)_{22}]^{2-}$	*283*	*283*	$[Fe_3Pt_3(CO)_{15}]^-$/MeCN, Δ	—	
$[Fe_4Cu_5(CO)_{16}]^{3-}$	*379*	*379*	CuBr + $[Fe_3Cu_3(CO)_{12}]^{3-}$	26	^{63}Cu, ^{13}C, ^{17}O NMR (*470*)
$Fe_4AuC(CO)_{12}H(PPh_3)$	*290*	*290*	$[Fe_4(CO)_{13}]^-$ + (i) $Au(PR_3)Cl$ + $TlPF_6$	47	^1H NMR, MS
			+ (ii) $HBF_4 \cdot Et_2O$		
$Fe_4Au_2C(CO)_{12}(PEt_3)_2$	*290*	*290*	$Fe_4AuC(CO)_{12}H(PEt_3)$ + (i) NEt_3	90	MS
			+ (ii) $Au(PEt_3)Cl$ + $TlPF_6$		
$Fe_4Cd_4(CO)_{16}$	*291*	*291*	$Fe(CO)_5$ + (i) $Cd(OAc)_2$ + NH_3 + H_2O	—	
			+ (ii) Δ, vacuum + (iii) acetone		
$[Fe_4Bi_4(CO)_{13}]^{2-}$	*292*	*292*	$[BiFe_3(CO)_{10}]^-$ + CO (35–50 atm)/CH_2Cl_2	—	
$[Fe_5RhC(CO)_{16}]^-$	*282*	*269*	$[Fe_5C(CO)_{14}]^{2-}$ + $[Rh(CO)_2Cl]_2$/MeOH	—	^{13}C NMR (*269*)
$Fe_5Au_2C(CO)_{14}(PEt_3)_2$	*293*	*293*	$[Fe_5C(CO)_{14}]^{2-}$ + $Au(PEt_3)Cl$ + $TlPF_6$	80	
$Fe_5Sn_2(CO)_{13}(C_5H_5)$	*294*	*294*	$[FeSn(CO)_4(C_5H_5)]_2$/toluene, Δ	33	
$[Fe_6Pd_6(CO)_{24}H]^{3-}$	*289*	*289*	$[Fe_4(CO)_{13}]^{2-}$ + $[PdCl_4]^{2-}$	5–10	
$RuCo_3Au(CO)_{12}(PPh_3)$	*295*	*295*	$[Co(CO)_4]^-$ + (i) $RuCl_3 \cdot xH_2O$ + $RuCl_3L_3$	60–70	
			(L = *o*-MePhCN, PhSMe) + (ii) $Au(PPh_3)Cl$		
$RuCo_4Hg(CO)_{16}$	*296*	*296*	$[RuCo_3(CO)_{12}]^-$ + (i) $HgBr_2$/toluene	32	
			+ (ii) $[Co(CO)_4]^-$		
$[RuRh_4(CO)_{15}]^{2-}$	*297*	*297*	$Ru_3(CO)_{12}$ + $Rh_4(CO)_{12}$ + CO + NaOH/MeOH	78	^{13}C NMR
$[RuIr_4(CO)_{15}]^{2-}$	*298*	*298*	$Ir_4(CO)_{12}$ + $RuCl_3 \cdot xH_2O$ + NaOH/MeOH + CO	30	

(*continued*)

TABLE I (*continued*)

Cluster[b]	References: X-Ray	References: Synthesis[c]	Reagents and conditions	Yield (%)	Spectroscopic and theoretical studies[d]
$Ru_2Co_2Au_2(CO)_{12}(PPh_3)_2$	*286*	*286*	$Ru_2Co_2(CO)_{12}H_2$ + (i) KH/THF + (ii) $Au(PPh_3)Cl$	38	
$Ru_3CoAu(CO)_{13}(PPh_3)$	*299*	*299*	$Ru_3(CO)_{12}$ + (i) $[Co(CO)_4]^-$ + (ii) $Au(PPh_3)Cl$	45	^1H NMR
$Ru_3CoAu_2(CO)_{12}H(PPh_3)_2$	*299*	*299*	$Ru_3Co(CO)_{13}H$ + $[(Ph_3PAu)_3O][BF_4]$	9	^1H NMR
$Ru_3CoAu_3(CO)_{12}(PPh_3)_3$	*299*	*299*	$[Ru_3Co(CO)_{13}]^-$ + $[(Ph_3PAu)_3O][BF_4]$	55	
$Ru_3Rh_2(CO)_{13}(PEt_3)(PPh)$	*300*	*300*	$Ru_3(CO)_9H_2(PPh)$ + (i) KOH/MeOH + (ii) $[Rh(CO)_3(PEt_3)_2]^+$	5	^1H NMR
$Ru_3Ni_2(CO)_8(C_5H_5)_2(PhCCPh)$	*301*	*301*	$Ru_3(CO)_{12}$ + $Ni_2(C_5H_5)_2(PhCCPh)$ + H_2/octane	6-10	^1H NMR
$Ru_3Au_2(CO)_8(PPh_3)_3S$	*302*	*302*	$Ru_3(CO)_9H_2S$ + $Au(PPh_3)Me$/toluene, Δ	18	^1H, $^{31}P\{^1H\}$ NMR, FABMS (*303*)
$Ru_3Au_2(CO)_9(PPh_3)_2S$	*304*	*304*	$Ru_3(CO)_9H_2S$ + (i) $K(HBBu^s_3)$/THF + (ii) $[(Ph_3PAu)_3O][BF_4]$	14	^1H NMR, FABMS
$Ru_3Au_2(CO)_9(CCHBu^t)(PPh_3)_2$	*305*	*305*	$Ru_3(CO)_9(CCHBu^t)H$ + (i) $K[HBBu^s_3]$ + (ii) $[(Ph_3PAu)_3O][BF_4]$	16	^1H NMR
$Ru_3Au_2(CO)_9(COMe)H(PPh_3)_2$	*306*	*306*	$Ru_3(CO)_9H_3(COMe)$ + $AuMe(PPh_3)$	21	^1H, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$ NMR
$Ru_3Au_3(CO)_9(COMe)(PPh_3)_3$	*306*	*306*	$Ru_3(CO)_9H_3(COMe)$ + $AuMe(PPh_3)$	12	$^{31}P\{^1H\}$, $^{13}C\{^1H\}$ NMR
$Ru_3Au_3(CO)_8(C_{12}H_{15})(PPh_3)_3$	*307*	*307*	$Ru_3(CO)_9H(C_{12}H_{15})$ + (i) $K(HBBu^s_3)$/THF + (ii) $[(Ph_3PAu)_3O][BF_4]$	29	FABMS (*303*)
$Ru_4Ni(CO)_9(CCPr^i)_2(PPh_2)_2$	*308*	*308*	$Ru_3(CO)_9(CCPr^i)(PPh_2)$ + $[(C_5H_5)Ni(CO)]_2$	—	
$Ru_4CuAg(CO)_{12}H_2(PPh_3)_2$	*309*	*309*	$[Ru_4(CO)_{12}H_2]^{2-}$ + $Cu(PPh_3)Cl$ + $Ag(PPh_3)I$ + $TlPF_6$	40	^1H, $^{31}P\{^1H\}$ NMR
$Ru_4Cu_2(CO)_{12}H_2(PPh_3)_2$	*309*	*309*	$[Ru_4(CO)_{12}H_2]^{2-}$ + $Cu(PPh_3)Cl$	40	^1H, $^{31}P\{^1H\}$ NMR
$Ru_4Ag_2(CO)_{12}H_2(PPh_3)_2$	*309*	*309*	$[Ru_4(CO)_{12}H_2]^{2-}$ + $Ag(PPh_3)I$ + $TlPF_6$	50	^1H, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$ NMR
$Ru_4RhC(CO)_{12}(C_5Me_5)$	*310*	*310*	$Ru_5RhC(CO)_{14}(C_5Me_5)$ + CO/heptane	35	MS
$Ru_4RhC(CO)_{11}H(C_5Me_5)I$	*310*	*310*	$Ru_4RhC(CO)_{12}(C_5Me_5)$ + (i) NEt_4BH_4/THF + (ii) I_2/CH_2Cl_2	10	

$Ru_4AuC(CO)_{12}H(PPh_3)$	*311*	*311*	$Ru_5Au_2C(CO)_{14}(PPh_3)_2 + HI$	—	^{31}P NMR, MS
$Ru_4AuC(CO)_{12}(PEt_3)I$	*311*	*311*	$Ru_5Au_2C(CO)_{14}(PEt_3)_2 + I_2$	—	^{31}P NMR, ^1H NMR, MS
$Ru_4Au_2C(CO)_{12}(PMe_2Ph)_2$	*311*	*311*	$Ru_5AuC(CO)_{14}(PMe_2Ph)_2$ + CO (80 atm) toluene, Δ	80	MS, ^{31}P NMR
$Ru_4Au_3(CO)_{12}H(PPh_3)_3$	*312*	*312*	$Ru_4(CO)_{12}H_4 + Au(PPh_3)Me$	59	^1H, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$ NMR, FABMS
$Ru_5RhC(CO)_{14}(C_5Me_5)$	*310*	*310*	$[Ru_5C(CO)_{14}]^{2-} + [Rh(C_5Me_5)(MeCN)_2][SbF_6]_2$	70	MS
$Ru_5RhAuC(CO)_{14}(COD)PPh_3$	*310*	*310*	$[Ru_5C(CO)_{14}]^{2-}$ + (i) $[Rh(COD)_2][SbF_6]/CH_2Cl_2$ + (ii) $Au(PPh_3)Cl/CH_2Cl_2$	70	
$Ru_5RhAuC(CO)_{16}PPh_3$	*310*	*310*	$Ru_5RhAuC(CO)_{14}(COD)PPh_3$ + CO/heptane	30	
$Ru_5AuC(CO)_{14}[C(Me)O](PPh_3)$	*314*	*314*	$Ru_5C(CO)_{15} + Au(PPh_3)Me$	64	^1H NMR (*314*)
$Ru_5AuC(CO)_{13}(C_5H_5)(PPh_3)$	*314*	*314*	$Ru_5C(CO)_{15}$ + (i) $Na[C_5H_5]$ + (ii) $[Au(PPh_3)][ClO_4]$	—	MS
$Ru_5AuC(CO)_{13}(PPh_3)_2I$	*26*	*26*	$Ru_5Au(CO)_{15}(PPh_3)I$ + (i) heptane, Δ + (ii) PPh_3	75	
$Ru_5AuC(CO)_{15}(PPh_3)Cl$	*315*	*315*	$Ru_5C(CO)_{15} + Au(PPh_3)Cl$	—	
$Ru_5AuC(CO)_{14}(PPh_3)Br$	*315*	*315*	$Ru_5C(CO)_{15} + Au(PPh_3)Br/CH_2Cl_2$, N_2	—	
$Ru_5Au_2C(CO)_{14}(PEt_3)_2$	*473*	*473*	$[Ru_5C(CO)_{14}]^{2-} + [Au(PEt_3)][ClO_4]$	95	$^{31}P\{^1H\}$ NMR
$Ru_6Cu_2C(CO)_{16}(MeCN)_2$	*316*	*316*	$[Ru_6C(CO)_{16}]^{2-} + [Cu(MeCN)_4][BF_4]$	77	^1H, ^{13}C NMR
$Ru_6Cu_2(CO)_{18}(C_6H_4\text{-}Me)_2$	*317*	*317*	$[Ru_6(CO)_{18}]^{2-}$ + (i) $[Cu(MeCN)_4][BF_4]$/acetone + (ii) toluene, Δ	—	
$Ru_6AuC(CO)_{15}(NO)(PPh_3)$	*51*	*51*	$[Ru_6C(CO)_{15}(NO)]^- + Au(PPh_3)Cl + TlPF_6$	—	
$Ru_6Au_2C(CO)_{16}(PMePh_2)_2$	*272*	*272*	$[Ru_6C(CO)_{16}]^{2-} + Au(PMePh_2)Cl$		^{31}P NMR
$Ru_6Hg(CO)_{18}(CCBu^t)_2$	*270*	*270*	$Ru_3(CO)_{12}$ + (i) Bu^tCCH + (ii) KOH/EtOH + HgI_2 + (iii) $[Ru_3(CO)_9(CCBu^t)]^-$	72	^1H NMR, MS
$Ru_6Hg(CO)_{20}(NO)_2$	*318*	*318*	$[Ru_3(CO)_{10}(NO)]^- + HgCl_2$	—	MS
$[Ru_{12}Tl(C)_2(CO)_{32}]^-$	*319*	*320*	$[Ru_6C(CO)_{16}]^{2-} + Tl(NO_3)_3/MeOH$	—	
$Os_3NiAu(CO)_9(C_5H_5)(PPh_3)$	*321*	*321*	$Os_3Ni(CO)_9(C_5H_5)H_3$ + (i) NaH/THF + (ii) $Au(PPh_3)Cl$/toluene	36	^1H NMR
$Os_3Ni_3(CO)_9(C_5H_5)_3$	*322*	*322*	$Os_3(CO)_{12} + [Ni(CO)(C_5H_5)]_2$/octane, Δ	40	^1H NMR, MS, ESR (*323*)
$Os_3Au_2(CO)_{11}H_2(PPh_3)_2$	*324*		Synthesis not reported		
$Os_3Au_2(CO)_{10}(PEt_3)_2$	*325*	*325*	$[Os_3(CO)_{11}H]^- + Au(PEt_3)Cl + TlPF_6/CHCl_3$, Δ	80	^1H NMR
$Os_4Au(CO)_{13}H(PEt_3)$	*326*	*326*	$[Os_4(CO)_{13}H]^- + Au(PEt_3)Cl + TlPF_6/CHCl_3$	65	^1H NMR
$Os_4Au(CO)_{12}H_3(PEt_3)$	*326*	*326*	$[Os_4(CO)_{12}H_3]^- + Au(PEt_3)Cl + TlPF_6/CHCl_3$	50	^1H NMR

(*continued*)

TABLE I (*continued*)

Cluster[b]	References: X-Ray	References: Synthesis[c]	Reagents and conditions	Yield (%)	Spectroscopic and theoretical studies[d]
$Os_4Au_2(CO)_{12}H_2(PPh_3)_2$	*327*	*327*	$Os_4Au(CO)_{12}H_3(PPh_3) + Au(PPh_3)Cl$ (two isomers)	—	MS
$Os_4Au_2(CO)_{13}(PEt_3)_2$	*328*	*328*	$[Os_4(CO)_{13}H]^- + 2Au(PEt_3)Cl + TlBF_4$	—	^{31}P NMR
$Os_4Au_2(CO)_{12}(PMePh_2)_2$	*328*	*328*	$Os_4Au_2(CO)_{13}(PMePh_2)_2/CH_2Cl_2$, Δ	—	^{31}P NMR
$Os_4Bi_2(CO)_{12}$	*329*	*329*	$Os_3(CO)_{12} + NaBiO_3$, Δ	—	
$Os_5AuH(CO)_{15}(PEt_3)$	*69*	*69*	$[Os_5(CO)_{15}H]^- + Au(PEt_3)Cl + TlPF_6/CH_2Cl_2$	—	
$Os_5Au_2C(CO)_{14}(PPh_3)_2$	*78*	*78*	$[Os_5C(CO)_{14}]^{2-} + Au(PPh_3)Cl + TlPF_6/CH_2Cl_2$	80	
$Os_6Au_2(CO_{17}(PMe_3)_2$	*330*	*330*	$Os_6(CO)_{18}$ + (i) Me_3NO/CH_2Cl_2 + (ii) $Au(PMe_3)Cl/TlPF_6/CH_2Cl_2$	50	^{31}P, ^1H NMR
$Os_6Au_2(CO)_{18}(PMe_3)_2$	*330*	*330*	$Os_6Au_2(CO)_{17}(PMe_3)_2) + CO/CH_2Cl_2$	90	
$Os_6Pt_2(CO)_{17}(C_8H_{12})_2$	*331*	*331*	$Os_6(CO)_{20} + Pt(C_8H_{12})_2$, toluene/$CH_3CN/C_2H_4$	15	
$Os_6Pt_2(CO)_{16}(C_8H_{12})_2$	*322*	*332*	$Os_6(CO)_{16}(MeCN)_2 + Pt(C_8H_{12})_2$, CH_2Cl_2	—	
$[Os_6Ag(CO)_{20}H_2]^-$	*333*	*333*	$[Os_3(CO)_{11}H]^- + AgPF_6/THF$, Δ		^{13}C, ^1H NMR
$[Os_6Au(CO)_{20}H_2]^-$	*334*	*334*	$Os_3Au(CO)_{10}H(PR_3) + [N(PPh_3)_2]Cl/CH_2Cl_2$ (R = Ph, Et)	90	^1H NMR
$Os_7Au_2(CO)_{20}(PEt_3)_2$	*335*	*335*	$[Os_7(CO)_{20}]^{2-} + Au(PEt_3)Cl + TlPF_6/CH_2Cl_2$	90	
$Os_8Au_2(CO)_{22}(PPh_3)_2$	*339*	*339*	$[Os_8(CO)_{22}]^{2-} + Au(PPh_3)Cl + TlPF_6/CH_2Cl_2$	65	
$Os_9Hg_3(CO)_{33}$	*336*	*336*	$[Os_3(CO)_{11}H]^- + Hg^{2+}$	60	
$[Os_{10}CuC(CO)_{24}(MeCN)]^-$	*337*	*337*	$[Os_{10}C(CO)_{24}]^{2-} + [Cu(MeCN)_4][BF_4]/CH_2Cl_2$	—	
$[Os_{10}AuC(CO)_{24}(PPh_3)]^-$	*337*	*337*	$[Os_{10}C(CO)_{24}]^{2-} + Au(PPh_3)Cl + TlPF_6/CH_2Cl_2$	—	
$[Os_{10}AuC(CO)_{24}Br]^-$	*338*	*338*	$[Os_{10}C(CO)_{24}]^{2-} + AuPPh_3Br + AgClO_4$	—	
$[Os_{11}CuC(CO)_{27}(MeCN)]^-$	*134*	*134*	$[Os_{11}C(CO)_{27}]^{2-} + [Cu(MeCN)_4][BF_4]/CH_2Cl_2$	—	
$[Os_{20}Au(C)_2(CO)_{48}]^{2-}$	*338*	*338*	$[Os_{10}C(CO)_{24}]^{2-} + M(PPh_3)X + AgClO_4$ (excess) (M = Cu, Ag, Au; X = Cl, Br)		
$[Os_{20}Hg(C)_2(CO)_{48}]^{2-}$	*338*	*338*	$[Os_{10}C(CO)_{24}]^{2-} + Hg^{2+}$ salts or $Hg/AgBF_4/CH_2Cl_2$	—	ESR
$[CoRh_6N(CO)_{15}]^{2-}$	*197*	*197*	$[Rh_6N(CO)_{15}]^{2-} + [Co(CO)_4]^-/THF$, Δ	70-80	

$Co_2Rh_4(CO)_{16}$	*340*	*340*	$Co_2Rh_2(CO)_{12}$/*n*-heptane, Δ	—	MS
$Co_2Pt_3(CO)_9(PEt_3)_3$	*341*	*341*	$[Co(CO)_4]^-$ + $Pt(PEt_3)_2Cl_2$/THF	66	
$Co_2Au_6(CO)_8(PPh_3)_4$	*342*	*342*	$[Au_8(PPh_3)_7]^{2-}$ + $[Co(CO)_4]^-$/THF	—	
$[Co_3Ni_7C_2(CO)_{15}]^{3-}$	*343*	*343*	$Co_3(CO)_9CCl$ + $[Ni_6(CO)_{12}]^{2-}$/THF	—	
$[Co_3Ni_9C(CO)_{20}]^{3-}$	*344*	*344*	$Co_3(CO)_9CCl$ + $[Ni_6(CO)_{12}]^{2-}$/THF	—	
$[Co_4Ni_2(CO)_{14}]^{2-}$	*345*	*346*	$NiCl_2$ + $[Co(EtOH]_x][(Co(CO)_4]_2$ + (i) Δ, vac. + (ii) KBr/H_2O	60	
$Co_4Cu_4(CO)_{16}$	*347*	*347*	$Na[Co(CO)_4]$/THF + CuCl/HCl	—	
$Co_4Ag_4(CO)_{16}$	*348*		Synthesis not reported		
$Co_4Zn_2(CO)_{15}$	*349*	*349*	$Hg[Co(CO)_4]_2$ + (i) Zn + (ii) octane/Δ	35	MS
$Co_4Ge(CO)_{16}$	*350*	*350*	Synthesis not reported		
$Co_4Ge(CO)_{14}$	*351*	*351*	$Na[Co(CO)_4]$ + GeI_4/benzene, hexane	52	MS
$Co_4Ge(CO)_{13}$	*352*	*352*	$Na[Co(CO)_4]$ + GeI_4/benzene, pet. ether	62	MS
$Co_4Ge_2(CO)_{11}(Me)_2$	*353*	*353*	MeGe + $Co_4Ge(CO)_{14}$/hexane, sealed tube, dark	—	MS
$[Co_5HgGe(CO)_{17}]^-$	*354*	*354*	$Co_2(CO)_8$ + (i) NaHg/THF + (ii) GeI_4/benzene, hexane	5	—
$[Co_5Ge(CO)_{16}]^-$	*355*	*355*	$[NEt_4][Co(CO)_4]$ + $Co_4Ge(CO)_{14}/CH_2Cl_2$, Δ	64	—
$[Co_5Sn_2(CO)_{19}Cl_2]^-$	*356*	*356*	$ClSn\{Co(CO)_4\}_3$ + $[HB(pyrazole)_3]^-$/THF	35	
$[Co_6Ni_2(C)_2(CO)_{16}]^{2-}$	*357*	*357*	$[NEt_4]_3[Co_3Ni_9C(CO)_{20}]$ + $[Co_3(CO)_9CCl]$/acetone	70	^1H NMR
$Co_6Ge_2(CO)_{19}$	*358*	*358*	GeH_2 + $Co_2(CO)_8$/hexane		
$Rh_4Pt(CO)_4(C_5Me_5)_4$	*359*	*359*	$Pt(C_2H_4)_3$ + $[Rh(CO)(C_5Me_5)]_2$/toluene	90	^{13}C, ^{195}Pt NMR
$[Rh_4Pt(CO)_{14}]^{2-}$	*360*	*361*	$RhCl_3 \cdot xH_2O$ + (i) $[PtCl_6]^{2-}$/MeOH + (ii) CO + NaOH	53	^{13}C, $^{13}C\{^{103}Rh\}$, ^{103}Rh NMR
$[Rh_4Pt(CO)_{12}]^{2-}$	*360*	*361*	$[Rh_4Pt(CO)_{14}]^{2-}$ + THF/N_2	92	^{195}Pt NMR (*361*)
$[Rh_5Pt(CO)_{15}]^-$	*362*	*361*	$[PtCl_6]^{2-}$ + $RhCl_3$ + Na_2CO_3 + CO/MeOH	87	^{195}Pt NMR (*250*), ^{13}C, $^{13}C\{^{103}Rh\}$, ^{103}Rh, ^{195}Pt NMR (*361*)
$[Rh_6Ni(CO)_{16}]^{2-}$	*363*	*363*	$[Rh_6(CO)_{15}]^{2-}$ + $Ni(CO)_4$/THF	90	^{13}C, $^{13}C\{^{103}Rh\}$, ^{103}Rh NMR (*364*)
$[Rh_6IrN(CO)_{15}]^{2-}$	*197*	*197*	$[Rh_6N(CO)_{15}]^{2-}$ + $[Ir(CO)_4]^-$/THF, Δ	79–80	
$Rh_6Cu_2C(CO)_{15}(MeCN)_2$	*365*	*365*	$[Rh_6C(CO)_{15}]^{2-}$ + $[Cu(MeCN)_4][BF_4]$/MeOH	70	
$[Rh_9Pt_2(CO)_{22}]^{3-}$	*366*	*366*	$[PtRh_5(CO)_{15}]^-$/MeOH, Δ	—	
$[Rh_{10}PtN(CO)_{21}]^{3-}$	*367*	*367*	$[Rh_6N(CO)_{15}]^-$ + $[Rh_4Pt(CO)_{12}]^{2-}$/acetone, Δ	15	
$[Rh_{11}Pt_2(CO)_{24}]^{3-}$	*368*	*368*	$[Rh_5Pt(CO)_{15}]^-$ + $NaHCO_3$/MeOH, Δ	15	^1H NMR, ESR

(*continued*)

TABLE 1 (*continued*)

Cluster[b]	References: X-Ray	References: Synthesis[c]	Reagents and conditions	Yield (%)	Spectroscopic and theoretical studies[d]
$[Rh_{12}Pt(CO)_{24}]^{4-}$	*368*	*368*	$[Rh_5Pt(CO)_{15}]^- + NaHCO_3/MeOH, \Delta$	—	
$[Rh_{12}AgC(CO)_{30}]^{3-}$	*369*	*369*	$[Rh_6C(CO)_{15}]^{2-} + AgBF_4$/acetone	75	
$[Rh_{12}Sb(CO)_{27}]^{3-}$	*370*	*370*	$Rh(CO)_2(acac) + CO/H_2$ (400 atm) + $Cs[C_6H_5COO] + SbPh_3$/tetraglyme, dimethyl ether, Δ	66	^{13}C NMR
$Ir_3Pt_3(CO)_6(C_5Me_5)_3$	*371*	*371*	$Ir(CO)_2(C_5Me_5) + Pt(C_2H_4)_3$/diethyl ether	100	$^{13}C\{^1H\}$, ^{195}Pt NMR
$Ir_8Au_2(CO)_{20}(PhPPPh)(PEt_3)_2$	*372*	*372*	$Ir_4CO_{11}PPhH_2$ + (i) DBU/THF + (ii) $AgClO_4$ + (iii) $Au(PEt_3)ClO_4$	30	
$[Ni_{38}Pt_6(CO)_{48}H_2]^{4-}$	*373*	*373*	$[Ni_6(CO)_{12}]^{2-} + 6PtCl_2$/MeCN	80	^{195}Pt NMR (*374*)
$[Ni_{38}Pt_6(CO)_{48}H]^{5-}$	*373*	*373*	$[Ni_{38}Pt_6(CO)_{48}H_2]^{4-} + NaCO_3$/MeCN		
$Pd_4Hg_2(CO)_4(PEt_3)_4(Br)_2$	*375*	*375*	$Pd(CO)_5(PEt_3)_4 + C_9H_8NCH(Me)HgBr$ + CO/benzene	24	

[a] Table is comprehensive up to September 1985.

[b] Clusters are listed under the earliest transition metal contained within their framework. Homometallic clusters are grouped together, followed by heterometallic clusters. Groups of the periodic table are listed in succession and within each group metals are arranged by period. The entries in each metal listing are further categorized according to the size of the clusters, which appear in order of increasing nuclearity. It must be noted that in the text cluster formulas are written in a more descriptive fashion.

[c] Where several synthetic routes have been reported, the synthesis giving the highest yield is given.

[d] References are given for spectroscopic studies, other $\nu_{(C-O)}$ IR. When these studies are reported in the synthetic/structural reference no further reference number is given. MS, mass spectrum; FABMS, fast atom bombardment mass spectrum; VT, variable-temperature.

[e] The author does not specify which isomer is produced by this method.

II. Synthesis of High-Nuclearity Carbonyl Clusters

The logical synthesis of HNCC presents a major problem. The transition metals exhibit a complex array of bonding modes and a far more extensive range of coordination numbers than their main group counterparts, which have dependable valences and, in the main, strongly directional bonds. This, combined with the relative similarities of M—M, M—CO, and M—H bond energies (*454*), makes the designed synthesis of HNCC difficult.

Initial studies seem to have been based upon chance discoveries. Early work by Chini *et al.* on the elements of the cobalt triad led to the discovery of useful but in general unsystematic routes (*196*). These methods, primarily concerned with redox–condensation reactions, have now been improved and extended to embrace the elements of adjacent triads. Similarly, pyrolytic syntheses, which were originally used to prepare osmium HNCC, have been shown to have a greater potential than initially anticipated and are now used to synthesize HNCC of other heavy metals. Recently, however, elegant work by Stone, Vahrenkamp, and others has shown that designed synthesis of clusters is possible (*118*, *458*, *471*, *472*). Use of the isolobal analogy in particular (*455*) has been most beneficial in devising routes for the preparation of many homo- and heteronuclear clusters. The synthetic strategies they have devised for small clusters have been applied with increasing frequency to the synthesis of HNCC.

Synthetic methods used for the preparation of HNCC may be classified in to two broad categories, depending on whether or not they involve the use of redox conditions; they are discussed below accordingly.

A. Syntheses Not Involving Redox Conditions

1. Pyrolytic or Photolytic Generation of Reactive Fragments

Pyrolysis reactions of mononuclear carbonyls and low-nuclearity cluster compounds have been used extensively in the syntheses of HNCC of osmium (*54*, *72*, *80*, *95*, *108*), ruthenium (*18*, *20*, *29*), and, more recently, rhenium (*2–4*). The reactions have been carried out either in inert solvents or, to facilitate the ejection of CO or other volatile ligands, in the solid state under vacuum. Condensation processes under pyrolytic conditions are rarely specific and, as such, lead to the formation of a wide range of products. In order to obtain optimum yields of a particular HNCC, the reaction conditions must be carefully screened. Solution reactions offer advantages such as the ability to monitor the progress of the reaction using IR spectroscopy. As they often give

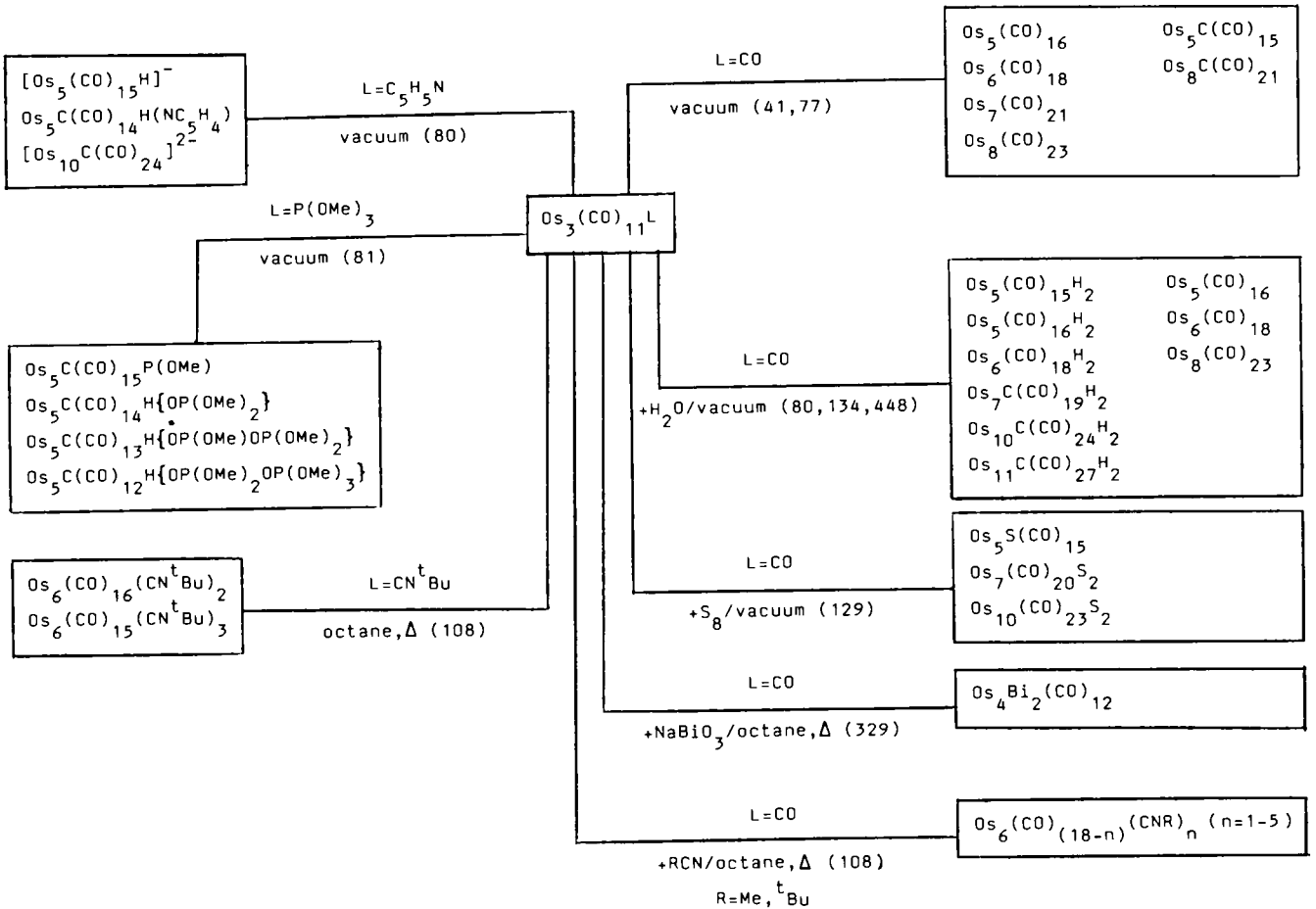
products or product distributions which differ from those under vacuum, both methods have been widely used.

A large number of HNCC of osmium have been produced from the vacuum pyrolysis of $Os_3(CO)_{12}$ and some of its derivatives (Scheme 1). The reaction of $Os_3(CO)_{12}$ has been shown to be extremely sensitive to temperature, time, and moisture, giving a series of products whose nuclearities range from 5 to 11 and possibly higher (*41*, *54*, *80*, *134*). By optimizing the conditions, yields up to 80% of $Os_6(CO)_{18}$ have been obtained (*41*). High specificity has also been observed in the vacuum pyrolysis of $Os_3(CO)_{11}(C_5H_5N)$, from which $[Os_{10}C(CO)_{245}]^{2-}$ has been obtained in 65% yield (*80*).

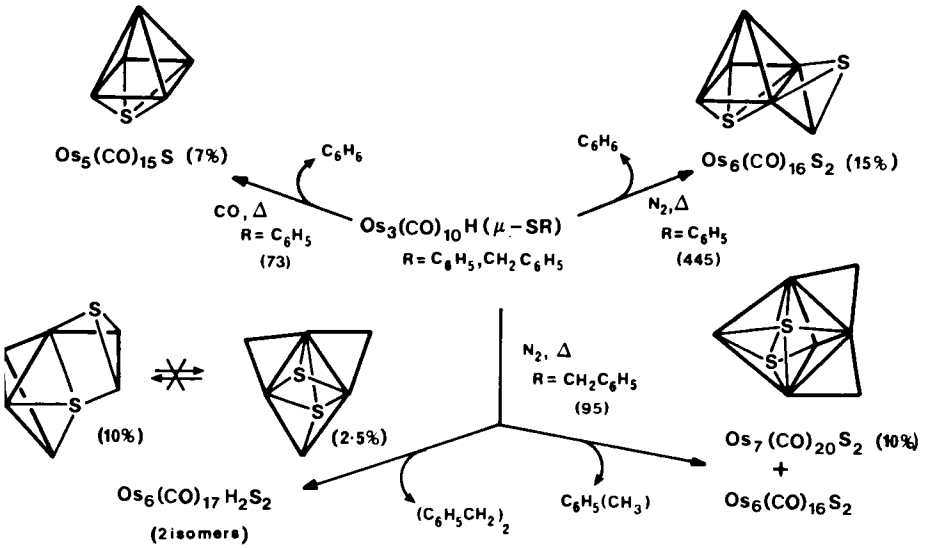
The HNCC of rhenium, $[Re_6C(CO)_{18}H_2]^{2-}$, $[Re_7C(CO)_{21}]^{3-}$, and $[Re_8C(CO)_{24}]^{2-}$, have been produced in high yields from the solution thermolysis of $[Re(CO)_4H_2]^-$ (*2–4*). In contrast, vacuum pyrolysis of $Re_2(CO)_{10}$ (182–300°C) has been shown to yield only rhenium metal (*41*), unless pyrolyzed in the presence of metallic indium, in which case $Re_4(CO)_{12}\{InRe(CO)_5\}_4$ was obtained in good yield (*279*).

The formation of carbido clusters under pyrolytic conditions is a common process. In a number of cases the carbon atom has been shown to be derived from a CO ligand, probably by disproportionation of CO to CO_2 and "C". In the case of the vacuum pyrolysis of $Ru_3(CO)_{12}$, from which $Ru_6C(CO)_{17}$ is formed in 65% yield, carbon dioxide was detected as a product of the reaction (*41*). Pyrolysis of the ^{13}CO-enriched species $Os_3(CO)_{11}(C_5H_5N)$ (*80*) and $[Re(CO)_4H_2]^-$ (*4*) as described above yields $[Os_{10}C(CO)_{24}]^{2-}$ and $[Re_8C(CO)_{24}]^{2-}$ with labeled carbide atoms and CO groups. The other possible sources of carbide atoms, the pyridine ligand in the osmium cluster and the *n*-tetradecane solvent used in the pyrolysis of $[Re(CO)_4H_2]^-$, can therefore be ruled out. This is in contrast with the pyrolysis of $Ru_5(CO)_{14}(CNBu^t)(\mu_5\text{-}CNBu^t)$ carried out in refluxing nonane, which yields the carbido cluster $Ru_6C(CO)_{16}(CNBu^t)$ (*46*). In this case the use of isotopically labeled $^{13}CNBu^t$ revealed that abstraction of a carbon atom from an isocyanide ligand had occurred. The fate of the NR portion of the fragmented isocyanide has not been established with any certainty.

Incorporation of other main group heteroatoms in pyrolysis products, as a consequence of the splitting of organic ligands under the reaction conditions, has also been observed. For example, the solution thermolysis of $Os_3(CO)_{10}H(\mu\text{-}SR)$ [R = C_6H_5 (*73*) and $CH_2C_6H_5$ (*445*)] (Scheme 2) results in the cleavage of a C—S bond in the thiolato ligands. For R = $CH_2C_6H_5$, the reaction was shown to occur by two competing processes: cleavage followed by elimination of toluene, and formation of sulfido clusters which do not contain hydrides, or homolysis of the C—S bond and formation of dibenzyl. The latter route yields two isomers of $Os_6(CO)_{17}H_2S_2$, which do not interconvert.



SCHEME 1. The pyrolysis reactions of $Os_3(CO)_{12}$ and some of its derivatives (see Table I for yields).

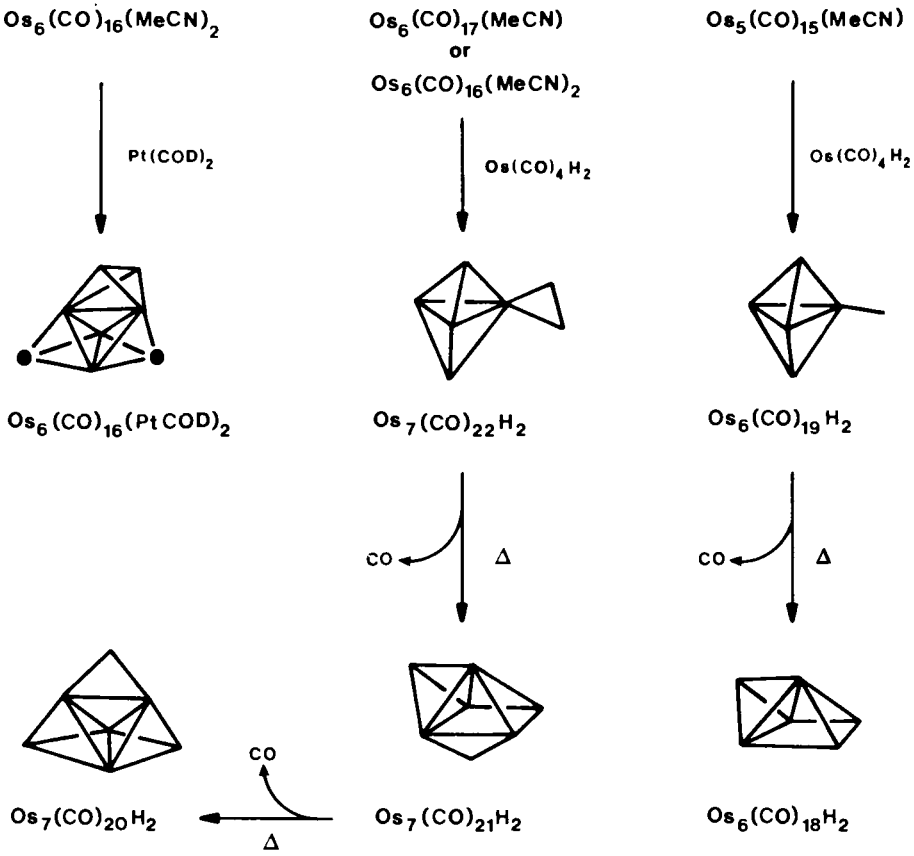


SCHEME 2. Pyrolysis reactions of $Os_3(CO)_{10}H(\mu\text{-SR})$ (R = C_6H_5 and $CH_2C_6H_5$).

2. *Chemical Activation of Carbonyl Clusters for Condensation under Pyrolytic Conditions*

The mechanism by which cluster expansion occurs in pyrolysis reactions is thought to involve formation of coordinatively unsaturated species by dissociation of ligands or cleavage of M—M bonds. These coordinatively unsaturated fragments are apparently the key intermediates that condense to give HNCC products (*456*). Major developments in HNCC synthesis have been achieved by using cluster precursors that contain a ligand such as acetonitrile, which is less strongly bound than CO. In this way milder conditions, which are less likely to lead to cluster fragmentation, can be employed.

Condensation of $Os_6(CO)_{16}(MeCN)_2$ with $Pt(COD)_2$ (COD = 1,2-cyclooctadiene), for example, has been found to yield $Os_6(CO)_{16}(PtCOD)_2$ (*332*). As shown in Scheme 3, this process is accompanied by a reorganization of the Os_6 polyhedron. Displacement of the MeCN ligands in $Os_6(CO)_{(18-n)}(MeCN)_n$ (n = 1, 2) has also been achieved by $Os(CO)_4H_2$ to give the heptanuclear hydrido clusters $Os_7(CO)_nH_2$ (n = 20, 21, and 22). The bicapped "bow tie" cluster $Os_7(CO)_{22}H_2$ loses CO under mild conditions to produce $Os_7(CO)_{21}H_2$ and $Os_7(CO)_{20}H_2$ with a sequential closing of the polyhedral framework (Scheme 3) (*119*). Similarly, substitution of the acetonitrile ligand in $Os_5(CO)_{15}(MeCN)$ by $Os(CO)_4H_2$ has



SCHEME 3. Synthesis of HNCC from $Os_6(CO)_{18-n}(MeCN)_n$ ($n = 1$, 2) and $Os_5(CO)_{15}(MeCN)$.

been performed successfully to give the spiked pentagonal-bipyramidal species $Os_6(CO)_{19}H_2$. This cluster also undergoes CO loss under mild conditions to give the capped square-based pyramidal cluster $Os_6(CO)_{18}H_2$ (*92*). The fortuitous condensation of two $Os_3(CO)_{10}(MeCN)_2$ clusters upon reaction with $PdCl_2$ has been reported to give the "raft" clusters $Os_6(CO)_{(21-n)}(MeCN)_n$ ($n = 0$, 1, 2) (*99*), while condensation of $Os_3(CO)_{10}(MeCN)_2$ with excess $HRe(CO)_5$ produces $Re_2Os_3H_2(CO)_{20}$ (*277*).

Sequential build-up of clusters, utilizing as coupling agents ligands that contain uncoordinated pairs of electrons, has been widely used by Vahrenkamp's group (*450*) and others in the synthesis of trinuclear and tetranuclear systems. This approach has been extended by Adams *et al.* to the synthesis of

sulfur-containing HNCC of osmium. The formation of $Os_6(CO)_{19}S$ (*114*), $Os_6(CO)_{17}S_2$ (*115*), $Os_7(CO)_{19}S$ (*120*), and $Os_7(CO)_{20}S_2$ (*121*) by condensation of $Os_3(CO)_{10}(MeCN)_2$ with trinuclear and tetranuclear μ_3-S-containing clusters is shown in Scheme 4. The mechanisms involved in these condensation reactions are not understood. An initial link has been suggested to occur via formation of a coordination bond between the sulfido atoms in the trinuclear and tetranuclear clusters and a metal atom in $Os_3(CO)_{10}(MeCN)_2$ upon displacement of an acetonitrile ligand. The sulfur atoms seem to play a key role not only in the initial linking to the acetonitrile clusters but also in preventing cluster breakdown during the reorganization of the hexanuclear compounds $Os_6(CO)_{17}S_2$ and $Os_6(CO)_{19}S$ upon loss of CO.

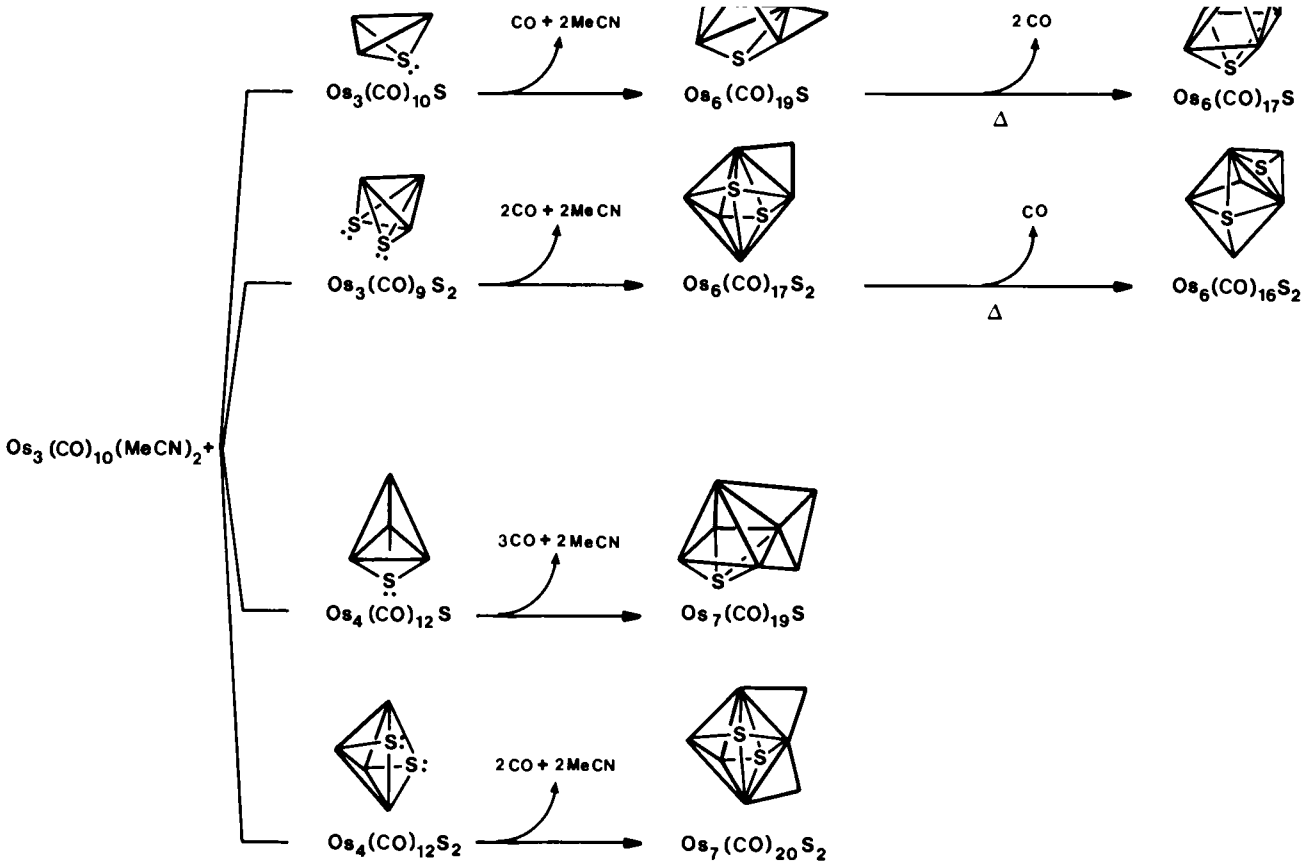
B. Syntheses Requiring Reducing or Oxidizing Conditions

1. Reduction of Mononuclear Carbonyl Complexes or Small Carbonyl Clusters

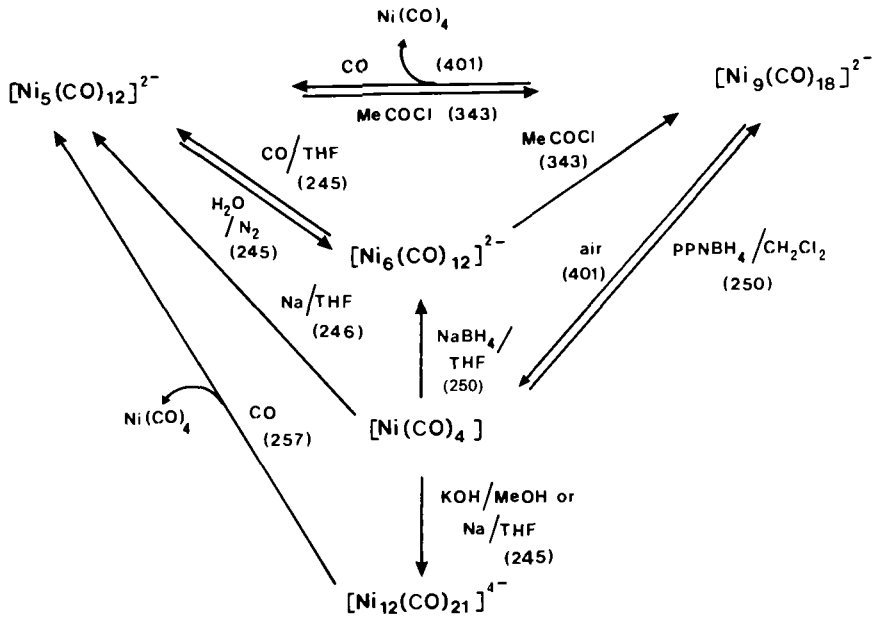
Synthesis of the great majority of HNCC of the cobalt and nickel subgroups involves the reduction of mononuclear carbonyls or small carbonyl clusters (*196*). In general, the reactive fragments for the condensation processes have been generated by the action of reducing agents such as alkali metals, alkali hydroxides, or carbonates. Soft nucleophiles such as halides, thiocyanate, and nitride, as well as phosphines and carbon monoxide, have also been used to this end. Alternatively, reactive fragments have been produced from the thermolysis reactions, particularly of small carbonyl cluster compounds, in coordinating high-boiling solvents.

a. Reactions Leading to Cluster Build-up. A range of HNCC of nickel has been prepared via the reduction of $Ni(CO)_4$ (*245, 250, 257, 401*). As shown in Scheme 5, the nuclearity of the products is critically dependent on the experimental conditions. For example, when alkali metals in tetrahydrofuran (THF) are used as reducing agent, $[Ni_5(CO)_{12}]^{2-}$ or $[Ni_{12}(CO)_{21}]^{4-}$ is produced. Alternatively, sodium borohydride yields $[Ni_6(CO)_{12}]^{2-}$ (68%) if the reaction is performed in tetrahydrofuran, but $[Ni_9(CO)_{18}]^{2-}$ (80%) if dichloromethane is used instead. Scheme 5 illustrates the lability of these clusters, which results in their facile interconversion under mild conditions.

Reduction of the carbonyls $M_4(CO)_{12}$ (M = Co, Rh, Ir) is the basis for the synthesis of many of the HNCC of the cobalt triad. Thus $Co_4(CO)_{12}$ is converted by the action of alkali metals in tetrahydrofuran to the hexanuclear dianion $[Co_6(CO)_{15}]^{2-}$. The dianion may be reduced further under these conditions to give $[Co_6(CO)_{14}]^{4-}$ (*142*). Reduction of $Ir_4(CO)_{12}$ under the



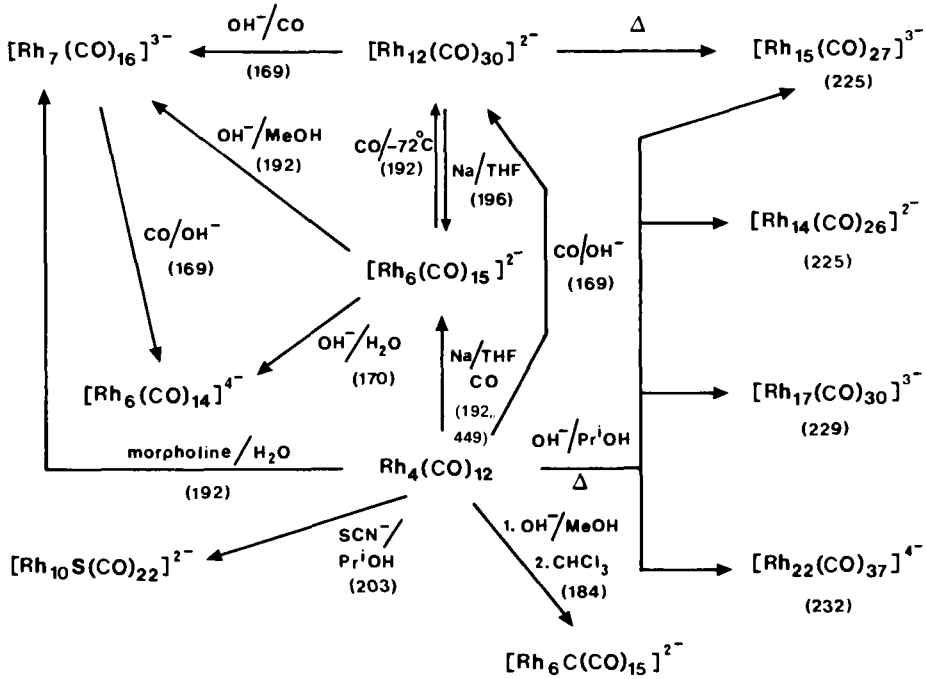
SCHEME 4. The formation of some Os_6 and Os_7 sulfur-containing clusters.



SCHEME 5. Synthesis of HNCC of nickel by reduction of $Ni(CO)_4$ and some redox interconversions between these clusters.

same conditions has also been shown to yield a hexanuclear dianion, $[Ir_6(CO)_{15}]^{2-}$ (*244*). In this case, however, the conversion has been shown to occur via the sequential formation of the octanuclear species $[Ir_8(CO)_{22}]^{2-}$ and $[Ir_8(CO)_{20}]^{2-}$. When the reduction of $Ir_4(CO)_{12}$ is carried out with potassium hydroxide in ethanol a mixture of brown anions possessing a high Ir/CO ratio is formed, whose components have not yet been characterized (*244*).

A large number of HNCC of rhodium have been produced from the reduction reactions of $Rh_4(CO)_{12}$ (Scheme 6). The reaction of this cluster with alkali hydroxides in isopropanol under thermolytic conditions has afforded binary carbonyl anions containing up to 22 rhodium atoms (*225*, *229*, *232*). The difficulties encountered in obtaining high yields of each product and in the separation process have led to the development of alternative synthetic routes to these clusters. Very selective, high-yield preparations of a series of rhodium HNCC have been achieved by high-pressure reduction of $Rh(CO)_2(acac)$ (acac, acetylacetone) with CO/H_2 mixtures in glyme solvents in the presence of bases (Scheme 7). In addition to the clusters previously prepared from the reduction of $Rh_4(CO)_{12}$, new species with encapsulated main-group atoms, $[Rh_9Y(CO)_{21}]^{2-}$



SCHEME 6. Synthesis of HNCC of rhodium by reduction of $Rh_4(CO)_{12}$ and some redox interconversions between these clusters.

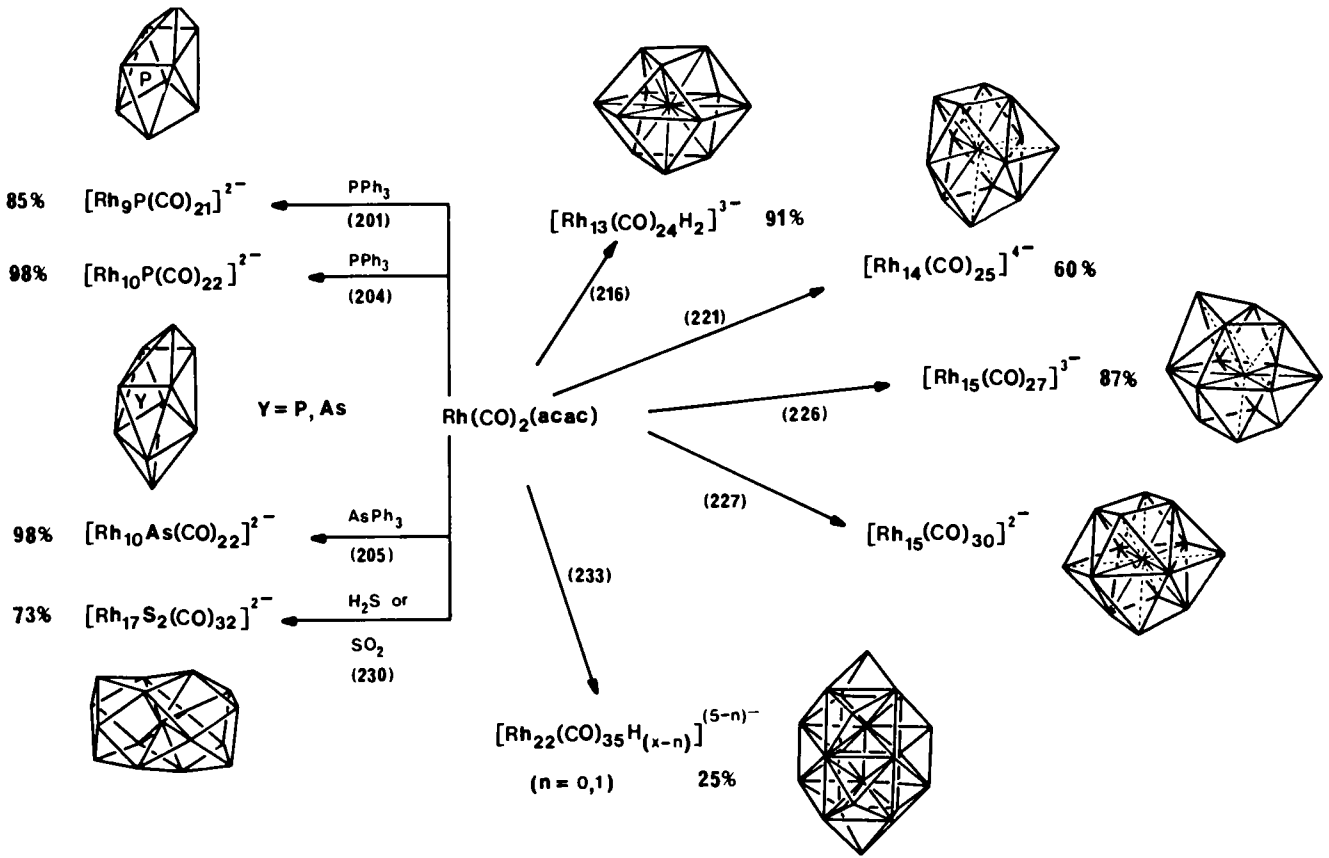
(*201*), $[Rh_{10}Y(CO)_{22}]^{3-}$ (*204*, *205*) $[Rh_{12}Sb(CO)_{27}]^{3-}$ (*370*), and $[Rh_{17}S_2(CO)_{32}]^{3-}$ (*230*) (Y = P, As) have been obtained when an external source of the heteroatom is added to the reaction mixture.

Halocarbons have been used successfully as a source of carbide atoms in the synthesis of carbido clusters of rhodium and nickel. For example, $[Rh_6C(CO)_{15}]^{2-}$ may be synthesized by the reduction of $Rh_4(CO)_{12}$ with alkali hydroxide in methanol followed by reaction with chloroform (*184*), or by the reaction of $[Rh(CO)_4]^-$ with CCl_4 according to Eq. (1).

$$6[Rh(CO)_4]^- + CCl_4 \xrightarrow[25°C]{Pr^iOH} [Rh_6C(CO)_{15}]^{2-} + 4Cl^- + 9CO \qquad (1)$$

In the latter case, the source of the carbide atom was established unequivocally by using $^{13}CCl_4$ in the reaction (*184*).

Carbide clusters of nickel have been obtained from the reaction of $[Ni_6(CO)_{18}]^{2-}$ with carbon tetrachloride, which yields $[Ni_9C(CO)_{17}]^{2-}$ (*252*) or $[Ni_{10}(C_2)(CO)_{16}]^{2-}$ (*254*), depending on the reaction conditions.



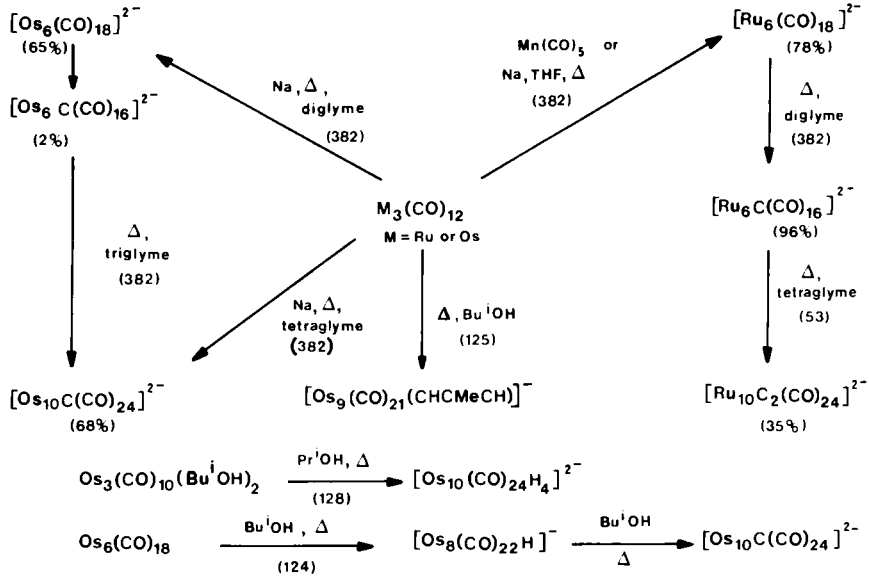
SCHEME 7. Synthesis of some HNCC of rhodium from $Rh(CO)_2(acac)$ (acac, acetylacetone).

The dicarbide is also formed if hexachloroethane is used as a source of carbide atoms (*254*).

The incorporation of a main group atom derived from the reducing agent itself has also been noted in a few cases. For example, reduction of $Rh_4(CO)_{12}$ with SCN^- in isopropanol has been found to give the sulfido cluster $[Rh_{10}S(CO)_{22}]^{2-}$ in high yield (*203*), while $[Ru_6N(CO)_{16}]^-$ was produced from the reduction of $Ru_3(CO)_{12}$ with N_3^- in refluxing tetrahydrofuran (*24*).

Reduction of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ with sodium in ether solvents at various reaction temperatures has been found to provide an effective route to HNCC of ruthenium and osmium (*382*). Although most of the dianions produced by this method had been isolated previously, the study of these reactions has allowed a better understanding of the build-up processes of these clusters.

As shown in Scheme 8 reduction of $M_3(CO)_{12}$ initially gives $[M_6(CO)_{18}]^{2-}$ (M = Ru, Os) in good yield (*382*). When heated in diglyme, $[Ru_6(CO)_{18}]^{2-}$ is quantitatively converted to the monocarbide $[Ru_6C(CO)_{16}]^{2-}$. Further thermolysis of this cluster in tetraglyme gives the dicarbide dianion $[Ru_{10}(C)_2(CO)_{24}]^{2-}$, whose structure has been shown to consist of two edge-sharing octahedra (*53*). In contrast, upon heating $[Os_6(CO)_{18}]^{2-}$ in triglyme, the anticipated carbido cluster $[Os_6C(CO)_{16}]^{2-}$ was only isolated in yields around 2% (*382*). Instead the reaction gave the tetracapped octahedral dianion $[Os_{10}C(CO)_{24}]^{2-}$ as the major product.



SCHEME 8. Synthesis of some HNCC of ruthenium and osmium under reducing conditions.

This suggests that $[Os_6C(CO)_{16}]^{2-}$ is probably generated as a reaction intermediate but under the reaction conditions it is converted to the thermodynamically more stable $[Os_{10}C(CO)_{24}]^{2-}$.

Prolonged thermolysis of $Os_3(CO)_{10}(OBu^i)_2$ in isobutanol has been found to produce a mixture of $[Os_{10}C(CO)_{24}]^{2-}$ and $[Os_{10}C(CO)_{24}H]^-$. However, when the reaction was carried out in isopropanol, the tetrahydrido dianion $[Os_{10}(CO)_{24}H_4]^{2-}$ was formed instead (*128*). The importance of the reaction temperature in the formation of the carbido species $[Os_{10}C(CO)_{24}]^{2-}$ is also evidenced by the thermolysis reactions of $Os_6(CO)_{18}$. When carried out in refluxing *n*-hexanol the only HNCC formed from the reaction is $[Os_{10}C(CO)_{24}H]^-$, while $[Os_8(CO)_{22}H]^-$ is produced in 30% yield when isobutanol is used (*124*).

Mixed-metal clusters have also been shown to undergo cluster build-up under reducing conditions. For instance, prolonged thermolysis of $[Rh_5Pt(CO)_{15}]^-$ in methanol in the presence of $NaHCO_3$ gives $[Rh_{11}Pt_2(CO)_{24}]^{3-}$ and $[Rh_{12}Pt(CO)_{24}]^{4-}$ (*368*). In the absence of base, $[Rh_9Pt_2(CO)_{22}]^{3-}$ is the major product of the reaction (*366*).

b. Syntheses Involving a Reduction in Cluster Nuclearity. The syntheses of HNCC under reducing conditions discussed above all result in cluster buildup. There are certain HNCC, however, which are best prepared by degradation of preformed clusters with nucleophiles such as CO, PR_3, or halides. The capped square-antiprismatic dianion $[Ni_9C(CO)_{17}]^{2-}$, for instance, is "decapped" by CO in tetrahydrofuran to give $[Ni_8C(CO)_{16}]^{2-}$ in 69% yield (*252*). Similarly, carbonylation of the octahedral species $Ru_6C(CO)_{17}$ and $[Ru_6N(CO)_{16}]^-$ is the method of choice for the preparation of the square-based pyramidal clusters $Ru_5C(CO)_{15}$ and $[Ru_5N(CO)_{14}]^-$, respectively (*24*, *25*). The synthesis of $Os_5(CO)_{19}$ is also achieved by carbonylation of $Os_6(CO)_{18}$. By using high-pressure infrared techniques to monitor the progress of the reaction, this cluster has been obtained in up to 80% yield (*56*).

2. *Redox Condensations*

The synthesis of HNCC by redox condensation involves the reaction of an anionic mononuclear or polynuclear carbonyl species with a neutral, cationic, or even anionic fragment.

a. Reactions of Carbonyl Metallates with Neutral Metal Complexes. Redox condensation reactions of mononuclear and cluster carbonyl metallates with neutral carbonyl compounds provide a selective synthetic route to homo- and heteronuclear HNCC anions. For example, reaction of

$[Rh(CO)_4]^-$ with the neutral cluster $Rh_4(CO)_{12}$ affords the trigonal-bipyramidal anion $[Rh_5(CO)_{15}]^-$ under mild conditions (*162*). Similarly, the octahedral species $[Fe_6C(CO)_{16}]^{2-}$ has been prepared by the condensation of $[Fe(CO)_4]^{2-}$ with stoichiometric amounts of $Fe(CO)_5$ under thermolytic conditions, which are necessary for the generation of the carbide atom [Eq. (2)] (*269*).

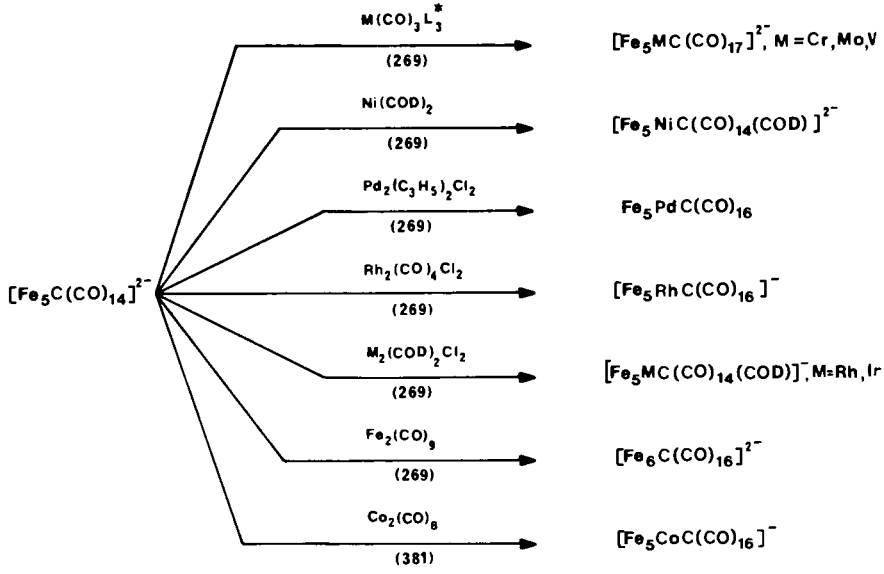
$$5Fe(CO)_5 + [Fe(CO)_4]^{2-} \xrightarrow[150-160°C]{\text{diglyme}} [Fe_6C(CO)_{16}]^{2-} \qquad (2)$$

Further examples of this synthetic technique are shown in Eqs. (3) (*363*) and (4) (*283*).

$$[Rh_6(CO)_{15}]^{2-} + Ni(CO)_4 \longrightarrow [Rh_6Ni(CO)_{16}]^{2-} + 3CO \qquad (3)$$

$$[Pt_3(CO)_6]^{2-} + 3Fe(CO)_5 \longrightarrow [Fe_3Pt_3(CO)_{15}]^{2-} + 6CO \qquad (4)$$

The condensation reactions of carbonyl metallates with neutral species, which are either coordinatively unsaturated or which will readily generate coordinatively unsaturated fragments, have also yielded a variety of mixed-metal clusters. The square-based pyramidal dianion $[Fe_5C(CO)_{14}]^{2-}$, for example, has been shown to react with a number of such species to yield octahedral Fe_5MC cluster compounds (Scheme 9) (*269*, *381*). In some cases,



*M=Cr, L=C_5H_5N; M=Mo, L=THF; M=W, L=MeCN.

SCHEME 9. Some reactions of $[Fe_5C(CO)_{14}]^{2-}$ with unsaturated metal fragments.

the unsaturation is achieved by the displacement of halides in halogenated metal complexes. Reaction of the dimer $Rh_2(CO)_2Cl_2$ with $[Fe(CO)_4H]^-$ affords $[FeRh_4(CO)_{15}]^{2-}$, $[FeRh_5(CO)_{16}]^-$, or $[Fe_2Rh_4(CO)_{16}]^{2-}$, depending on the reaction conditions employed (*281*). Interestingly, both hexanuclear clusters were found to be isostructural with the octahedral $Rh_6(CO)_{16}$ species, while $[FeRh_4(CO)_{15}]^{2-}$ possesses a different carbonyl distribution to that found for $[Rh_5(CO)_{15}]^-$ both in solution and in the solid state (*281*).

The chloromethynyl derivative $Co_3(CO)_9CCl$ has been used as a source of "$Co_3(CO)_9C$" fragments for the synthesis of large cobalt and mixed-metal carbido clusters. The chlorine atom in this species has been found to be easily displaced by mononuclear and cluster carbonyl metallates. Reaction of $Co_3(CO)_9CCl$ with $[Co(CO)_4]^-$ yields $[Co_6C(CO)_{15}]^{2-}$ (*145*), while $[Co_3Ni_9C(CO)_{20}]^{3-}$ is one of the products from the reaction of $Co_3(CO)_9CCl$ with $[Ni_6(CO)_{12}]^{2-}$ (*344*). The monocarbido cluster $[Co_3Ni_9C(CO)_{20}]^{3-}$ reacts further with $Co_3(CO)_9CCl$ to yield $[Co_6Ni_2(C)_2(CO)_{16}]^{2-}$, according to Eq. (5) (*357*).

$$2[Co_3Ni_9C(CO)_{20}]^{3-} + 4Co_3(CO)_9CCl \longrightarrow 3[Co_6Ni_2(C)_2(CO)_{16}]^{2-} + 2NiCl_2 + 7Ni(CO)_4 + 3Ni \quad (5)$$

Even simple metal halides have been used as sources of metal atoms for the condensation reactions of carbonyl metallates [e.g., Eq. (6)] (*379*).

$$3[Fe(CO)_4]^{2-} + 3CuBr \longrightarrow [Fe_3Cu_3(CO)_{12}]^{3-} + 3Br^- \quad (6)$$

Another example of this synthetic method is the reaction of $[Ni_6(CO)_{12}]^{2-}$ with $PtCl_2$ in acetonitrile, which yields $[Ni_{38}Pt_6(CO)_{48}H_2]^{4-}$, the largest metal carbonyl cluster characterized to date (*373*).

Clusters of the heavier elements undergo coupling reactions with salts of Ag(I), Au(I), Hg(I), Hg(II), and Tl(III), in which the basic metal cluster geometry is preserved. Even in these cases it is difficult to predict the nuclearity of the mixed species formed. These reactions may result in the simple coupling of two cluster units, as in the formation of $[\{Ru_6C(CO)_{16}\}_2Tl]^-$ (Fig. 1a) shown in Eq. (7) (*320*).

$$2[Ru_6C(CO)_{16}]^{2-} + Tl(NO_3)_3 \longrightarrow [\{Ru_6C(CO)_{16}\}_2Tl]^- + 3NO_3^- \quad (7)$$

Dissociation of CO ligands may occur concomitantly with the condensation process as examplified by the formation of $\{RuCo_3(CO)_9\}_2Hg$ (Fig. 1b) from the reaction shown in Eq. (8) (*453*).

$$2[RuCo_3(CO)_{12}]^- + HgBr_2 \longrightarrow \{RuCo_3(CO)_9\}_2Hg + 6CO + 2Br^- \quad (8)$$

The formation of the dianions $[Os_{20}(C)_2(CO)_{48}M]^{2-}$ (M = Au and Hg) (Fig. 1c) from the reactions of $[Os_{10}C(CO)_{24}]^{2-}$ with $Au(PPh_3)Br$ in the

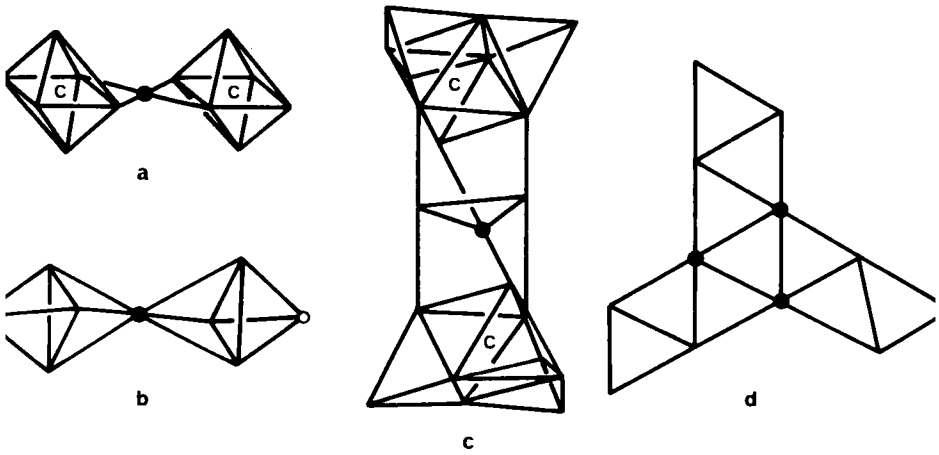


FIG. 1. Metal core geometry of (a) $[\{Ru_6C(CO)_{16}\}_2Tl]^-$, (b) $\{RuCo_3(CO)_9\}_2Hg$, (c) $[Os_{20}M(C)_2(CO)_{48}]^{2-}$ (M = Au, Hg), and (d) $Os_9Hg_3(CO)_{33}$.

presence of $AgClO_4$ and RHgY (R = C_6F_5, C_6H_5, Cl, CF_3COO; Y = CF_3COO or Cl), respectively, has been shown to occur via the formation of the intermediates $[Os_{10}C(CO)_{24}(AuBr)]^-$ and $[Os_{10}C(CO)_{24}(HgR)]^-$, which undergo ligand disproportionation and condensation on standing in solution (*338*).

Condensation of more than two metal clusters has been found to occur in some cases. For example, $[Os_3(CO)_{11}H]^-$ reacts with $HgBr_2$ to yield the "raft" $Os_9Hg_3(CO)_{33}$ (Fig. 1d) (*336*). Reaction of the trigonal-prismatic dianion $[Rh_6C(CO)_{15}]^{2-}$ with $AgBF_4$ yields a series of oligomers containing Rh_6 prismatic units bridged by Ag(I) atoms. The nature of these species was found to be critically dependent upon the ratio Ag(I): $[Rh_6C(CO)_{15}]^{2-}$. The condensation process was studied by monitoring the ^{13}C and $^{13}C\{^{103}Rh\}$ NMR spectra of both $[Rh_6C(^{13}CO)_{15}]^{2-}$ and $[Rh_6{}^{13}C(CO)_{15}]^{2-}$ after sequential addition of $AgBF_4$, and is summarized in Fig. 2 (*369*).

b. Reactions of Anionic Carbonyl Clusters with Cationic Mononuclear Complexes. A number of heterometallic HNCC have been synthesized by the condensation reactions of anionic carbonyl clusters with the cationic fragments $[M(MeCN)]^+$ and $[M(PR_3)]^+$, generated from $[M(MeCN)_4][Y]$ (M = Cu, Ag, Y = BF_4, PF_6) and $M(PR_3)X$ (M = Cu, Ag, Au; X = Cl, Br, I; R = alkyl or aryl), respectively. While formation of the coordinatively unsaturated fragments $[M(MeCN)]^+$ occurs readily in solution, the $[M(PR_3)]^+$ species have either been prepared with silver salts or, in the case of the chloride complexes, generated *in situ* by reaction with $TlPF_6$.

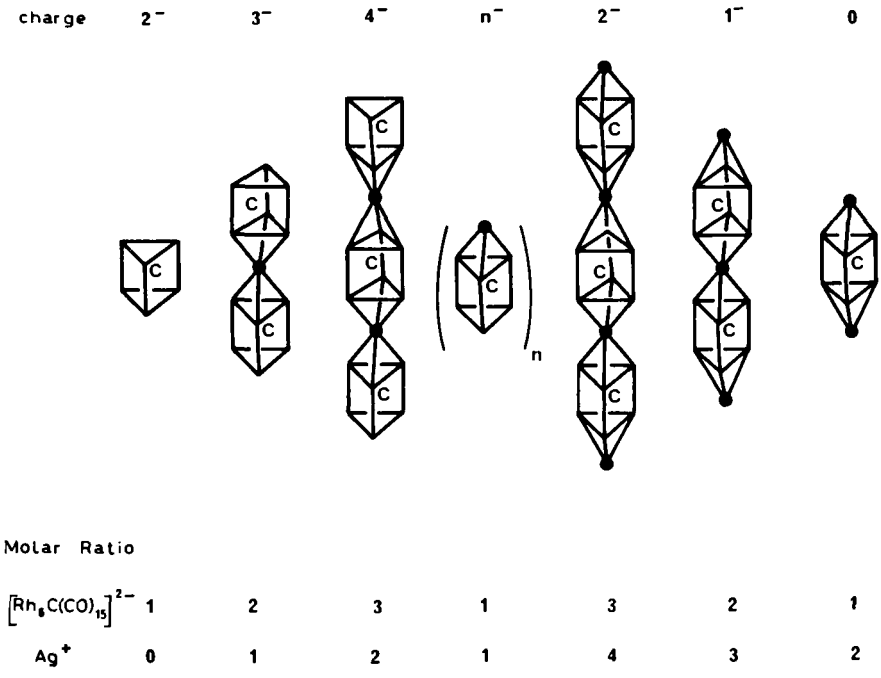
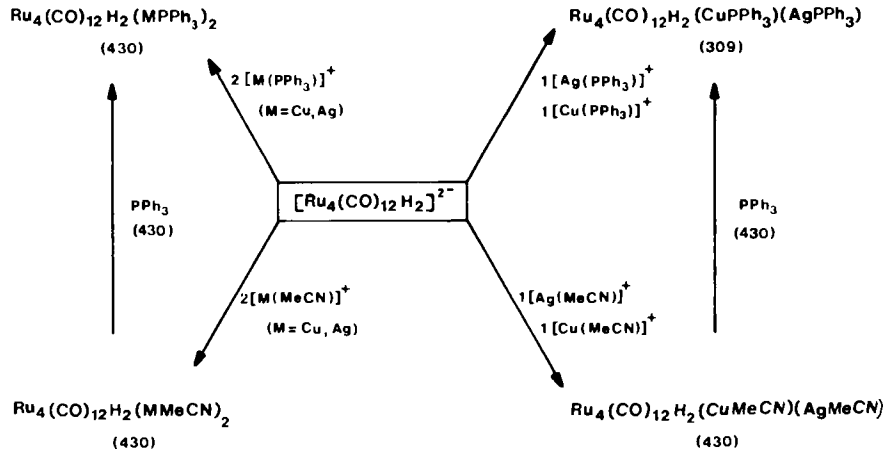


FIG. 2. $[Rh_6C(CO)_{15}]^{2-}/Ag^+$ adducts formed on progressive addition of $AgBF_4$ (*369*).

The condensation reactions of the dianion $[Ru_4(CO)_{12}H_2]^{2-}$ with $[M(MeCN)]^+$ and $[M(PPh_3)]^+$ (M = Cu and Ag) are shown in Scheme 10 and demonstrate the flexibility of this synthetic method (*309*, *430*). The number of metal fragments incorporated in the anionic clusters can often be controlled by using stoichiometric amounts of the metal cations. In the case of the dianion $[Os_{10}C(CO)_{24}]^{2-}$, however, only $[Os_{10}C(CO)_{24}(AuPPh_3)]^-$ is formed, even in the presence of excess $[Au(PPh_3)]^+$ (*337*). In contrast, both the mono- and dicopper species $[Os_{10}C(CO)_{24}(CuMeCN)]^-$ and $Os_{10}C(CO)_{24}(CuMeCN)_2$ are produced from the reaction of the dianion with $[Cu(MeCN)_4]^+$ (*337*). In fact, $[Au(PR_3)]^+$ and $[Cu(MeCN)]^+$ have often been found to bind differently to the same HNCC due to their different electronic and steric requirements (*451*). Examples are $Ru_6C(CO)_{16}(AuPMePh_2)_2$ (*272*) and $Ru_6C(CO)_{16}(CuMeCN)_2$ (*316*), whose structures are shown in Fig. 3. More surprising perhaps is the difference in the bonding modes of the $AuPR_3$ groups in the series of closely related compounds $M_5C(CO)_{14}(AuPR_3)_2$ (M = Fe, (*293*) Ru (*473*), Os (*78*)] (Fig. 4).

According to electron counting rules, the electrophilic addition of $[M(MeCN)]^+$ and $[M(PPh_3)]^+$ fragments to anionic carbonyl clusters



SCHEME 10. Condensation reactions of $[Ru_4(CO)_{12}H_2]^{2-}$ with $[M(MeCN)]^+$ and $[M(PPh_3)]^+$ (M = Cu, Ag).

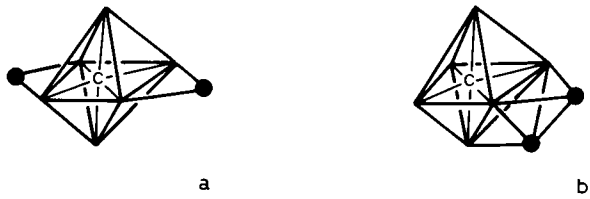


FIG. 3. Metal core geometry of (a) $Ru_6C(CO)_{16}(AuPMePh_2)_2$ and (b) $Ru_6C(CO)_{16}(CuMeCN)_2$.

FIG. 4. Metal core geometry of (a) $M_5C(CO)_{14}(AuPEt_3)_2$ (M = Fe, Ru) and (b) $Os_5C(CO)_{14}(AuPR_3)_2$ (R = Et, Ph).

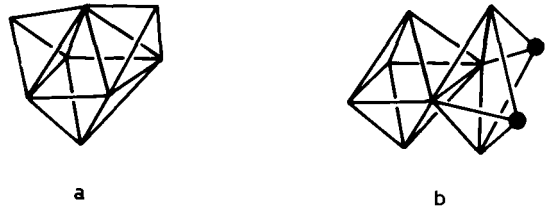


FIG. 5. Metal arrangements in (a) $[Os_8(CO)_{22}]^{2-}$ and (b) $Os_8(CO)_{22}(AuPPh_3)_2$.

should not lead to any metal polyhedral changes as these species donate no electrons to the cluster. Clearly, these rules do not always hold true for HNCC. The addition of $[Au(PPh_3)]^+$ to $[Os_8(CO)_{22}]^{2-}$ gives $Os_8(CO)_{22}(AuPPh_3)_2$, which exhibits an Os_8 polyhedral geometry different from that of the dianion (*339*) (Fig. 5).

The reagent $[(R_3PAu)_3O][BF_4]$ has also been used for the synthesis of clusters containing "$AuPR_3$" fragments, e.g. (*452*),

$$[H_3Ru_4(CO)_{12}]^- + [(Ph_3PAu)_3O]^+ \longrightarrow$$
$$H_3Ru_4(CO)_{12}AuPPh_3 + H_2Ru_4(CO)_{12}(AuPPh_3)_2 + HRu_4(CO)_{12}(AuPPh_3)_3 \quad (9)$$

In this case, however, the reaction does not always involve a simple addition of the gold moiety; often a carbonyl ligand is replaced by two or three $AuPR_3$ fragments [e.g., Eq. (10)] (*299*).

$$[Ru_3Co(CO)_{13}]^- + [(Ph_3PAu)_3O]^+ \longrightarrow Ru_3(CO)_{12}(AuPPh_3)_3 \quad (10)$$

A few homometallic HNCC have also been produced by the condensation reactions of anionic carbonyl clusters with cationic complexes. For instance, sequential buildup of rhodium HNCC via incorporation of "$Rh(CO)_2$" fragments has been achieved by reacting $[Rh(CO)_2(MeCN)_2]^+$ in acetonitrile with a series of anionic rhodium clusters as illustrated by the reactions shown in Eqs. (11) and (12) (*223*).

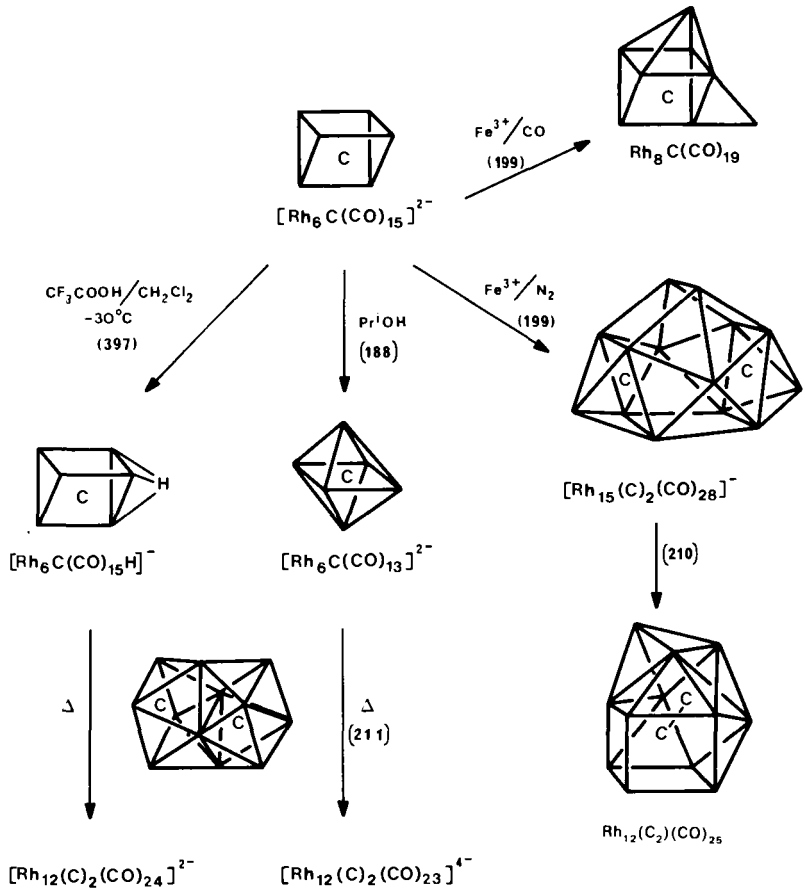
$$[Rh(CO)_2(MeCN)_2]^+ + [Rh_{13}(CO)_{24}H]^{4-} \longrightarrow [Rh_{14}(CO)_{25}H]^{3-} \quad (11)$$
$$[Rh(CO)_2(MeCN)_2]^+ + [Rh_{14}(CO)_{25}]^{4-} \longrightarrow [Rh_{15}(CO)_{27}]^{3-} \quad (12)$$

In spite of the relatively mild reaction conditions employed, further condensation of unstable products has been shown to occur. For example, reaction of $[Rh_6C(CO)_{15}]^{2-}$ with $[Rh(CO)_2(MeCN)_2]^+$ yields $[Rh_{14}(C)_2(CO)_{23}]^{2-}$ rather than the anticipated Rh_7C cluster (*224*). This contrasts with the condensation reaction of $[Rh_6(CO)_{15}]^{2-}$ with the same rhodium complex, which yields $[Rh_7(CO)_{16}]^{3-}$ (*170*).

3. *Oxidation of Carbonyl Clusters*

Only a relatively small number of HNCC have been synthesized by oxidation of other carbonyl clusters.

a. Oxidation Reactions Resulting in Expansion of Cluster Size. The oxidation reactions of anionic HNCC of rhodium have often been found to result in cluster expansion. For instance, reaction of $[Rh_6C(CO)_{15}]^{2-}$ with ferric ammonium alum gives $Rh_8C(CO)_{19}$, $[Rh_{15}(C)_2(CO)_{28}]^-$, or $Rh_{12}(C_2)(CO)_{25}$, depending on the reaction conditions, while oxidation of $[Rh_6C(CO)_{15}]^{2-}$ with sulfuric acid gives $[Rh_{12}(C)_2(CO)_{24}]^{2-}$ (*211*) (Scheme 11).



SCHEME 11. Synthesis of large carbido clusters of rhodium from $[Rh_6C(CO)_{15}]^{2-}$.

Oxidative aggregation of two Rh_6 clusters was also observed in the reaction of $[Rh_6(CO)_{15}]^{2-}$ with acids giving $[Rh_{12}(CO)_{30}]^{2-}$. It was established by variable-temperature multinuclear NMR studies that the protonation of both $[Rh_6(CO)_{15}]^{2-}$ and $[Rh_6C(CO)_{15}]^{2-}$ proceeds first with formation of the intermediate species $[Rh_6(CO)_{15}H]^-$ and $[Rh_6C(CO)_{15}H]^-$, which were fully characterized at low temperatures. Warming the solution was shown to result in the loss of hydrogen and formation of $[Rh_{12}(CO)_{30}]^{2-}$ and $[Rh_{12}(C)_2(CO)_{24}]^{2-}$, respectively (*397*). It is interesting to note that the reaction of the hexacobalt dianion $[Co_6(CO)_{15}]^{2-}$ with acids does not lead to an increase in nuclearity following formation of $[Co_6(CO)_{15}H]^-$ (*144*), and the large carbido clusters $[Co_{11}(C_2)(CO)_{22}]^{3-}$ and $[Co_{13}(C)_2(CO)_{24}]^{4-}$ have only been produced by the thermolysis of $[Co_6C(CO)_{15}]^{2-}$ in diglyme (*158*, *159*).

The reaction of $[Rh_7(CO)_{16}]^{3-}$ with trifluorosulfonic acid also results in selective oxidative coupling of two Rh_7 clusters to give $[Rh_{14}(CO)_{26}]^{2-}$. Even though neither of the protonated species $[Rh_7(CO)_{16}H_{(3-x)}]^{x-}$ ($x = 1$, 2) were detected by ^1H NMR spectroscopy over a range of temperatures during the course of the reaction (*216*), the reaction probably follows a similar pathway to that of the hexanuclear dianions.

Oxidative aggregation is not restricted to rhodium HNCC. The dianions $[Ni_{12}(CO)_{21}H_{(4-x)}]^{x-}$ ($x = 2$, 3), for example, have been produced from the reaction of $[Ni_6(CO)_{18}]^{2-}$ with acids (*257*). In this case it was established by IR and ^1H NMR spectroscopy that the condensation processes occur through the sequence of reactions given by Eqs. (13)–(15).

$$3[Ni_6(CO)_{12}]^{2-} + 2H^+ \longrightarrow 2[Ni_9(CO)_{18}]^{2-} + H_2 \tag{13}$$

$$2[Ni_9(CO)_{18}]^{2-} + H^+ \longrightarrow [Ni_{12}(CO)_{21}H]^{3-} + 3Ni(CO)_4 + 3Ni + 3CO \tag{14}$$

$$[Ni_{12}(CO)_{21}H]^{3-} + H^+ \rightleftharpoons [Ni_{12}(CO)_{21}H_2]^{2-} \tag{15}$$

Interestingly, the only example of oxidative cluster aggregation in the iron triad is the formation of $[Ru_6(CO)_{18}H]^-$ in the reaction of $[Ru_3(CO)_{11}H]^-$ with mineral acids (*31*).

b. Selective Oxidative Degradation. The oxidation reactions of a number of large carbide clusters have been found to provide relatively selective synthetic routes to clusters of reduced nuclearity. For example, polyhedral contraction of the octahedral species $[Fe_5MC(CO)_x]^{y-}$ to the square-based pyramidal clusters $[Fe_4MC(CO)_z]^{w-}$ has been achieved selectively with

ferric chloride as shown in Eqs. (16)–(20) (*269*).

$$[Fe_5CrC(CO)_{17}]^{2-} \xrightarrow{FeCl_3} Fe_4CrC(CO)_{16} \quad (16)$$

$$[Fe_5MoC(CO)_{17}]^{2-} \xrightarrow{FeCl_3} Fe_4MoC(CO)_{16} \quad (17)$$

$$[Fe_5WC(CO)_{17}]^{2-} \xrightarrow{FeCl_3} Fe_4WC(CO)_{16} \quad (18)$$

$$[Fe_5RhC(CO)_{16}]^{2-} \xrightarrow{FeCl_3} [Fe_4RhC(CO)_{14}]^{-} \quad (19)$$

$$[Fe_6C(CO)_{16}]^{2-} \xrightarrow{FeCl_3} Fe_5C(CO)_{15} \quad (20)$$

Similarly, the octahedral cluster $[Re_6C(CO)_{19}]^{2-}$ has been synthesized by the oxidation of $[Re_7C(CO)_{21}]^{3-}$ with iodine, which leads to abstration of the capping rhenium unit (*376*).

III. Reactions of High-Nuclearity Carbonyl Clusters

In attempting to rationalize the reactivity of HNCC one faces an extremely complex problem. Compared with the boranes, which have been the subject of detailed electron-density calculations, our knowledge of the electronic properties of HNCC is still insufficient for correlations with reactivity patterns and prediction of the nature and structure of the products.

A full understanding of HNCC reactivity is hampered by several factors. First, HNCC exhibit a large number of polyhedral shapes, and within each given structure transition metals are found with coordination numbers ranging from five to nine and on occasion even more. It is therefore difficult to be sure of the site of attack of a substrate, whether it is a nucleophile or an electrophile. There is some evidence to suggest that nucleophilic attack occurs at sites of lowest coordination number, but this has not been established with certainty outside a few systems (*387*, *388*). It has also been suggested that electrophilic attack occurs at sites of high electron density, viz, M—M bonds (*408*). The problem then is that of understanding the precise nature of the M—M bond in a metal cluster. To be more precise, one cannot overemphasize that polyhedral edges do not necessarily correspond to chemical bonds. Secondly, it is often difficult to predict the nature of the products formed. A number of pathways are always available for these reactions, and, depending on the type of metal and on the cluster nuclearity, the course of the reaction may vary considerably. This is complicated by the fact that in various reactions a large number of products are formed. In many

instances it is clear that cluster degradation followed by recombination of the fragments occurs during the course of the reaction, leading to the formation of both lower and higher nuclearity compounds. This is particularly the case for HNCC of cobalt, nickel, iron, and rhodium. For clusters of the heavier metals, which normally require vigorous conditions to induce chemical reactivity, subsequent transformation of the products is often a problem. Thirdly, HNCC have a tendency to undergo polyhedral rearrangements. These often result from the addition of electron density to or its removal from the cluster as charge or as ligand. However, even more subtle changes resulting, for example, from the substitution of carbonyls by related ligands with different electronic and steric properties have been found to lead to changes in geometry.

For all these reasons it is difficult to suggest mechanisms for reactions of HNCC on the basis of product distribution and structure. These problems cannot be resolved readily. At present there is a paucity of kinetic data available and it may be that because of the complexity of these reactions such data will not be forthcoming. Nevertheless this is clearly an area where further studies are necessary.

Because of the difficulties discussed above, our classification of the reactions of HNCC is based on the products obtained from those reactions. They are discussed in six separate sections: A. Oxidation Reactions, B. Protonation and Deprotonation Reactions, C. Reduction Reactions, D. Electron-Transfer Reactions and Electrochemical Studies, E. Reactions with Soft Nucleophiles, and F. Oxidative Addition of the Small Molecules H_2, I_2, and HX.

A. Oxidation Reactions

Oxidation of HNCC often results in cluster fragmentation or, as a consequence of redox condensation, cluster expansion as discussed in Section II,B,3. The systematic formation of oxidized species of unchanged nuclearity has been investigated only recently. Depending on the reagent, the products of oxidation reactions may or may not incorporate the oxidant and these reactions are classified below accordingly.

1. Oxidation of HNCC Anions without Incorporation of the Oxidant

Simple two-electron oxidation of anionic HNCC has been shown to proceed with or without concomitant addition of CO. For example, while oxidation of $[Os_5(CO)_{15}]^{2-}$ with $FeCl_3$ under CO gives $Os_5(CO)_{16}$ (*383*), $Os_6(CO)_{18}$ is the product of the oxidation of $[Os_6(CO)_{18}]^{2-}$ under the same

reaction conditions (*383*). In the first case the cluster electron count is not altered in the process and the accommodation of an extra CO ligand results in only a slight distortion of the metal polyhedron in the dianion in comparison to the neutral species. Oxidation of the $[Os_6(CO)_{18}]^{2-}$ dianion though brings about reorganization of the metal polyhedron from an octahedral to a bicapped tetrahedral geometry. Cluster rearrangement is also observed in the oxidation of the 90-electron trigonal-prismatic $[Co_6C(CO)_{15}]^{2-}$ to give the 87-electron octahedral monoanion $[Co_6C(CO)_{14}]^{-}$ [Eq. (21)] (*145*, *147*).

$$[Co_6C(CO)_{15}]^{2-} + FeCl_3 \longrightarrow [Co_6C(CO)_{14}]^{-} + FeCl_2 + Cl^{-} + CO \quad (21)$$

As oxidation reactions may often be complicated by further attack on the product by the oxidant, the choice of both oxidant and reaction conditions is critical. Ferric chloride under CO is the oxidant of choice, but even this sometimes causes cluster breakdown or buildup (see Section II,B.3). Mercuric salts have been used in the oxidation of $[Co_6(CO)_{14}]^{4-}$ and $[Co_6(CO)_{15}]^{2-}$ to give $Co_6(CO)_{16}$ (*138*, *389*), but condensation of two cluster species incorporating atomic Hg may occur, as in the oxidation of $[Os_{10}C(CO)_{24}]^{2-}$ to $[Os_{20}Hg(C)_2(CO)_{48}]^{2-}$ (*338*). Iodine has been used successfully in a few cases, for example in the one-electron oxidation of $[Fe_3Pt_3(CO)_{15}]^{2-}$ to the monoanion $[Fe_3Pt_3(CO)_{15}]^{-}$ (*283*), as well as in the two-electron oxidation of $[Os_6(CO)_{18}]^{2-}$ to $Os_6(CO)_{18}$ (*88*). As discussed in Section III,A,2, however, the use of iodine as oxidant often results in the addition of I^+ to the anionic cluster.

Oxidation via intermediate formation of hydrido species has been achieved but only with clusters of the cobalt triad. At least two isomers of $Ir_6(CO)_{16}$ (*235*) have been isolated from the oxidation of $[Ir_6(CO)_{15}]^{2-}$ by varying the conditions employed, [Eqs. (22) (*235*) and (23) (*236*)].

$$[Ir_6(CO)_{15}]^{2-} + MeCOOH + CO \xrightarrow{CH_2Cl_2} Ir_6(CO)_{16}\,(black) \quad (22)$$

$$[Ir_6(CO)_{15}]^{2-} + CO \xrightarrow{MeCOOH} Ir_6(CO)_{16}\,(red) \quad (23)$$

Both isomers have an octahedral arrangement of metal atoms but with different CO distributions: the four COs that are not terminally bound in these species are edge-bridging in the black isomer but face-capping in the red one.

The nature of the oxidation products of $[Rh_6(CO)_{14}]^{4-}$ with acids shows a greater dependence on the H^+ to tetraanion ratio and on the strength of the acid. *p*-Toluenesulfonic acid in a 1 to 2 ratio with respect to $[Rh_6(CO)_{14}]^{4-}$ in acetonitrile gives $[Rh_6(CO)_{15}]^{2-}$, while an excess of the acid results in the formation of $Rh_6(CO)_{16}$; the use of an excess of the weaker acetic acid,

however, gives mainly $[Rh_{12}(CO)_{30}]^{2-}$ (*170*). This illustrates the extremely sensitive balance between formation of M—M and M—CO bonds as well as the kinetic dependence of the oxidation reactions.

2. *Addition of I^+ and NO^+ to Anionic HNCC*

The reactions of anionic HNCC with I_2 and $NOBF_4$ resulting in the oxidative addition of I^+ and NO^+, respectively, have been studied in only a few systems. Even so it is becoming increasingly possible to see a pattern emerging in these processes. Because of a lack of kinetic data for these reactions, only a simplified discussion based on their final products is possible.

The nature of the products may well depend on the site of attack of the electrophile, among other factors. The metal atoms in HNCC are effectively shielded by a close-packed CO ligand envelope (*384*), which renders direct attack upon them difficult; however, oxygen atoms in compounds containing bridging COs provide electron-rich sites for attack. Kinetic studies have suggested that the formation of transition adducts of the type μ-{COE} takes place during the initial stages of the reaction of a number of polynuclear metal carbonyl derivatives and halogens (*437*).

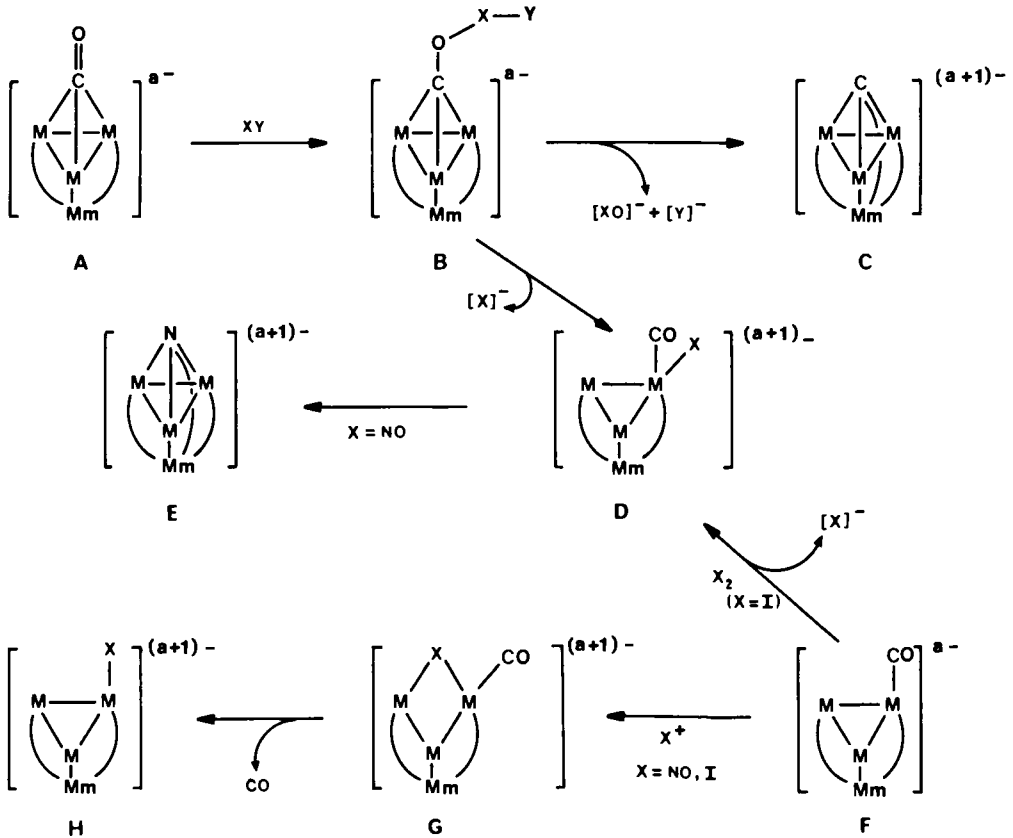
This site of attack has also been postulated in the reaction of $[Co_6(CO)_{15}]^{2-}$ with acetyl chloride [Eq. (24)] (*390*).

$$3[Co_6(CO)_{15}]^{2-} + 2MeCOCl \xrightarrow{CO} 2[Co_6C(CO)_{14}]^- + 4[Co(CO)_4]^- + 2Co^{2+} + 2Cl^- + 2MeCOO^- \quad (24)$$

Addition of the acylium ion is believed to give $[Co_6(CO)_{14}\{CO—C(=O)—Me\}]^-$ as an intermediate (Scheme 12,B). There is a precedent for such a ligand: In $Fe_3(CO)_{10}\{\mu_2$-$CO—C(=O)—Me\}]^-$ (*438*), the acyl group is indeed attached to the oxygen atom of a bridging CO. Upon scission of this CO, the carbido cluster $[Co_6C(CO)_{14}]^-$ (Scheme 12,C) is formed and acetate is liberated. The site of I_2 attack in the reaction with $[Rh_6(CO)_{15}]^{2-}$ might also be at an oxygen of a bridging CO. Loss of I^- and formation of $[Rh_6(CO)_{15}I]^-$ with a terminally bound iodine atom (Scheme 12,D) occur in this case [Eq. (25)] (*173*).

$$[Rh_6(CO)_{15}]^{2-} + I_2 \longrightarrow [Rh_6(CO)_{15}I]^- + I^- \quad (25)$$

The formation of the nitrido cluster $[Co_6N(CO)_{15}]^-$ (Scheme 12,E) from the reaction of $[Co_6(CO)_{15}]^{2-}$ and NO^+ (*152*) may similarly involve initial formation of $[Co_6(CO)_{15}(NO)]^-$ related to $[Rh_6(CO)_{15}I]^-$, followed by reduction of the coordinated NO to nitrogen by the cluster or by CO.



SCHEME 12. Pathways for the reactions of electrophiles with anionic HNCC (see text).

For anionic HNCC that do not contain bridging COs, as is often the case with compounds of osmium and ruthenium (Scheme 12,F), one could envisage the negatively charged oxygen layer orientating the attacking molecule XY for the tunneling process through the CO barrier (*439*). Dissociation of Y^- and attack of X^+ at a center of high electron density on the metal core might be followed by migration of X and metal polyhedral rearrangements. The nature of the addition product may depend not only on the electrophile but probably also on the type of cluster and charge distribution within it. For example, addition of I^+ to the "electron precise" trigonal-bipyramidal dianion $[Os_5(CO)_{15}]^{2-}$ gives $[Os_5(CO)_{15}I]^-$ (Scheme 12,D). The metal polyhedron in the dianion is slightly distorted in $[Os_5(CO)_{15}I]^-$. The iodine atom that is terminally bound and formally acts as a two-electron donor bears some negative charge and is easily abstracted by Ag^+ (*75*). In contrast, addition of I^+ to the tetracapped octahedral dianion $[Os_{10}C(CO)_{24}]^{2-}$ involves a sequential opening up of two capping tetrahedra to give $[Os_{10}C(CO)_{24}(\mu\text{-}I)]^-$ and $Os_{10}C(CO)_{24}$ $(\mu\text{-}I)_2$, which contain Os_4 butterflies bridged by iodine atoms acting as three-electron donors (Scheme 12,G) (*133*). For all HNCC studied to date, dissociation of bridging iodine ligands is effected by I^-, even when major structural rearrangements have occurred upon I^+ addition, e.g., in $Os_8(CO)_{22}H(\mu\text{-}I)$ (*124*). Addition of NO^+ to the dianion $[Os_{10}C(CO)_{24}]^{2-}$ initially gives the NO-bridged species $[Os_{10}C(CO)_{24}(\mu\text{-}NO)]^-$ with a structure similar to that of the monoiodine derivative. The final product of the reaction, though, is $[Os_{10}C(CO)_{23}(NO)]^-$, which results from the closure of the Os_4 butterfly upon CO ejection and a change in coordination of the NO from bridging to terminal (*132*) (Scheme 12,H). The same mechanism involving coordination of NO^+ prior to CO ejection might also be involved in the reaction of $[Fe_6C(CO)_{16}]^{2-}$ with NO^+ to give $[Fe_6C(CO)_{15}(NO)]^-$. Further reaction of this monoanion with excess NO^+ affords $Fe_6C(CO)_{11}(NO)_4$ but the mechanism of the formation of this cluster is not clear, although it must involve an oxidative reduction step (*17*).

B. Protonation and Deprotonation Reactions

The protonation reactions of anionic HNCC are often complicated by further chemical transformations of unstable hydride derivatives, as discussed in Sections II,B,3 and III,A,1. There are, however, several examples of straightforward protonation reactions to yield hydrido clusters of unchanged nuclearity. In many cases, by choosing acids and solvents correctly, sequential protonation of the anions may be achieved.

Acidification of the dianions $[Os_5(CO)_{15}]^{2-}$ (*58*), $[Os_6(CO)_{18}]^{2-}$ (*88*), $[Os_7(CO)_{20}]^{2-}$ (*410*), $[Os_8(CO)_{22}]^{2-}$ (*410*), and $[Os_{10}C(CO)_{24}]^{2-}$ (*130*) with sulfuric acid in dichloromethane or tetrahydrofuran, for example, gives the respective monohydrides, while reaction in acetonitrile results in the precipitation of the dihydrides. The acidic nature of the dihydrides $[Os_m(CO)_nH_2]$ ($m = 6, 7, 8$; $n = 18, 20, 22$, respectively) and $[Os_{10}C(CO)_{24}H_2]$ is evidenced by their facile deprotonation by halides to give the corresponding monoanions; further deprotonation requires stronger bases such as KOH, DBU, or proton sponge (*409*, *410*). The mechanism of this reaction is not understood but ^1H NMR studies on the reaction of $Os_7(CO)_{20}H_2$ with Cl^- suggest that formation of the monoanion $[Os_7(CO)_{20}H]^-$ occurs via the intermediate $[Os_7(CO)_{20}H_2Cl]^-$ (*474*). Interestingly, reaction of $Os_5(CO)_{15}H_2$ with I^- does not lead to deprotonation, but rather to formation of the adduct $[Os_5(CO)_{15}H_2I]^-$ (*65*), demonstrating that reduction in nuclearity and acidity occur concomitantly in these systems.

The isolation and full characterization of a number of large hydrido clusters have in many cases been hampered by their extremely high acidity. The clusters $[Ni_{38}Pt_6(CO)_{48}H_{(6-n)}]^{n-}$ ($n = 3$–6), for instance, exist as an equilibrium mixture of anions **a** ($n = 3$), **b** ($n = 4$), **c** ($n = 5$), and **d** ($n = 6$) in acetonitrile solution. This mixture has been found to be easily converted into one of its components by controlled addition of acid or base [Eq. (26)] (*373*).

$$\mathbf{a} \underset{H^+}{\overset{MeCN}{\rightleftharpoons}} \mathbf{b} \underset{H^+}{\overset{CO_3^{2-}}{\rightleftharpoons}} \mathbf{c} \underset{H_2O}{\overset{OH^-}{\rightleftharpoons}} \mathbf{d} \tag{26}$$

The hydrides **b** and **c** were isolated in a crystalline state. Isolation of **a**, however, was not possible due to the ready deprotonation of its salts on dissolution both in acetone and acetonitrile, the only solvents in which the mixture of **a**–**d** is soluble.

1. Sites of Protonation

It is not known whether proton transfer from the medium to the metal atoms through the carbonyl shell is direct or whether intermediates containing protonated ligands are formed. Protonation at the oxygen of a CO group in small clusters has been shown to occur [e.g., in $Fe_3(CO)_{10}H(COH)$ (*440*)] but not a single example has yet been reported for HNCC hydrides. Protonation of the exposed carbide atom in the pyramidal clusters $[M_5C(CO)_{14}]^{2-}$ [M = Fe (*411*, *414*), Ru (*412*), and Os (*78*)] does not occur either. This is in contrast with the butterfly species $[Fe_4C(CO)_{14}]^{2-}$, which is attacked by acid to give first $[Fe_4C(CO)_{14}H]^-$, with the hydride attached to the metal framework, and then $Fe_4(CH)(CO)_{14}H$, in which the second

hydride bridges an Fe—C vector (*413*, *414*). Theoretical studies by Shriver *et al.* (*411*) have correlated the greater reactivity of the carbon atom in the butterfly cluster to the fact that the highest occupied molecular orbital (HOMO) of the butterfly carbide contains a significant negative charge on this atom. Hoffmann *et al.* (*415*) have also carried out calculations on this system and their results are in general agreement with the earlier calculations, except that the HOMO-LUMO (LUMO, lowest unoccupied molecular orbital) gap is less in the butterfly cluster than in the square-pyramidal species.

These and other MO calculations (*416*) indicate that the positions preferred by hydrogen atoms tend to reflect the electron distribution in clusters. In general, hydrides occupy edge-bridging sites, but a few examples of face-capping hydrides in HNCC are known [e.g., $Ru_6(CO)_{18}H_2$ (*35*) and $Os_8(CO)_{22}HI$ (*124*)]. The only reported species containing terminal hydrides are $Os_6(CO)_{19}H_2$ (*92*) and $[Rh_6(CO)_{15}H]^-$ (*397*). A number of clusters with semiinterstitial [e.g., $[Rh_{14}(CO)_{25}H]^{3-}$ (*223*)] and interstitial hydrides are also known (Table II). It is currently impossible to relate and predict the hydride position in a homologous series of compounds (Scheme 13). While $[Co_6(CO)_{15}H]^-$ and $[Ru_6(CO)_{18}H]^-$ contain interstitial hydrides, for example, the hydride in $[Rh_6(CO)_{15}H]^-$ occupies a terminal site in solution (*397*) and in $[Os_6(CO)_{18}H]^-$ the hydride caps an Os_3 face in the solid state (*88*).

2. *Structural Characterization of Large Hydrido Clusters*

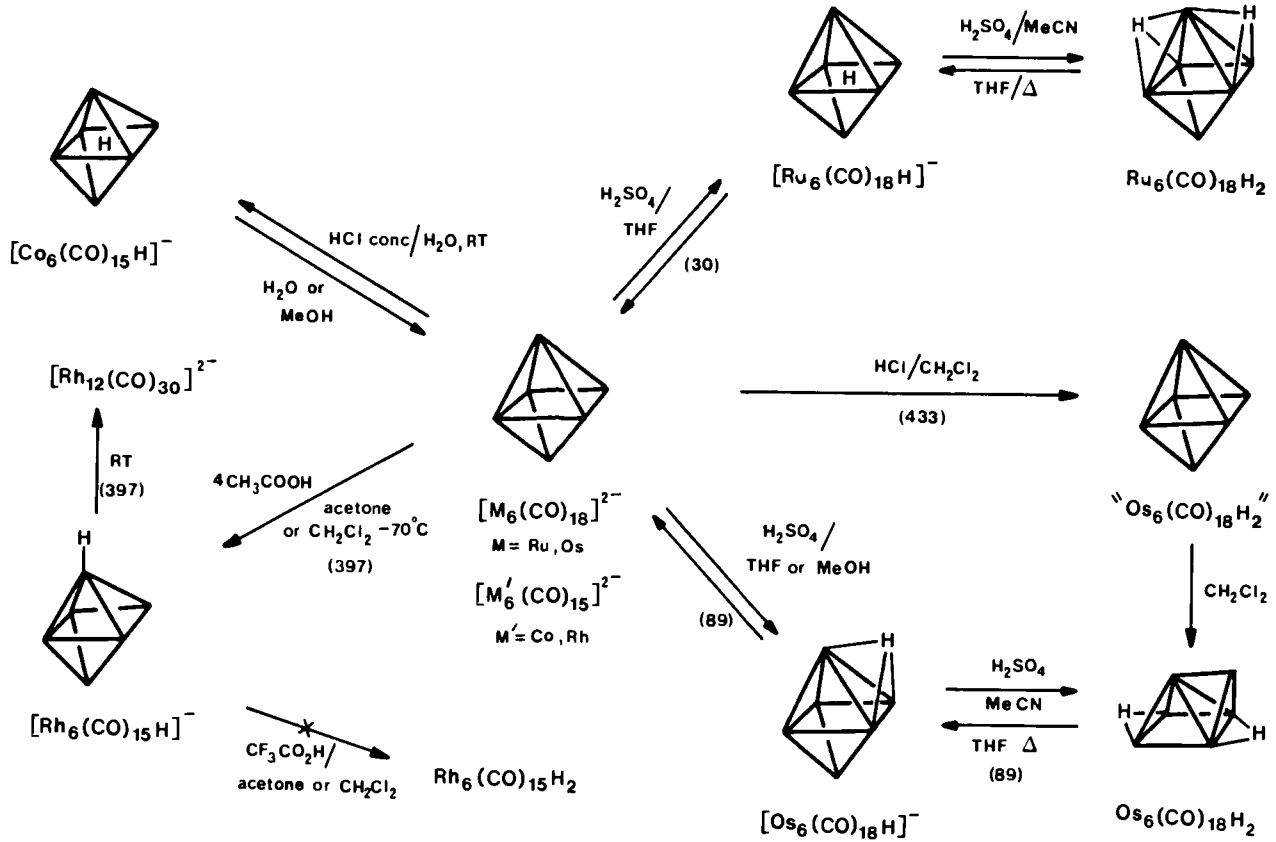
X-Ray diffraction has often been successful in the determination of hydrogen atom position in HNCC hydrides. Direct location from Fourier

TABLE II

^{1}H NMR DATA OF INTERSTITIAL HYDRIDO HNCC

Cluster hydride	Environment	^{1}H NMR shift (δ)	Other studies[a]
$[Co_6(CO)_{15}H]^-$	Octahedral	23.2	N and X
$[Ru_6(CO)_{18}H]^-$	Octahedral	16.4	N and X
$[Os_{10}C(CO)_{24}H]^-$	Tetrahedral	−14.4	X
$[Os_{10}(CO)_{24}H_4]^{2-}$	?	−16.5 (broad) at RT, −14.7 and −19.1 (1:1) at 198 K	
$[Ni_{12}(CO)_{21}H]^{3-}$	Distorted, octahedral	−24	N and X
$[Ni_{12}(CO)_{21}H_2]^{2-}$	Distorted, octahedral	−18	N and X

[a] N, Neutron diffraction; X, X-ray diffraction.



SCHEME 13. Protonation reactions of $[M_6(CO)_{18}H_{(2-n)}]^{n-}$ (M = Ru, Os; n = 2, 1) and $[M'_6(CO)_{15}H_{(2-n)}]^{n-}$ (M' = Co, Rh; n = 2, 1) and deprotonation reactions of the hydrido derivatives.

difference maps is rarely achieved, but instead indirect methods such as stereochemical considerations of the ligands' disposition about the metal atoms (*446*), M—M bond lengthening, metal cluster face or cavity expansion, and potential energy calculations (*447*) have been used with success. Precise representation of the hydrogen bonding in these systems, however, is possible only with the use of single-crystal neutron diffraction.

The use of this technique to study the hydrido clusters $[Ni_{12}(CO)_{21}H_{4-n}]^{n-}$ ($n = 2, 3$) (*417*) has provided the most detailed stereochemical study on the bonding of an interstitial hydrogen atom. The X-ray structures of $[Ni_{12}(CO)_{21}H_2]^{2-}$ and $[Ni_{12}(CO)_{21}H]^{3-}$ (*256*) consist of a 12-atom nickel fragment of a hexagonal-close-packed (hcp) metal lattice surrounded by 9 terminal and 12 bridging carbonyls (Fig. 6). Neutron diffraction studies have shown that the hydrogen atoms in both dianion and trianion are localized in octahedral sites as suggested by the X-ray analysis. However, the hydride in the trianion was found to be much closer to the central hexanickel plane (0.73 Å) than to the outer triangular plane (1.69 Å), effectively being coordinated to only three of the six nickel atoms. In the dihydride the two interstitial hydrogen atoms are closer to the centers of the octahedral sites. This has been ascribed both to competition for electron density on the central nickel triangle and mutual repulsion between the two hydrogen nuclei in neighboring octahedral holes.

It has been found (*257*) that once the two octahedral cavities have been occupied in $[Ni_{12}(CO)_{21}H_2]^{2-}$, this cluster cannot be protonated further. The fact that protonation of the monohydride $[Fe_6Pd_6(CO)_{24}H]^-$ also cannot be achieved has been used to support the tentative hydride location in the Pd_6 octahedron on the basis of the long average Pd—Pd distance (*289*).

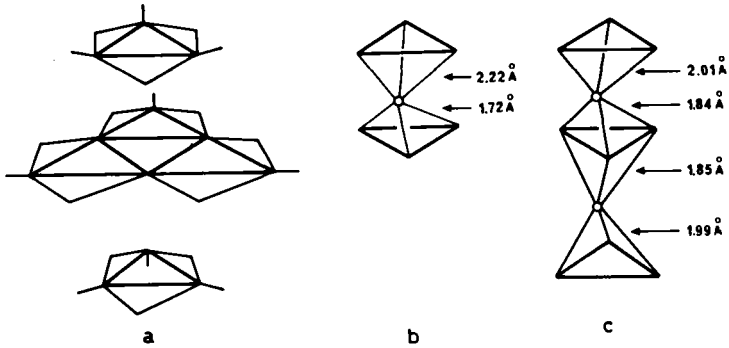


FIG. 6. (a) Schematic architecture of the hydrido clusters $[Ni_{12}(CO)_{21}H_{(4-n)}]^{n-}$ ($n = 2, 3$). Both anions are constructed from the planar $Ni_6(CO)_3(\mu_2\text{-}CO)_6$ capped by two $Ni_3(CO)_3(\mu_2\text{-}CO)_3$ fragments through Ni-Ni interactions. Fragments of the structures showing the hydrogen atoms in the octahedral interstices in (b) $[Ni_{12}(CO)_{21}H]^{3-}$ and in (c) $[Ni_{12}(CO)_{21}H_2]^{2-}$ (mean Ni-H distances given) (*417*).

Proton NMR cannot be used as an indication of the position occupied by hydrides in HNCC in solution as the range of chemical shifts observed is enormous (*441*). For example, all fully characterized carbonyl clusters that contain interstitial hydrides are listed in Table II, with chemical shifts from 23.2 δ in $[Co_6(CO)_{15}H]^-$ to $-24\,\delta$ in $[Ni_{12}(CO)_{21}H]^{3-}$. The octahedral $[Ru_6(CO)_{18}H]^-$ was the first reported cluster for which an interstitial hydride was assigned on the basis of X-ray (*30, 31*) and solid-state infrared spectroscopy studies (*33*). However, because of the extremely low field position of the NMR signal (16.4 δ), it was suspected to be of the formyl type (*417*). Its interstitial position was later unequivocally established by neutron diffraction studies (*32*). The observation of the ^{191}Os–^1H satellites in the proton NMR of $[Os_{10}C(CO)_{24}H]^-$ has allowed in this case conclusive location of the hydride in one of the tetrahedra of the tetracapped octahedral cluster. This supports the results of X-ray studies that evidenced slight expansion of the tetrahedral site (*131*).

Multinuclear NMR has been used extensively to investigate the structures of rhodium clusters in solution. Where X-ray quality crystals are not available, as is the case for $[Rh_6(CO)_{15}H]^-$, the study of ^1H,^1H-$\{^{103}Rh\}$, ^{13}C, ^{13}C-$\{^{103}Rh\}$, and ^{103}Rh NMR has allowed determination of the cluster structure (Scheme 13) (*397*). A combination of this technique with X-ray diffraction studies in the hydrido species $[Rh_{13}(CO)_{24}H_{(5-n)}]^{n-}$ ($n = 2, 3$) has helped to establish the nature of the hydrogen atoms in these clusters. Both clusters have a centered twinned cuboctahedral arrangement of rhodium atoms (Fig. 7). Their hydrides were located in the square-pyramidal holes for which a comparison of the mean Rh—Rh bonds of cavities showed that lengthening had occurred. A ^1H,^1H-$\{^{103}Rh\}$ INDOR and ^{13}C NMR spectroscopic solution study was consistent with a rapid migration of the interstitial hydrogen atoms inside the hcp rhodium cluster. As the accepted radius of a hydrogen atom, 0.37 Å, is much greater than the hole in the triangular Rh_3 face (0.22 Å) in the inside of the cluster, these studies suggest

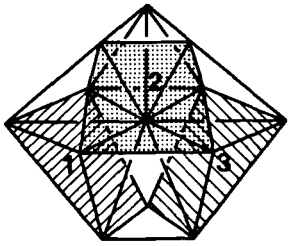


FIG. 7. The twinned cuboctahedral rhodium atoms arrangement in the hydrido clusters $[Rh_{13}(CO)_{25}H_{(5-n)}]^{n-}$ ($n = 2, 3, 4$). The hydrogen atoms occupy the square-based pyramidal holes 1 ($n = 4$), 1 and 2 ($n = 3$), and 1, 2, and 3 ($n = 2$).

that the hydrogen atom is protonic in character (*217*). A more attractive picture, however, is that of a "breathing cluster" with Rh—Rh bonds expanding and contracting as the CO ligands exchange and the hydrogens migrate.

3. Metal Polyhedral Rearrangements in Protonation Reactions

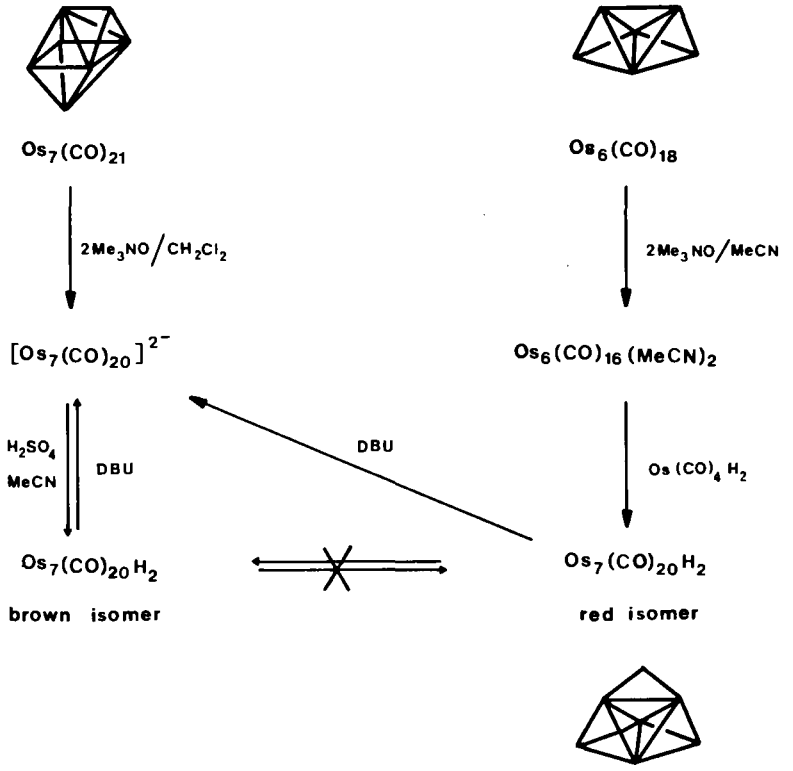
Addition of protons to anionic clusters to generate hydrides leaves the cluster electron count unaffected, yet the process is sometimes accompanied by structural changes. For example, both $[Os_6(CO)_{18}]^{2-}$ (*87*) and $[Os_6(CO)_{18}H]^-$ (*88*) have octahedral arrangements of metal atoms as predicted by Wade's rules. In the dihydride $Os_6(CO)_{18}H_2$, however, the metal atoms describe a capped square-based pyramid (*87*).

Recent molecular orbital (MO) calculations by Wade *et al.* (*408*) using the series $[B_6H_6]^{2-}$, $[B_6H_7]^-$, and B_8H_8 as models for the protonation of hexanuclear metal carbonyls have attempted to rationalize these findings. The charge distribution is symmetrical in an octahedral $[B_6H_6]^{2-}$ but asymmetrical in the capped square-based pyramidal isomer. It was found that upon protonation, significant charge redistribution occurs. This results in a substantial decrease in the symmetry of the octahedral cluster framework, which is disfavored in comparison with the capped square-based pyramidal structure much less affected by the protonation process.

Further evidence for the stabilization of this structure in the Os_6 system comes from the fact that the octahedral isomer of $Os_6(CO)_{18}H_2$, isolated by varying the conditions for protonation of $[Os_6(CO)_{18}]^{2-}$ (*433*), slowly rearranges in solution to the more thermodynamically stable capped square-based pyramidal structure. The dihydride $Ru_6(CO)_{18}H_2$, however, does not show preference for this structure and retains the octahedral metal atom geometry observed for $[Ru_6(CO)_{18}]^{2-}$ and $[Ru_6(CO)_{18}H]^-$ (*30, 31, 35*) even on warming.

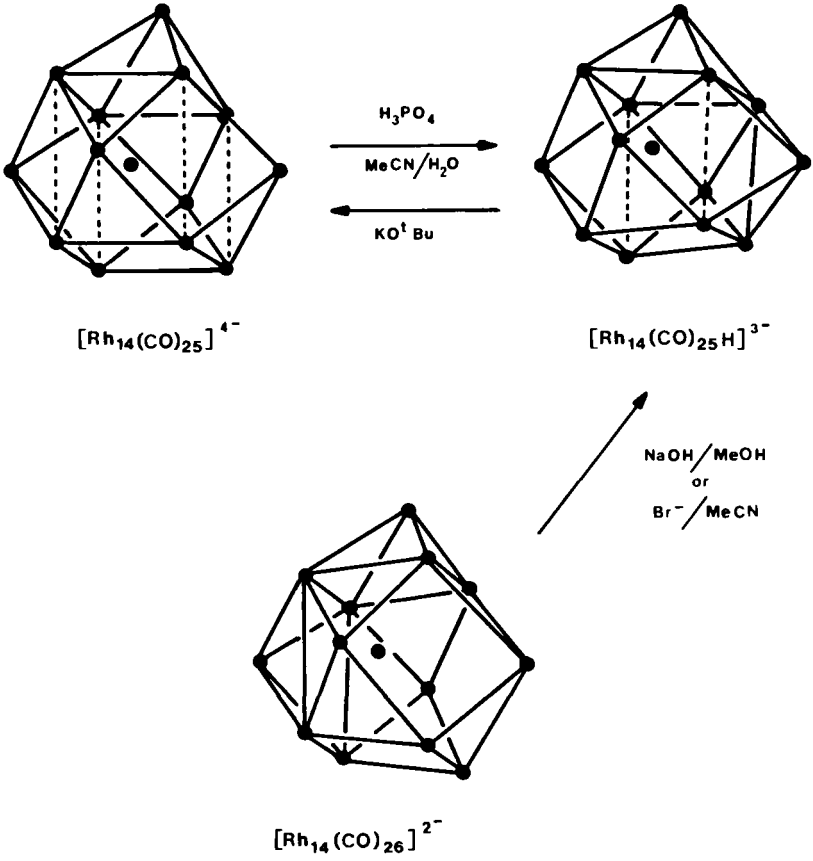
The dihydride $Os_7(CO)_{20}H_2$ also exists in two isomeric forms, which, in this case, are formed by two very different routes (Scheme 14). Protonation of $[Os_7(CO)_{20}]^{2-}$ gives the brown isomer (*118*). Only the red isomer, synthesized via the addition of $Os(CO)_4H_2$ to $Os_6(CO)_{16}(MeCN)_2$, has been structurally characterized (*118*). Instead of the monocapped octahedron predicted by Wade's Rules and observed for the isoelectronic $Os_7(CO)_{21}$, it has a structure based on the $Os_6(CO)_{18}$ bicapped tetrahedral metal atoms arrangement, with an edge bridged by an $Os(CO)_4$ unit. These two species do not interconvert. Deprotonation of both isomers yields the same dianion and the red species, once deprotonated, even singly, cannot be reformed (*474*).

It has become evident that as cluster nuclearity increases, the simple relationship between their electron count and structure is lost, particularly



SCHEME 14. Synthetic routes to the two isomers of $Os_7(CO)_{20}H_2$.

when they contain ligands other than CO. In these cases the packing of the metal atoms and the ligand stereochemistries are optimized in a way that has not yet been rationalized. Comparison of the structures of $[Rh_{14}(CO)_{25}]^{4-}$ (*220*), $[Rh_{14}(CO)_{25}H]^{3-}$ (*223*), and $[Rh_{14}(CO)_{26}]^{2-}$ (*219*) (all with the same electron count) shows that isoelectronic replacement of two negative charges by a CO and protonation of the tetraanion lead to distortions from a body-centered cubic (bcc) arrangement of rhodium atoms to arrays intermediate between ccp and bcc (Scheme 15). In the similar isoelectronic series $[Os_8(CO)_{22}]^{2-}$, $[Os_8(CO)_{22}H]^{-}$, and $Os_8(CO)_{23}$, no significant distortion in the bicapped octahedral metal geometry is observed in going from the neutral carbonyl to the dianion. In contrast, the hydrido species $[Os_8(CO)_{22}H]^{-}$ has a fused tetrahedral structure (*124*). This emphasizes once again the ability of hydrides to stabilize alternative metal cluster geometries.



SCHEME 15. Structural transformations in the Rh_{14} system.

C. REDUCTION REACTIONS

Under this heading only reactions with hard nucleophiles that result in reduced species that do not incorporate the nucleophilic reagent are considered. The additions of soft nucleophiles to HNCC are discussed in Section III,E.

1. Two-Electron Reduction with Concomitant Loss of CO

As with oxidation, the reduction of HNCC can be complicated by redox condensation reactions and by cluster degradation induced by free carbon monoxide. The latter is most commonly observed when reduction is effected

by alkali metals (see Section II,B,1) [e.g., Eq. (27)] (*196*).

$$10[Co_6(CO)_{15}]^{2-} + 22Na \longrightarrow 9[Co_6(CO)_{14}]^{4-} + 6[Co(CO)_4]^- + 22Na^+ \quad (27)$$

The ejection of CO and subsequent cluster degradation may be avoided if nucleophiles such as OH^-, OR^-, H^-, and R^- are used instead. These species oxidize CO to CO_2 simultaneously with cluster reduction. It is believed that the mechanism for this reaction in HNCC is similar to that known for mononuclear complexes [Eqs. (28) and (29)] (*418*).

$$M_m(CO)_n + OH^- \longrightarrow [M_m(CO)_{(n-1)}(CO_2H)]^- \quad (28)$$

$$[M_m(CO)_{(n-1)}(CO_2H)]^- \longrightarrow [M_m(CO)_{(n-1)}]^{2-} + CO_2 + H^+ \quad (29)$$

Although no CO_2H-containing cluster has been isolated, there have been reports of related species in the reactions of OR^- and R^- with $Rh_6(CO)_{16}$ (*168*, *172*, *173*) (Scheme 16) and $Ru_6C(CO)_{17}$ [Eqs. (30) and (31)] (*39*).

$$Ru_6C(CO)_{17} \xrightarrow{Na_2CO_3/MeOH} [Ru_6C(CO)_{16}(COOMe)]^- \quad (30)$$

$$[Ru_6C(CO)_{16}(COOMe)]^- \xrightarrow{OH^-/H_2O} [Ru_6C(CO)_{16}]^{2-} \quad (31)$$

The reduction of neutral carbonyls with alkali metal hydroxides or carbonates is an important route to HNCC dianions. In a few instances reduction of rhodium clusters has been reported to proceed further with oxidation of another CO. Examples are the formation of $[Rh_6(CO)_{14}]^{4-}$ from $[Rh_6(CO)_{15}]^{2-}$ (*170*) (Scheme 16) and the reduction of the dicarbide $[Rh_{12}(C)_2(CO)_{24}]^{2-}$ to give $[Rh_{12}(C)_2CO_{23}]^{4-}$ (*213*). In the latter case, the unstable paramagnetic intermediate $[Rh_{12}(C)_2(CO)_{23}]^{3-}$ has also been isolated upon slight alteration of the reaction conditions [Eqs. (32) and (33)].

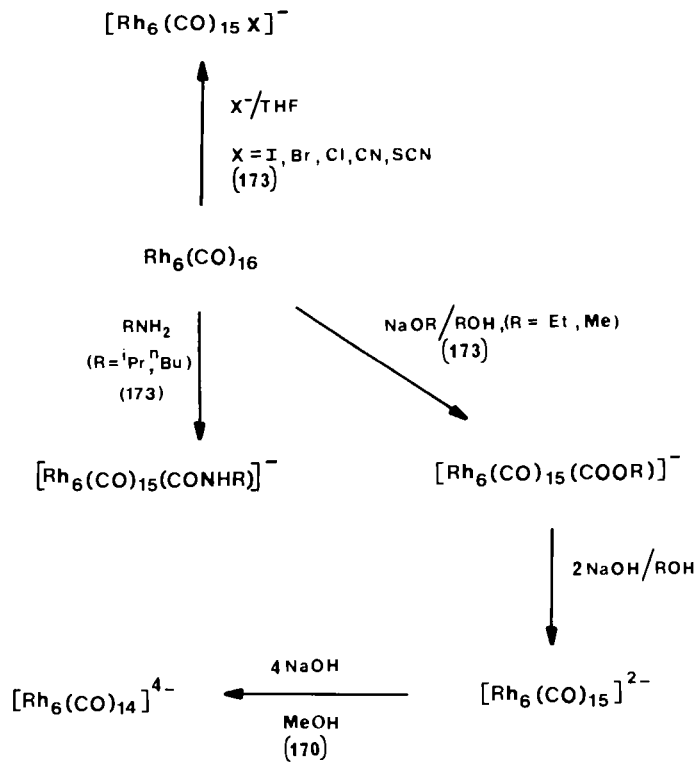
$$[Rh_{12}(C)_2(CO)_{24}]^{2-} \xrightarrow{OH^-/MeOH} [Rh_{12}(C)_2(CO)_{23}]^{3-} \quad (32)$$

$$[Rh_{12}(C)_2(CO)_{23}]^{3-} \xrightarrow[i\text{-PrOH}, \Delta]{OH^-(excess)} [Rh_{12}(C)_2(CO)_{23}]^{4-} \quad (33)$$

The reduction of the trianion to $[Rh_{12}(C)_2(CO)_{23}]^{4-}$ is easily reversed by I_2 but the dianion $[Rh_{12}(C)_2(CO)_{24}]^{2-}$ cannot be regenerated under these reaction conditions.

2. *Reduction Reactions of Osmium Binary Clusters* $Os_m(CO)_n$

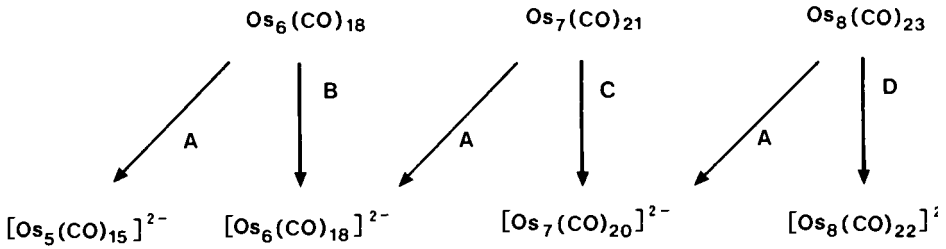
The reduction of $Os_5(CO)_{16}$ with excess potassium hydroxide proceeds to give $[Os_5(CO)_{15}]^{2-}$. In contrast the series $Os_m(CO)_n$ ($m = 6, 7, 8$; $n = 18, 21, 23$) undergoes fragmentation under similar conditions with the ejection



SCHEME 16. Reduction reactions of $Rh_6(CO)_{16}$.

of an "$Os(CO)_3$" unit, resulting in the formation of the dianions $[Os_{(m-1)}(CO)_{(n-3)}]^{2-}$ (Scheme 17) (*386*). It has been proposed that the difference in behavior on reduction may be related to the electron-precise nature of $Os_5(CO)_{16}$. Having six skeletal electron pairs ($s = 6$), this cluster adopts a fundamental polyhedron (trigonal-bipyramid). In contrast, the electron-deficient clusters $Os_6(CO)_{18}$ ($s = 6$), $Os_7(CO)_{21}$ ($s = 7$), and $Os_8(CO)_{23}$ ($s = 7$) possess capped polyhedral geometries, and, by loosing $Os(CO)_3$ groups, generate the electron-precise anions $[Os_5(CO)_{15}]^{2-}$ and $[Os_6(CO)_{18}]^{2-}$, and the less electron-deficient $[Os_7(CO)_{20}]^{2-}$, respectively.

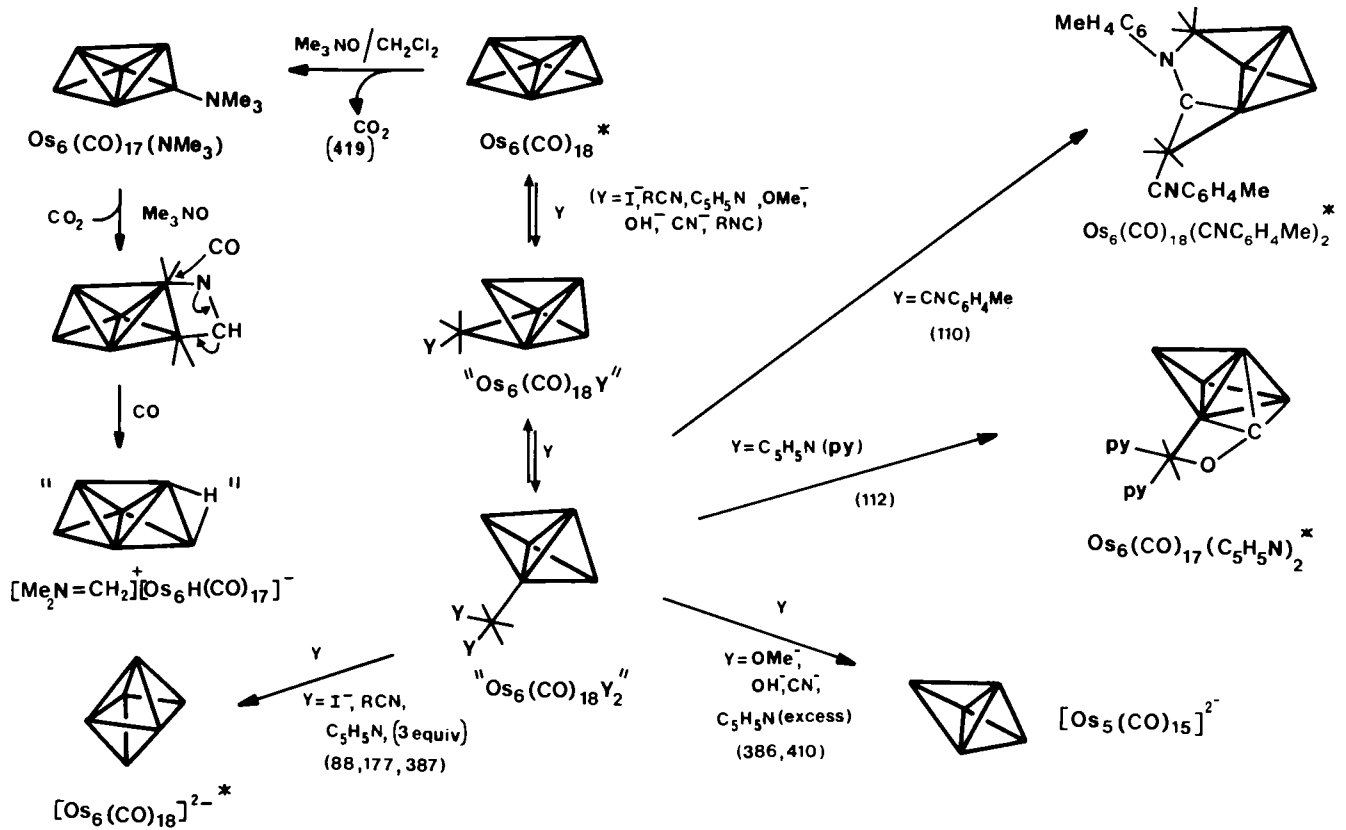
Reduction of the binary carbonyls $Os_m(CO)_n$ ($m = 6, 7, 8$; $n = 18, 21, 23$) to their respective dianions $[Os_6(CO)_{18}]^{2-}$ and $[Os_m(CO)_{(n-1)}]^{2-}$ ($m = 7, 8$) is achieved with weaker bases such as nitriles (*387*) and halides (*388*, *335*, *123*). The importance in the choice of the reducing conditions for this cluster series is summarized in Scheme 17.



SCHEME 17. Reduction reactions of $Os_6(CO)_{18}$, $Os_7(CO)_{21}$, and $Os_8(CO)_{23}$. A, KOH/MeOH; B, I^-, Na–Hg, or Zn/CH_2Cl_2, nitriles; C, Me_3NO or $[BH_4]^-/CH_2Cl_2$; D, I^- or $[BH_4]^-$/THF.

The reduction reactions of $Os_6(CO)_{18}$ have been investigated in great detail. Studies on the reduction of this cluster by donor ligands Y ($Y = I^-$, RCN, CN^-, pyridine, OMe^-, and OH^-) suggest that successive additions of Y probably occur at the same osmium atom to give $Os_6(CO)_{18}Y$ and $Os_6(CO)_{18}Y_2$ (Scheme 18). Kinetic studies of the nitrile reaction revealed a third-order rate dependence on the nitrile concentration, suggesting that the formation of the dianion $[Os_6(CO)_{18}]^{2-}$ is brought about by the attack of a third ligand (*387*). A similar process has been invoked to account for the formation of $[Os_5(CO)_{15}]^{2-}$ on reaction of $Os_6(CO)_{18}$ with strong bases such as OH^-, OMe^-, and concentrated CN^- (*410*), discussed above. In this case, addition of a third molecule of Y serves to eliminate the electron deficient group. Evidence for these propositions comes from the reaction of $Os_6(CO)_{18}$ with pyridine, which leads to production either of $[Os_6(CO)_{18}]^{2-}$ or $[Os_5(CO)_{15}]^{2-}$, depending on the molar ratio of $Os_6(CO)_{18}$ over pyridine employed (*177*). The neutral $Os_6(CO)_{17}(C_5H_5N)_2$ was also isolated in low yield from this reaction (*112*). It adopts a spiked trigonal-bipyramidal structure with the two pyridine ligands on the terminal osmium. It may derive from $Os_6(CO)_{18}(C_5H_5N)_2$ through nucleophilic attack by the oxygen of a terminal CO at the terminal osmium of the trigonal bipyramid, and elimination of CO (*112*).

A different mechanism has been proposed for the reduction of $Os_6(CO)_{18}$ by R_3NO (two equivalents, R = Me, Et) to give $[Os_6(CO)_{17}H]^-$ (*419*). The reaction of $Os_6(CO)_{18}$ with trialkylamine oxide in the presence of reagents such as MeCN gives $Os_6(CO)_{(18-n)}(MeCN)_n$ ($n = 1, 2$) (see Section III,E,2,b). It is believed that, in the absence of acetonitrile, the initial product formed is the monosubstituted species $Os_6(CO)_{17}(R_3N)$, which, by transfer of an α hydrogen from the amine ligand to the metal cluster and accompanying elimination of the iminium ion $[R_2N{=}CHR]^+$, yields $[Os_6(CO)_{17}H]^-$ (Scheme 18).



SCHEME 18. Reactions of $Os_6(CO)_{18}$ with nucleophiles Y (Y = I^-, RCN, C_5H_5N, OMe^-, OH^-, CN^-, RNC). Asterisks denote structures determined by X-ray studies.

D. Electron-Transfer Reactions and Electrochemical Studies

The electrochemistry of HNCC is a new and rapidly expanding field which has not been covered in previous reviews of electrochemical studies of transition metal clusters (*420*). In a similar way to smaller clusters, HNCC have been found to exhibit both reversible and irreversible redox behavior. These processes will be discussed separately in the following sections.

1. Characterization of Paramagnetic, Electrochemically Generated HNCC Species

It has been shown that clusters often undergo oxidation or reduction by single electron-transfer steps. A number of paramagnetic HNCC species have been obtained, particularly radical anion clusters. Characterization of these radicals is afforded by solution electron spin resonance (ESR) spectroscopy. Further characterization of these species has often been hampered by their instability toward oxidation or reduction and the difficulty of separating them from the base electrolyte. Only a few HNCC radicals have been found to be stable enough to allow isolation in the solid state. These species were in fact generated chemically by a variety of methods discussed in Sections III,A and III,C. In these cases, ESR studies were substantiated by X-ray structural data and a detailed picture of their bonding has been established, for example, for $[Co_6C(CO)_{14}]^-$, $[Rh_{12}(C)_2(CO)_{23}]^{3-}$, $[Co_{13}(C)_2(CO)_{24}]^{4-}$, (*148*) and $[Fe_3Pt_3(CO)_{15}]^-$ (*284*).

The g values for many radical HNCC species are close to the free electron values, e.g., $[Ru_6C(CO)_{17}]^-$ ($g = 2.001$ at 223 K) (*385*). This suggests that there is little mixing of excited or lower energy levels with the orbital containing the odd electron and that this orbital is delocalized and largely metallic in character. Deviations of g values from the free electron values denote the contribution from the spin–orbit coupling of metal atoms between various states, e.g., $[Rh_{12}(C)_2(CO)_{23}]^{3-}$ ($g_1 = 2.282$, $g_2 = 2.198$, $g_3 = 2.038$, from 120 to 4.2 K) (*148*).

2. Reversible Electrochemical Generation of Different Oxidation States

a. Redox Behavior of $Os_6(CO)_{18}$. Studies of the electrochemical reduction of $Os_6(CO)_{18}$ (*421*) have shown it to proceed in a chemically reversible two-electron wave to the cluster dianion $[Os_6(CO)_{18}]^{2-}$ at either Pt or Au electrodes in tetrahydrofuran solution [Eq. (34)].

$$Os_6(CO)_{18} + 2e^- \longrightarrow [Os_6(CO)_{18}]^{2-} \quad [E^\circ = 0.04 \text{ V (vs. SCE)}] \qquad (34)$$

Cyclic voltammetry results were shown to be consistent with a redox model involving two stepwise one-electron transfers, in which the structural rearrangement of the bicapped tetrahedron of $Os_6(CO)_{18}$ occurs during the first electron-transfer step to give an octahedral structure. From the temperature dependence of the electron-transfer rate, the cluster reorganization energy was estimated to be $\Delta H^{\ddagger} = 8$ kcal/mol. This is lower than the activation energy for carbonyl scrambling in the cluster (*85*). In other words, the breaking and remaking of M—M bonds in the formation of a transient state in this cluster is energetically more favorable than similar processes involving M—CO bonds. This observation is consistent with both the $Os_6(CO)_{18}$ redox chemistry discussed in Sections III,A and III,B and with the fact that the reactivity of this cluster with nucleophiles under mild conditions is dominated by opening up of the cluster rather than CO substitution (see Section III,E).

Further two-electron reduction of the dianion at -2.15 V was also achieved electrochemically, and gave a highly unstable species formulated as $[Os_6(CO)_{18}]^{4-}$. This is in contrast with the chemical reduction of the related cluster $[Ru_6(CO)_{18}]^{2-}$ with stoichiometric amounts of $Na[(C_6H_5)_2CO]$ in tetrahydrofuran, which affords $[Ru_6(CO)_{17}]^{4-}$ and $[Ru_6(CO)_{16}]^{6-}$ sequentially with CO dissociation (*423*). The electrochemical oxidation of $[Ru_6(CO)_{18}]^{2-}$ is also different from that of $[Os_6(CO)_{18}]^{2-}$ as it is chemically irreversible (*421*).

b. Redox Behavior of "Raft" Os_6 Clusters. Predictions of the reduction potentials of the raft Os_6 clusters have been made by Evans and Mingos (*422*) on the basis of studies of the electronic requirements of the hypothetical planar $[Os_6(CO)_{24}]^{6+}$ cluster. These predictions may also be applied to $Os_6(CO)_{21}$, which can be derived from $[Os_6(CO)_{24}]^{6+}$ by isolobal replacement of three $[Os(CO)_4]^{2+}$ by three $Os(CO)_3$ groups. Their calculations have indicated the existence of a low-lying empty molecular orbital of $a_2{}^1$ symmetry in these clusters (Fig. 8), which is antibonding between the osmium atoms of the central triangle and bonding between the triangle and the bridging osmium groups. As a consequence, two-electron reduction of $Os_6(CO)_{21}$ should occur easily and the occupation of this orbital should lead to an increase in bond lengths in the central triangle and a decrease in the bond lengths to the bridging groups.

Electrochemical studies of the series of phosphite and phosphine substituted compounds $Os_6(CO)_{(21-n)}\{PR_3\}_n$ (R = OMe, n = 1-6; R = Ph, n = 1-3) (*99*) are in accord with the predictions of Evans and Mingos. These compounds undergo two well-defined reversible one-electron reductions and one irreversible oxidation (Table III). A correlation has been established between the values of $E_{1/2}$ for the first wave potential and the number of

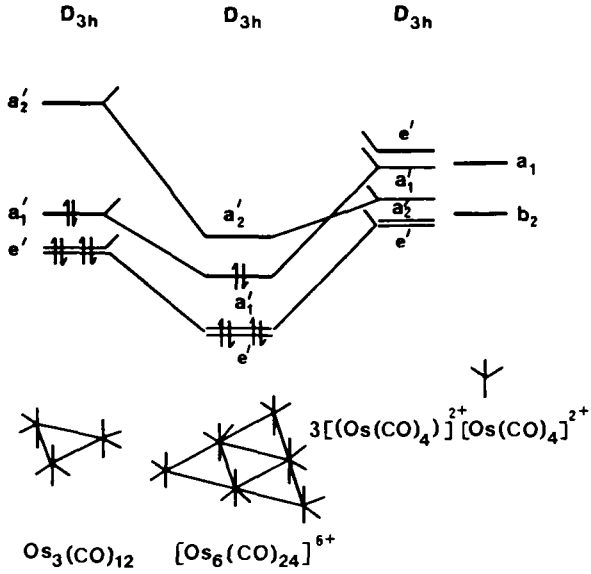


FIG. 8. Construction of the molecular orbitals for the "raft" cluster $[Os_6(CO)_{24}]^{6+}$ from $Os_3(CO)_{12}$ and three $[Os(CO)_4]^{2+}$ fragments.

TABLE III

REDUCTION POTENTIAL FOR SOME $P(OMe)_3$, $P(OPh)_3$, PPh_3, AND MeCN DERIVATIVES OF $Os_6(CO)_{21}$

Cluster	$E_{1/2}(1)$ (V)[a]	E_p (mV)	$E_{1/2}$ (2) (V)	E_p (mV)
$Os_6(CO)_{20}P(OMe)_3$ (ax.)	−0.96	65	−1.12	90
$Os_6(CO)_{20}P(OPh)_3$ (ax.)	−1.01	62	−1.27	57
$Os_6(CO)_{20}(PPh_3)$ (eq.)	−1.02	67	−1.30	62
$Os_6(CO)_{20}P(OMe)_3$ (eq.)	−1.09	67	−1.28	85
$Os_6(CO)_{20}P(OPh)_3$ (eq.)	−1.15	64	−1.38	72
$Os_6(CO)_{19}\{P(OMe)_3\}_2$, isomer I	−1.24	80	−1.46	85
$Os_6(CO)_{19}\{P(OMe)_3\}_2$, isomer II	−1.24	60	−1.43	75
$Os_6(CO)_{18}\{P(OMe)_3\}_3$, isomer I	−1.42	68	−1.62	125
$Os_6(CO)_{18}\{P(OMe)_3\}_3$, isomer II	−1.28	75	−1.49	140
$Os_6(CO)_{17}\{P(OMe)_3\}_4$	−1.43	—	−1.60	—
$Os_6(CO)_{16}\{P(OMe)_3\}_5$	−1.58	64	−1.78	85
$Os_6(CO)_{15}\{P(OMe)_3\}_6$	−1.84	62	−2.04	75
$Os_6(CO)_{20}(MeCN)$	−0.98	68	−1.22	114
$Os_6(CO)_{19}(MeCN)_2$	−1.20	—	—	—

[a] Conditions: MeCN solutions, 298 K, Pt electrode with Ag/Ag^+ reference electrode, $FeCp_2$ internal calibrant, and $[Bu_4N][BF_4]$ electrolyte.

phosphites and phosphines in the two series. As expected on the basis of electronic arguments, an increase in the degree of substitution of the cluster by PR_3 is accompanied by a decrease in the tendency to undergo further substitution; however, changing PPh_3 to $P(OMe)_3$ has no effect within experimental error.

The stability of the reduced products was found to be highly dependent on the nature of the ligands attached to these raft species. For example, the series $Os_6(CO)_{(21-n)}(MeCN)_n$ ($n = 1, 2$) does not undergo reversible reduction, that is, breakdown of the reduced species occurs. This is probably due to the fact that MeCN is a poorer π acceptor than PR_3 and therefore is not able to stabilize the reduced species produced during the cyclic voltammetry.

Reduced species of the type $[Os_6(CO)_{21}]^{2-}$ have not yet been characterized crystallographically, but evidence to support the existence of the orbital described above is provided by X-ray and ESR studies of the related species $[Fe_3Pt_3(CO)_{15}]^{n-}$ ($n = 1, 2$). The $a_2{}^1$ symmetry orbital is fully occupied in the dianion of this mixed-metal cluster, which is easily oxidized to the paramagnetic species $[Fe_3Pt_3(CO)_{15}]^-$ [Eq. (35)] (*283*).

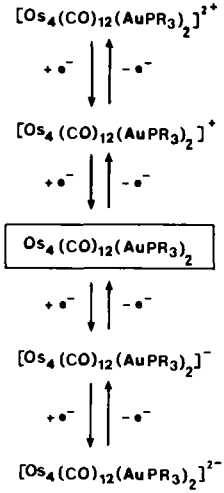
$$[Fe_3Pt_3(CO)_{15}]^{2-} \underset{OH^-/MeOH}{\overset{H_3PO_4 \text{ or } H_2SO_4 \text{ or } Cu^+ \text{ or } Ag^+ \text{ salts}}{\rightleftharpoons}} [Fe_3Pt_3(CO)_{15}]^- \qquad (35)$$

X-ray diffraction studies have indeed shown a significant shortening of the average Pt—Pt bond distance in going from $[Fe_3Pt_3(CO)_{15}]^{2-}$ (2.750 Å) to the monoanion (2.656 Å). Also, ESR and electronic diffuse-reflectance spectra (*284*) were found to agree with the location of the unpaired electron in $[Fe_3Pt_3(CO)_{15}]^-$ in an orbital corresponding to that described above.

c. The Redox Reactions of $Os_4(CO)_{12}(AuPR_3)_2$. The hexanuclear clusters $Os_4(CO)_{12}(AuPR_3)_2$ ($R_3 = Et_3$, Ph_2Me, Ph_3) may be considered as true electron reservoirs (Scheme 19) (*425*). They have been shown to undergo two fully reversible one-electron reduction steps corresponding to the formation of $[Os_4(CO)_{12}(AuPR_3)_2]^-$ ($g = 1.775$) and $[Os_4(CO)_{12}(AuPR_3)_2]^{2-}$. The reduced species $[Os_4(CO)_{12}(AuPR_3)_2]^{2-}$ were also generated chemically by reaction of $Os_4(CO)_{12}(AuPR_3)_2$ with Na/Hg, but these species were too unstable to be further characterized. The neutral compounds $Os_4(CO)_{12}(AuPR_3)_2$ also undergo two fully reversible one-electron oxidations (Scheme 19).

3. Irreversible Electrochemical Redox Reactions

a. The reduction of $M_5C(CO)_{15}$ ($M = Fe, Ru, Os$). Cyclic voltammetry of $M_5C(CO)_{15}$ (M = Ru, Os) at a Pt electrode in dichloromethane shows



A-OXIDATION		
PR_3	$E_{1/2}(1)$ (V)*	$E_{1/2}(2)$ (V)
PEt_3	0.60	0.78
PPh_2Me	0.68	0.83
PPh_3	0.68	0.80

B-REDUCTION				
PR_3	$E_{1/2}(1)$ (V)*	Ep	$E_{1/2}(2)$ (V)	Ep
PEt_3	−0.64	65mV	−0.89	60mV
PPh_2Me	−0.57	60mV	−0.79	60mV
PPh_3	−0.58	70mV	−0.81	65mV

SCHEME 19. Electrochemical reactions of $Os_4(CO)_{12}(AuPR_3)_2$ and potentials (relative to NHE) for the two-step two-electron oxidation (CH_2Cl_2 solution, 298 K) and reduction (258 K, $FeCp_2$ internal calibrant) processes.

two-electron irreversible reductions at −1.78 V (M = Ru) and −1.50 V (M = Os) versus Ag/Ag^+ at a scan rate of 1 V sec^{-1} at 298 K. No ESR-active intermediates were detected during the formation of the dianions $[M_5C(CO)_{14}]^{2-}$, which have also been generated chemically by the action of alkali metals, hydroxides, or carbonates on $M_5C(CO)_{15}$ (*78*). Cyclic voltammetry of $Fe_5C(CO)_{15}$ at a carbon electrode in the same solvent, however, suggests that the process proceeds through two steps at 253 K: one quasi-reversible, assigned to a two-electron transfer [step A, Eq. (36)], followed by irreversible loss of CO [step B, Eq. (36)] (*13*).

$$Fe_5C(CO)_{15} + 2e^- \xrightarrow{A} [Fe_5C(CO)_{15}]^{2-} \xrightarrow{B} [Fe_5C(CO)_{14}]^{2-} + CO \qquad (36)$$

If this is so, then the formation of $[Fe_5C(CO)_{15}]^{2-}$ could be compared with the generation of the bridged butterfly $M_5C(CO)_{15}L$ (M = Ru, Os) species from the square-based pyramid $M_5C(CO)_{15}$ upon addition of L as discussed in Section III,E,2,a.

The complexes $[M_5C(CO)_{14}]^{2-}$ show irreversible oxidation waves in dichloromethane at +0.15 V (M = Ru) and +0.35 V (M = Os) versus Ag/Ag^+, and the reformation of $M_5C(CO)_{15}$ has been attributed to scavenging of CO by the electron-deficient "$M_5C(CO)_{14}$" (*78*).

b. Electrochemical Reactions of $[Rh_{12}(CO)_{30}]^{2-}$ *(426).* Cyclic voltammetry of $[Bu_4N]_2[Rh_{12}(CO)_{30}]$ in tetrahydrofuran at 298 K shows two reductions at -1.00 and -1.45 V versus Ag/Ag^+. The first reduction is a two-electron process that gives $[Rh_6(CO)_{15}]^{2-}$. However, at 233 K and a scan rate of 2.0 V sec^{-1}, fragmentation is slower and the process is partly reversible, leading to the formation of $[Rh_{12}(CO)_{30}]^{4-}$. The second reduction is irreversible even at 223 K and is attributed to the reduction of $[Rh_6(CO)_{15}]^{2-}$ to unidentified products. The cyclic voltammogram of $[Rh_{12}(CO)_{30}]^{2-}$ also exhibits a two-electron oxidation at $+0.80$ V which is partly reversible at 233 K. These processes are summarized in Eqs. (37) and (38).

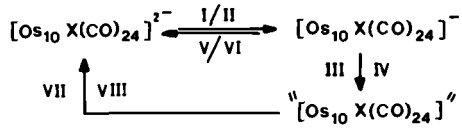
$$[Rh_{12}(CO)_{30}]^{2-} \underset{-1.00\ V}{\overset{+2e^-}{\rightleftharpoons}} [Rh_{12}(CO)_{30}]^{4-} \xrightarrow{k = 14.5\ sec^{-1}}$$

$$2[Rh_6(CO)_{15}]^{2-} \xrightarrow[-1.45\ V]{} \text{products} \qquad (37)$$

$$[Rh_{12}(CO)_{30}]^{2-} \underset{}{\overset{-2e^-}{\rightleftharpoons}} Rh_{12}(CO)_{30} \xrightarrow{k = 11.5\ sec^{-1}} \text{products} \qquad (38)$$

c. The Redox Chemistry of $[Os_{10}C(CO)_{24}]^{2-}$ *and* $[Os_{10}(CO)_{24}H_4]^{2-}$. Cyclic voltammetry studies of $[Os_{10}X(CO)_{24}]^{2-}$ (X = C, H_4) in dichloromethane at a Pt electrode show that these species undergo two one-electron oxidation steps (*427*) (Scheme 20). The first of these is fully reversible for both compounds. As the potential required to oxidize $[Os_{10}C(CO)_{24}]^{2-}$ (0.78 V versus Ag/Ag^+) is much higher than that for $[Os_{10}(CO)_{24}H_4]^{2-}$ (0.39 V), it has been suggested that the carbide atom somehow stabilizes the paired electron with respect to oxidation. Both of the oxidized species $[Os_{10}X(CO)_{24}]^-$ (X = C, H_4) exhibit paramagnetic behavior up to 200 K. Their g values of 2.295 (X = C) and 2.277 (X = H_4) are indicative of spin-orbit coupling between the various states in these species. In the case of the hydride radical, two weak signals associated with the interstitial hydrogen atoms were also observed. The second oxidation step is irreversible in both species. The diamagnetic solid formed, presumably $Os_{10}X(CO)_{24}$, gives $[Os_{10}X(CO)_{24}]^{2-}$ when taken up in donor solvents.

The voltammetry of $[Os_{10}C(CO)_{24}]^{2-}$ at a hanging drop mercury electrode is a complex process whose nature is not fully understood. Controlled electrolysis at a mercury pool of 0.8 V leads to a product that upon standing reacts slowly to yield $[Os_{20}Hg(C)_2(CO)_{48}]^{2-}$. This compound has also been generated chemically by reaction of $[Os_{10}C(CO)_{24}]^{2-}$ with mercuric salts or $AgBF_4$ and mercury (*338*) (see Section II,B,2,a).



Conditions for oxidation of the $[Os_{10}X(CO)_{24}]^{2-}$ species		
	CHEMICAL	ELECTROCHEMICAL
I	X = C, 1 equiv $AgBF_4$ or $FeCl_3$	+1.0V at Pt electrode
II	X = H_4, 1 equiv $AgBF_4$ or $FeCl_3$	+0.50V at Pt electrode
III	X = C, 2 equiv $AgBF_4$ or $FeCl_3$	+1.40V at Pt electrode
IV	X = H_4, 2equiv $AgBF_4$ or $FeCl_3$	+0.80V at Pt electrode
V	X = C air, 2–3 min	
VI	X = H_4 air, 12hrs	
VII	X = C, acetone, CH_3CN or Δ	
VIII	X = H_4 acetone, CH_3CN or Δ	

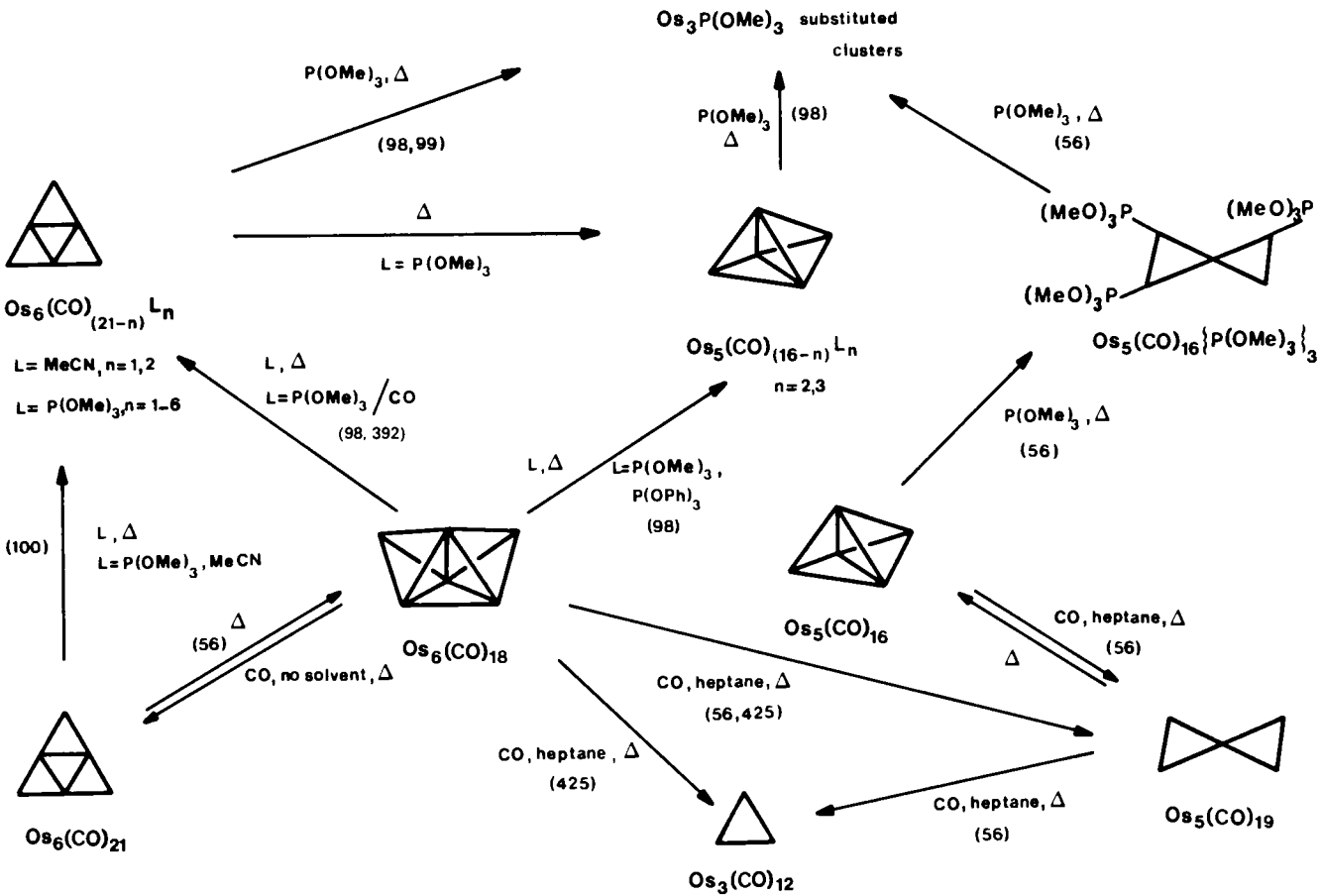
SCHEME 20. Redox chemistry of $[Os_{10}X(CO)_{24}]^{2-}$ (X = C, H_4). Unless specified, chemical reactions are as in CH_2Cl_2. Electrochemical potentials versus Ag/Ag^+.

E. REACTIONS WITH SOFT NUCLEOPHILES

The reactions of HNCC with soft nucleophiles (CO, PR_3, RCCR, R_2CCR_2, pyridine, NO_2^-, and halides) result either in the formation of addition or substitution products, or in cluster breakdown. The nature of the species formed depends on the nucleophile (which may or may not undergo transformation on the cluster surface), the type of metal cluster, and the conditions employed in the reaction. Generally, clusters of the lighter elements tend to fragment even under mild conditions, while those of the heavier elements, which are more robust, often afford addition and substitution products.

1. Addition Reactions

Simple nucleophilic addition at the metal centers of a cluster results in an increase in the number of electrons available for skeletal bonding. As a consequence, breakage of M—M bonds resulting in an opening of the cluster framework, sometimes followed by cluster breakdown, may be observed.



SCHEME 21. Reactions of $Os_6(CO)_{18}$ with CO and PR_3.

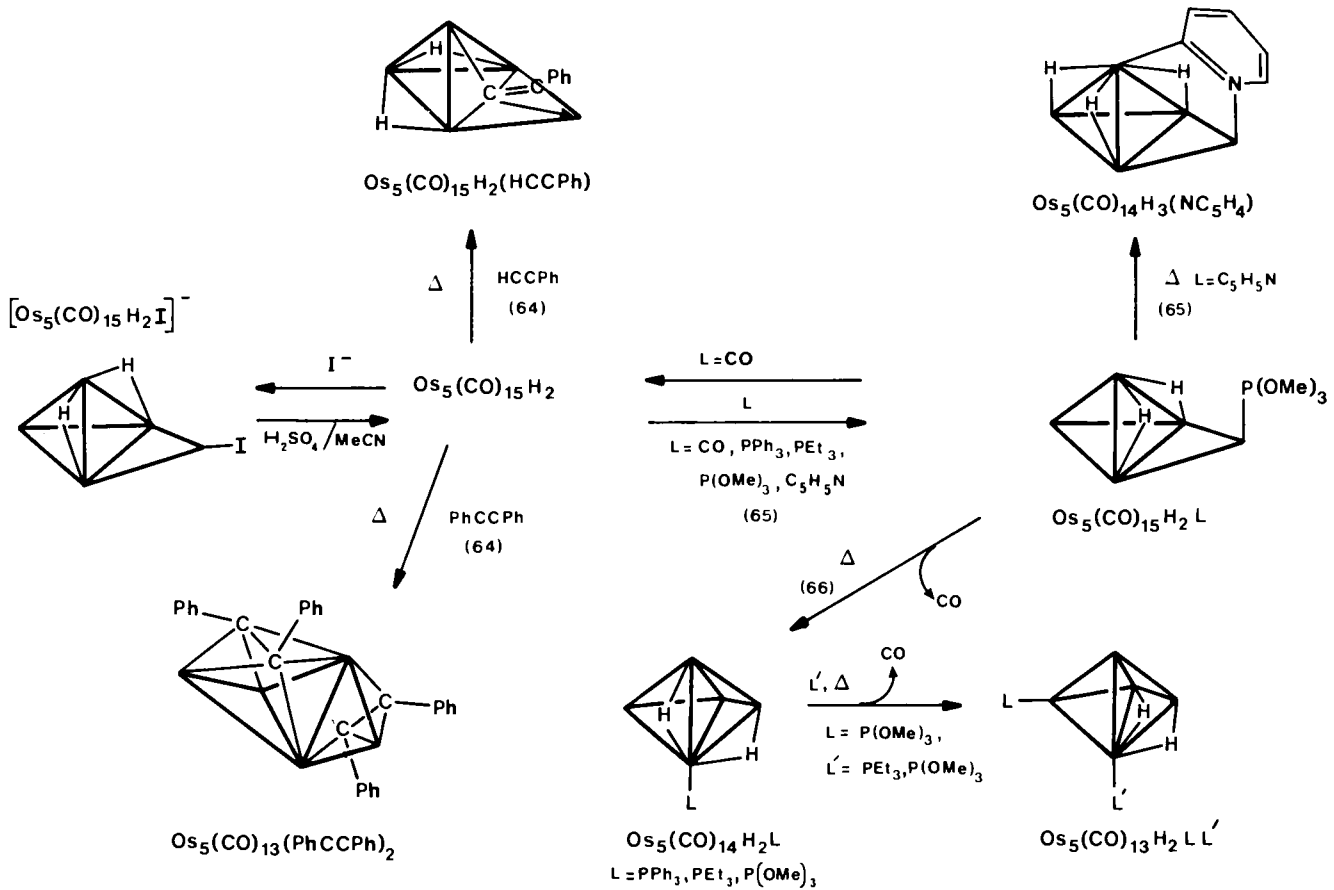
For example, the thermal reactions of $Os_6(CO)_{18}$ with CO (*56*, *425*) and $P(OMe)_3$ (*56*, *98*, *392*) lead to the open "raft" species $Os_6(CO)_{21}$ and $[Os_6(CO)_{21-n}\{P(OMe)_3\}_n]$ ($n = 1$-6), respectively, probably by sequential bond fission in the bicapped tetrahedral cluster. As indicated in Scheme 21, under slightly different reaction conditions, elimination of an osmium vertex occurs, resulting in the formation of clusters containing a trigonal-bipyramidal metal framework. These react further with nucleophiles to give open Os_5 clusters and finally substituted triosmium species. Cluster unfolding has also beeen observed in the reactions of $Os_5(CO)_{15}H_2$ with a variety of nucleophiles (Scheme 22).

Certain ligands have been found to act as anchors by preventing cluster breakdown upon addition of nucleophiles. The acetylene-phosphido ligand in $Ru_5(CO)_{13}(\mu_5\text{-}CCPPh_2)(\mu\text{-}PPh_2)$, for example, allows extensive metal cluster rearrangement upon addition of two equivalents of CO (Scheme 23a) (*22*). Similarly, the square-based pyramidal clusters $Os_5C(CO)_{15}$ and $Ru_5(CO)_{13}(\mu_4\text{-}\eta^2\text{-}CCPh)(\mu\text{-}PPh_2)$ (*20*) are safely opened up through breakage of axial and equatorial edges, respectively, in order to accommodate a variety of nucleophiles, under mild conditions (Scheme 23b). It is interesting to note that the related compounds $Os_5S(CO)_{15}$ and $Os_5(CO)_{15}PPh$ do not react with halides or phosphines under similar reaction conditions (*428*). This behavior must reflect a difference in the bonding of the capping groups in these clusters compared with $Os_5C(CO)_{15}$. As shown in Fig. 9, the S and P atoms in $Os_5S(CO)_{15}$ and $Os_5(CO)_{15}P(OMe)$ interact only with the four atoms of the basal plane. This seems to impose rigidity on the Os_5 skeleton, preventing the opening up of the polyhedron exhibited by the carbido species or by $Ru_5(CO)_{13}(\mu_4\text{-}\eta^2\text{-}CCPh)(\mu\text{-}PPh_2)$ upon addition of nucleophiles.

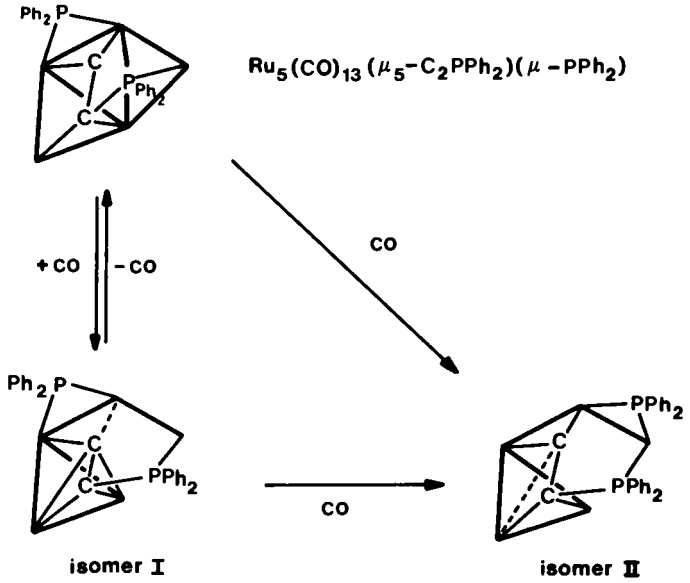
2. *Substitution Reactions*

a. Thermal Activation. The addition of a nucleophile L is sometimes followed by thermally induced dissociation of a carbonyl ligand with reformation of an M—M bond, resulting in the generation of a substituted derivative. Substitution via an associative process has been widely observed in the chemistry of HNCC of osmium. For example, $Os_5(CO)_{15}H_2\{P(OMe)_3\}$ looses CO under thermolytic conditions to give $Os_5(CO)_{14}H_2\{P(OMe)_3\}$ (Scheme 22). Subsequent CO substitution by PR_3 to give $Os_5(CO)_{13}H_2\{P(OMe)_3\}(PR_3)$ (R = Et, OMe) probably follows the same mechanism, although a more drastic polyhedral rearrangement during the course of the reaction has been invoked to explain the structure of the products (*66*).

For most HNCC, however, it is difficult to establish whether substitution occurs via an associative or dissociative mechanism due to the absence of

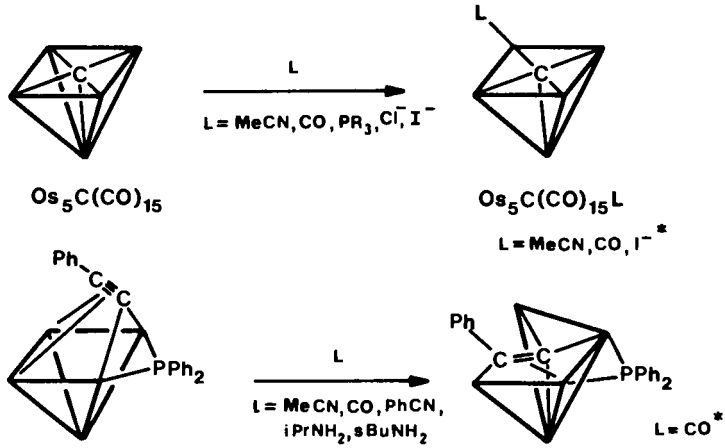


SCHEME 22. Reactions of $Os_5(CO)_{15}H_2$ with nucleophiles.



$Ru_5(CO)_{15}(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)$

a

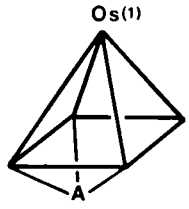


$Ru_5(CO)_{13}(\mu_4 - \eta^2\text{-}C_2Ph)(\mu\text{-}PPh_2)$ $Ru_5(CO)_{13}L(\mu_4 - \eta^2\text{-}C_2Ph)(\mu\text{-}PPh_2)$

b

* X-ray structures

SCHEME 23. Structural transformations of some M_5 clusters upon addition of nucleophiles.



$Os_5A(CO)_{15}$

A = C ; $Os_{(1)}$– C = 2.13, 2.09 Å *

A = S ; $Os_{(1)}$– S = 3.44 Å

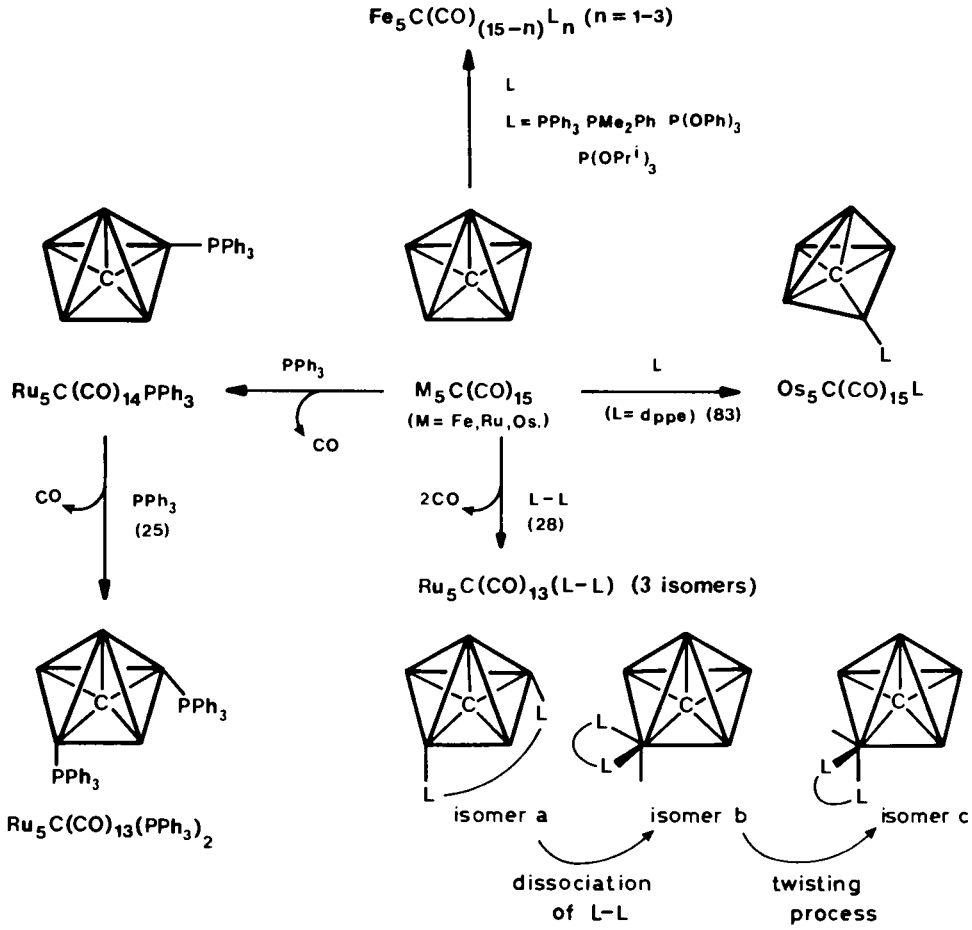
A = POMe; $Os_{(1)}$– P = 3.17 Å

FIG. 9. Distances between the apical Os atom and the capping atoms in $Os_5C(CO)_{15}$ (*434*), $Os_5S(CO)_{15}$ (*73*), and $Os_5(CO)_{15}(POMe)$ (71). Asterisk indicates that there are two independent $OS_5C(CO)_{15}$ molecules in the unit cell.

kinetic data and the infrequent isolation of the intermediates. The reactions of $Ru_5C(CO)_{15}$ with PPh_3 and diphosphines (diphos), for example, proceed directly to give the substituted species $Ru_5C(CO)_{(15-n)}(PPh_3)_n$ ($n = 1, 2$) (*25*) and $Ru_5C(CO)_{13}$(diphos) (*28*), respectively, no intermediate adducts having been detected. By analogy with $Os_5C(CO)_{15}$, the $Ru_5C(CO)_{15}$ cluster is nevertheless believed to react via an associative mechanism (Scheme 24).

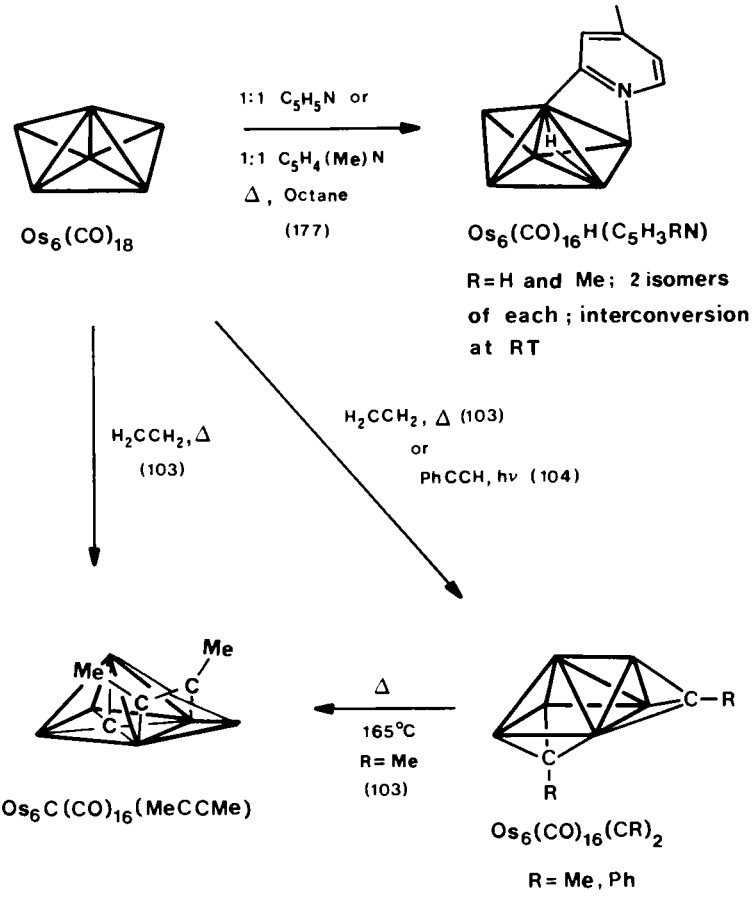
Ligand reorganization on the cluster surface induced by thermolysis is a common process. The pyridine ligand in $Os_5(CO)_{15}H_2(C_5H_5N)$ (*177*) and $Os_5C(CO)_{15}(C_5H_5N)$ (*429*), for instance, undergoes ortho-metallation with hydrogen transfer to the metal core and ejection of a CO ligand from the clusters to give $Os_5(CO)_{14}H_3(C_5H_4N)$ and $Os_5C(CO)_{14}(H)(C_5H_4N)$, respectively. A similar mechanism has been proposed for the formation of $Os_6(CO)_{16}(H)(C_5H_3RN)$ (R = H, Me) (*177*) from the reactions of $Os_6(CO)_{18}$ with pyridine and picoline, respectively, in apolar solvents (Scheme 25). Under the extreme conditions used for CO substitution in $Os_6(CO)_{18}$ by acetylenes, even more drastic modifications have been observed in the ligands attached to the cluster. These changes may have involved splitting of a C—C bond in the organic fragment, and possibly of the C—O bond of the carbonyl leading to carbide formation (Scheme 25).

Among the cobalt subgroup, only the $M_6(CO)_{16}$ (M = Rh, Ir) clusters have been shown to react with phosphines and related nucleophiles (*396*) to afford substituted products (Scheme 26). Facile replacement of four carbonyl ligands by $P(OR)_3$ (R = Ph, Me) has been achieved in both systems (*176*, *239*) but the substitution of a fifth ligand was observed only for the less bulky $P(OMe)_3$ ligand giving $Ir_6(CO)_{11}\{P(OMe)_3\}_5$ (*240*). Attempts at further substitution in the rhodium systems gave only breakdown products, unless the reaction was performed under vacuum and with stoichiometric amounts of $P(OMe)_3$ or 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (ETPO) in which case a sixth CO could be substituted (*391*). Similarly a maximum of six carbonyl ligands was substituted in the reactions of $Rh_6(CO)_{16}$ with



Isomerization process of $Ru_5C(CO)_{13}(L-L)$	
L–L	
dppm	c ⇌ b
dppe	c(solution) ⇌ b(solid state)
dppp	c ⇌ b ← a
dppb	a ← c ⇌ b

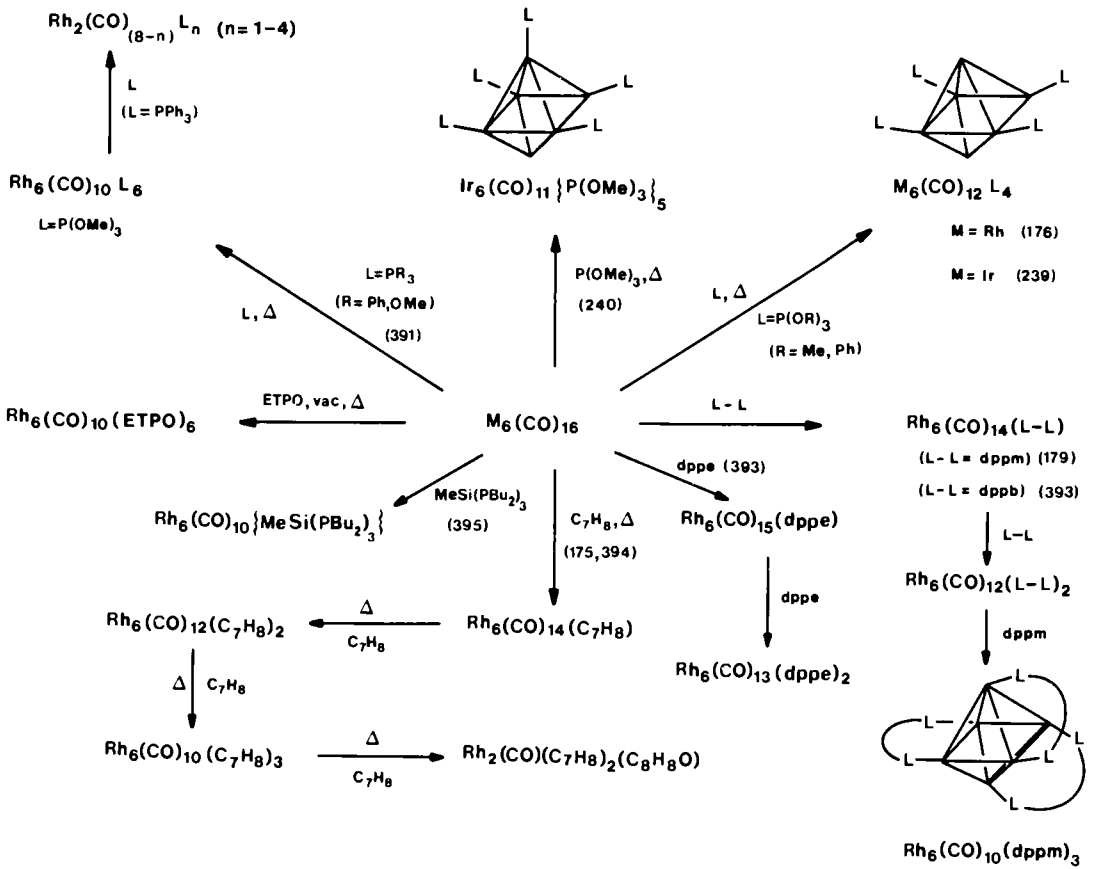
SCHEME 24. Reactions of $M_5C(CO)_{15}$ (M = Fe, Ru, Os) with phosphines and diphosphines and the mechanism of isomerization of the $Ru_5C(CO)_{13}(L-L)$ species (L–L = dppm, dppe, dppp, and dppb).



SCHEME 25. Reactions of $Os_6(CO)_{18}$ with C_5H_4RN (R = H, Me), PhCCH, and CH_2CH_2 under thermolytic conditions.

dppm (*179*) or norbonadiene (*175*, *394*), but breakdown to a rhodium dimer also occurred if further substitution was attempted.

Generally, second-row metal clusters do not need to be thermally activated to afford CO substitution. The degree of substitution in these clusters therefore can often be controlled by kinetic factors, such as concentration and ratio of the reagents as well as reaction times. In this way high yields of each compound in the series $Ru_6C(CO)_{(17-n)}\{P(OMe)_3\}_n$ (n = 1-4) (*52*) and $Rh_6(CO)_{(16-2n)}(L\text{-}L)_n$ (n = 1, 2, 3, L-L = dppm) (*179*) have been obtained. For HNCC of the heavier metal atoms, however, thermal activation must be employed. Because the temperatures necessary to activate CO substitution



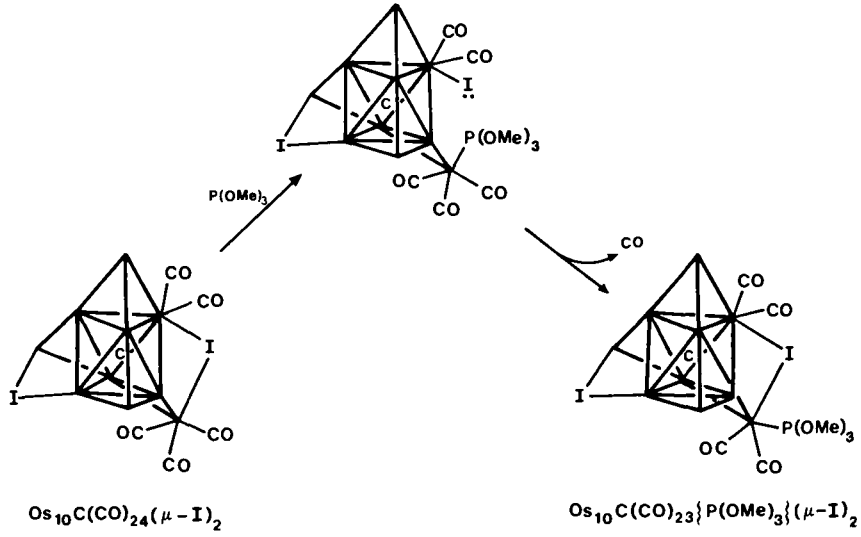
SCHEME 26. Reactions of $M_6(CO)_{16}$ (M = Rh, Ir) with phosphines, diphosphines, and norbornadiene. ETPO, 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane.

often lead to degradation of the desired products, these are obtained in low yields. Photochemical activation has been applied with relative success only in isolated cases and is still an open field in HNCC chemistry. Chemical activation of osmium clusters has given spectacular results. The methods used for this purpose discussed below have great potential in the investigation of the chemistry of HNCC of rhenium and iridium.

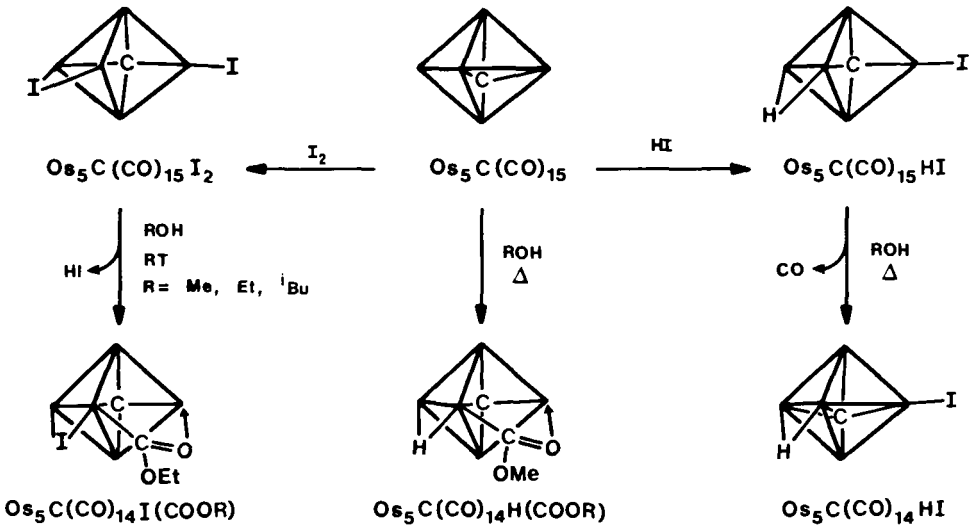
b. Chemical Activation. Basically three strategies have been employed to activate HNCC of osmium in the reactions with nucleophiles.

i. Introduction of ligands, such as nitrosyl, halogens, and thiols, that can exhibit more than one oxidation state. A bridging halogen, for example, acts as a three-electron donor and can convert to a terminal one-electron donor; through this process of bridge opening, a vacant site may be created on one metal atom. Such a mechanism has been proposed in the reaction of $[Os_{10}C(CO)_{24}(\mu\text{-}I)_2]$ with $P(OMe)_3$ (Scheme 27). (*133*). Activation can also occur through charge polarization in the molecule caused by the ligand, which may direct the nucleophilic attack as well as reduce the activation energy for the process. One example is the reaction of $Os_5C(CO)_{15}I_2$ with alcohols to give $Os_5C(CO)_{14}(COOR)I$. This reaction needs much milder conditions that the analogous reaction of $Os_5C(CO)_{15}$ to give $Os_5C(CO)_{14}(H)(COOR)$ (*79*) (Scheme 28).

ii. Synthesis of coordinatively unsaturated species. A series of unsaturated hexaosmium compounds has recently been reported (*313*, *330*). The key



SCHEME 27. Substitution of CO by $P(OMe)_3$ in $Os_{10}C(CO)_{24}(\mu\text{-}I)_2$.

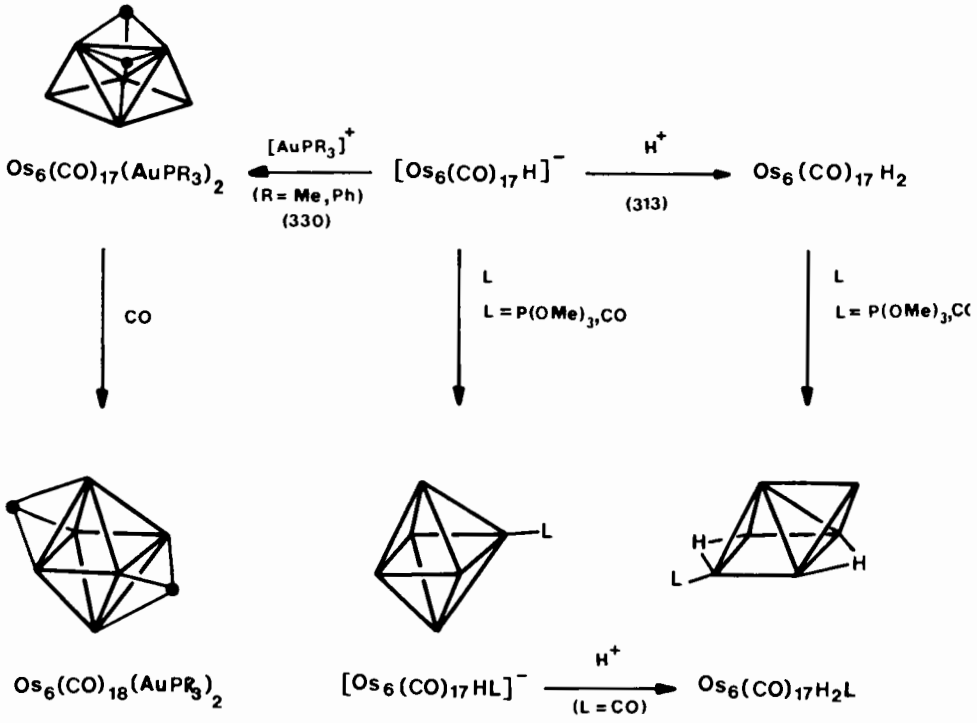


SCHEME 28. Chemical activation of $Os_5C(CO)_{15}$ by iodine ligand towards ROH addition.

species, $[Os_6(CO)_{17}H]^-$, was prepared from $Os_6(CO)_{18}$ by oxidation of a carbonyl ligand with trimethylamine oxide (see Section III,C,2); the neutral 84-electron species $Os_6(CO)_{17}H_2$ and $Os_6(CO)_{17}(AuPR_3)_2$ (R = Me, Ph) were obtained by addition of H^+ and $AuPR_3^+$ fragments, respectively, to the monoanion. These three bicapped tetrahedral compounds isoelectronic with $Os_6(CO)_{18}$ all add 2-electron donor ligands such as CO and PR_3 to afford 86-electron species (Scheme 29).

Other examples of formally unsaturated clusters are provided by the series $Os_4(CO)_{12}(AuYR_3)$ (Y = P, As; $R_3 = Et_3$, Ph_2Me, Ph_3) (*328*). Some of their reactions are depicted in Scheme 30. A parallel can be drawn between these unsaturated clusters and $Os_3(CO)_{10}H_2$, which has been used for the synthesis of a multitude of Os_3 derivatives.

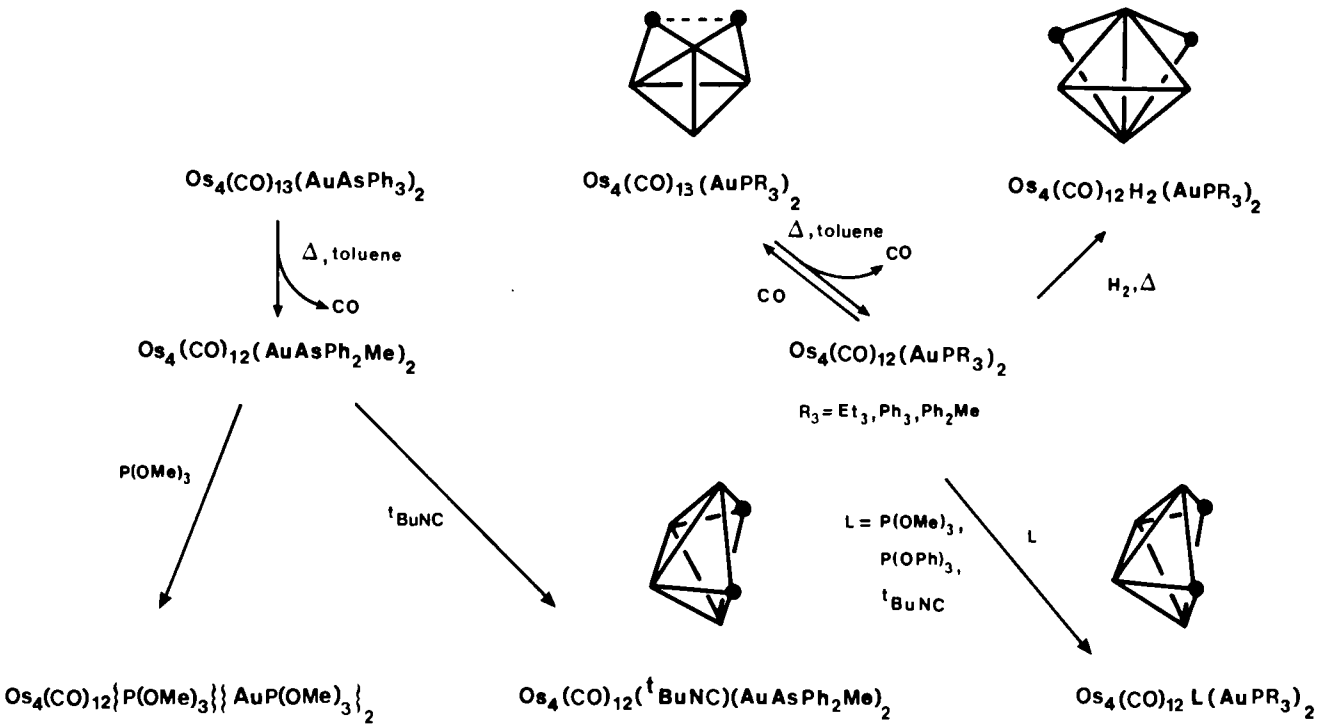
iii. Synthesis of species containing ligands which can be displaced more easily than CO. This is also an extension of the technique employed to activate $Os_3(CO)_{12}$ and has been widely used in Os_6 chemistry. When oxidative displacement of carbon monoxide from $Os_6(CO)_{18}$ and $Os_5(CO)_{16}$ by trimethylamine oxide is carried out in the presence of acetonitrile, the substituted products $Os_6(CO)_{17}(MeCN)$, $Os_6(CO)_{16}(MeCN)_2$ (*97*, *118*), and $Os_5(CO)_{15}(MeCN)$ (*92*) are isolated in good yields. The acetonitrile derivatives of the raft "$Os_6(CO)_{21}$" species $Os_6(CO)_{(21-n)}(MeCN)_n$ (n = 1, 2) have alternatively been synthesized by condensation of $Os_3(CO)_{10}(MeCN)_2$ using $PdCl_2$ (*99*).



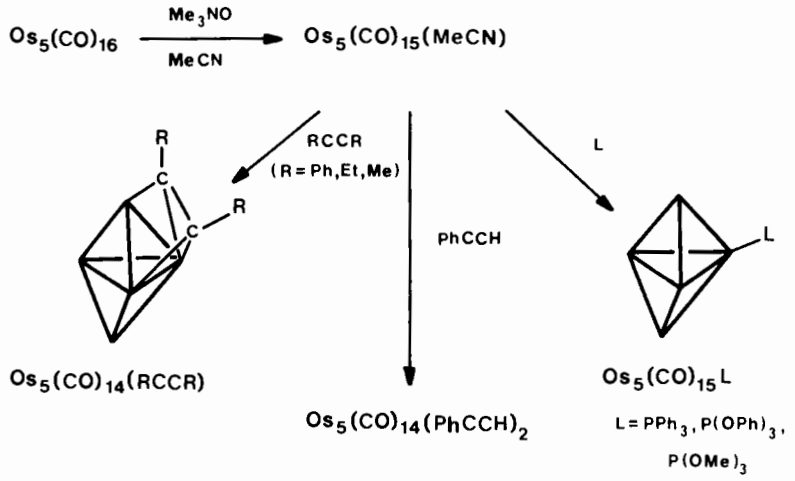
SCHEME 29. Reactions of $[Os_6(CO)_{17}H]^-$, $Os_6(CO)_{17}H_2$, and $Os_6(CO)_{17}(AuPR_3)_2$ (R = Me, Ph) with PR_3 and CO.

The reactions involving nucleophilic displacement of MeCN in the species $Os_5(CO)_{15}(MeCN)$, $Os_6(CO)_{(18-n)}(MeCN)_n$ ($n = 1, 2$), and $Os_6(CO)_{(21-n)}(MeCN)_n$ ($n = 1, 2$) have been studied extensively (Schemes 31, 32, and 33).

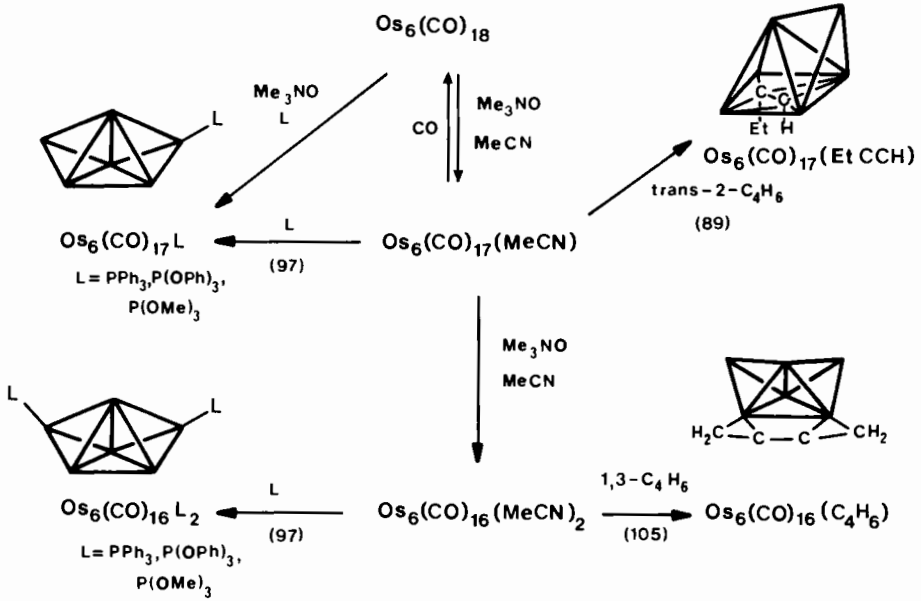
Facile substitution of the MeCN ligand by a variety of trisubstituted phosphines has been observed for the three systems with no structural changes in the metal geometry. The reactions of the raft $Os_6(CO)_{20}(MeCN)$ with primary and secondary phenylphosphines (*93*) show a pattern similar to those reported for $Os_3(CO)_{11}(MeCN)$ (*442*); initial substitution of MeCN by PPh_2H and $PPhH_2$ is followed by hydrogen transfer to the metal frame. Consequently a change in the coordination mode of the phosphines occurs from terminal to μ_2-PPh_2 and μ_3-PPh, respectively. This process is induced by thermal activation. As a result, unpredictable modifications in the phosphido-substituted Os_6 polyhedra, including cluster close-up with CO ejection or cluster breakdown, have been shown to occur (Scheme 33).



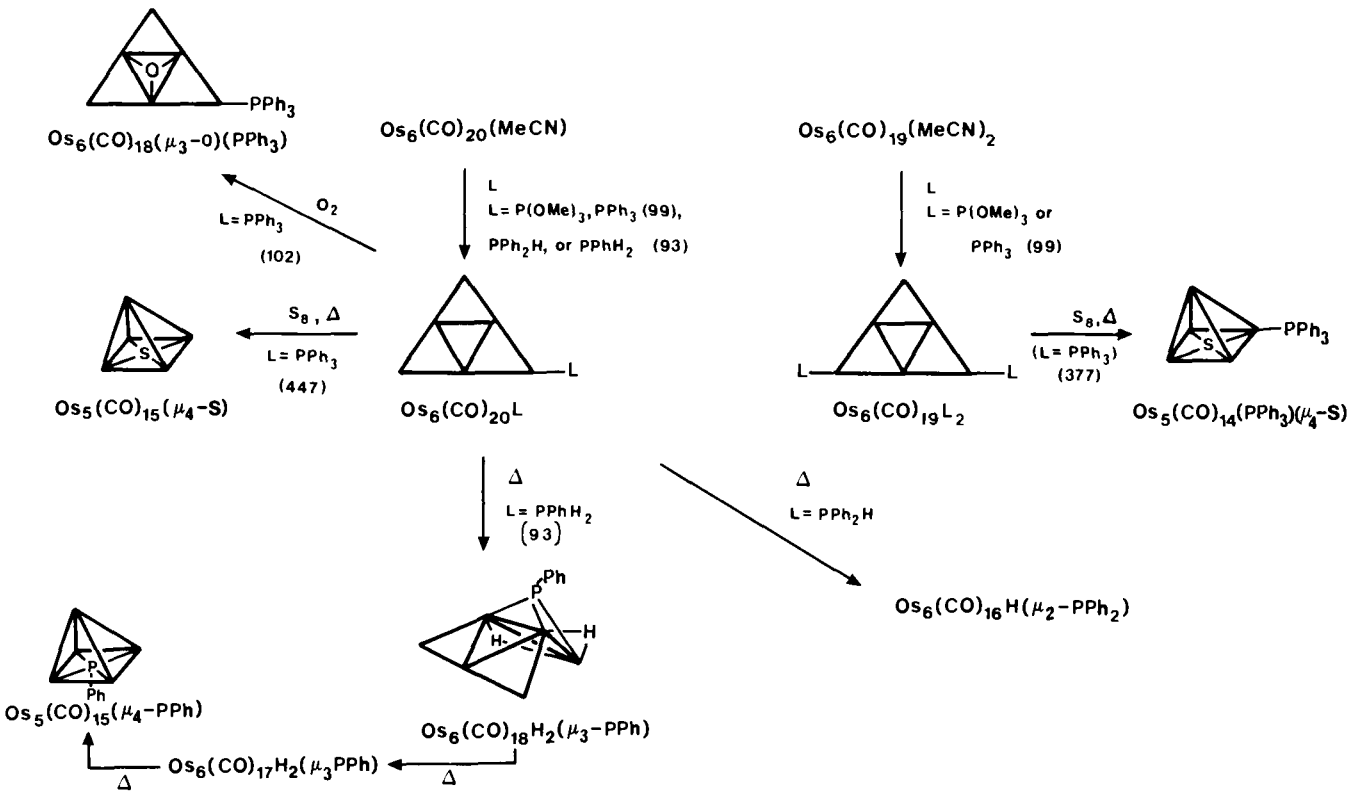
SCHEME 30. Reactions of the unsaturated clusters $Os_4(CO)_{12}(AuZR_3)_2$ (Z = P, As) (*328*).



SCHEME 31. Reactions of $Os_5(CO)_{15}(MeCN)$ with nucleophiles (*69*).



SCHEME 32. Reactions of $Os_6(CO)_{(18-n)}(MeCN)_n$ ($n = 1, 2$) with nucleophiles.



SCHEME 33. Reactions of $Os_6(CO)_{20}(MeCN)$ and $Os_6(CO)_{19}(MeCN)_2$ with phosphines.

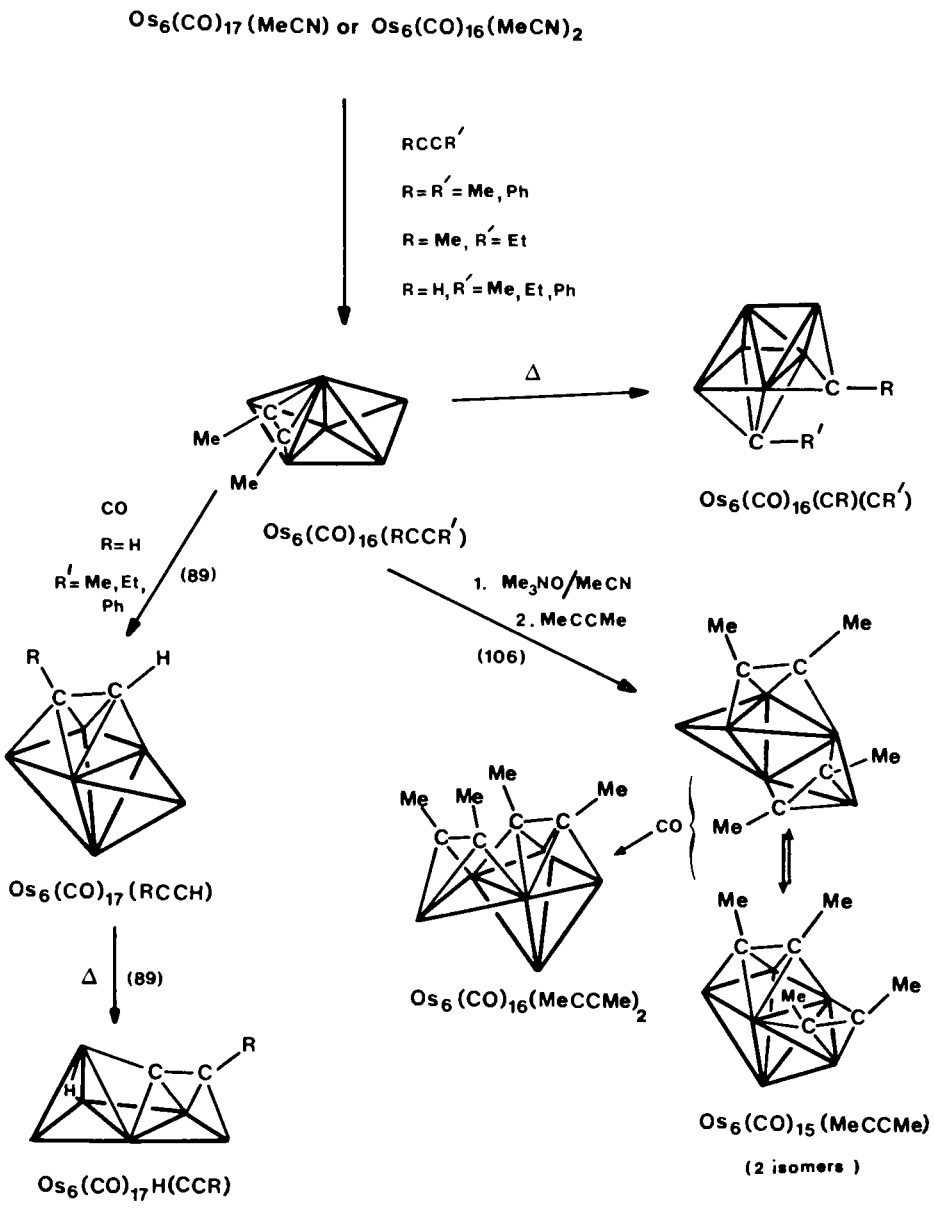
Reactions of $Os_6(CO)_{(18-n)}(MeCN)_n$ ($n = 1, 2$) with a variety of acetylenes have also been investigated. Generally, analogous reactions of this species and $Os_6(CO)_{18}$ have been found to give similar final products. However, as a result of the much milder conditions employed in the reactions of the acetonitrile derivative, intermediates have been isolated, allowing a better understanding of these reactions. For example, the reactions of $Os_6(CO)_{(18-n)}(MeCN)_n$ ($n = 1, 2$) with RCCR′ (R = R′ = Me, Ph; R = Me, R′ = Et) and RCCH (R = Me, Et, Ph) (*89*) have been shown to lead initially to substitution of MeCN and CO ligands to give the 84-electron species $Os_6(CO)_{16}(RCCR')$ and $Os_6(CO)_{16}(RCCH)$ with the same bicapped tetrahedron of osmium atoms as the starting material (Scheme 34). Upon heating $Os_6(CO)_{16}(RCCR')$, a two-electron reduction occurs as a consequence of the change in the donor properties of the acetylene upon splitting. The structural rearrangement that follows results in the formation of the capped square-based pyramidal cluster $Os_6(CO)_{16}(CR)_2$, which was previously isolated from the thermolytic reaction of $Os_6(CO)_{18}$ and ethylene (*103*) (Scheme 25).

Oxidative displacement of another CO ligand by trimethylamine oxide in $Os_6(CO)_{16}(MeCCMe)$ in the presence of acetonitrile has also been described (*106*). Subsequent substitution of the MeCN ligand in $Os_6(CO)_{15}(MeCN)$-$(MeCCMe)$ with dimethylacetylene gave $Os_6(CO)_{15}(MeCCMe)_2$. This cluster was shown by X-ray crystallography to exist in two interconvertible isomeric forms, one of which exhibits a capped square based pyramidal arrangement of metal atoms, while the other has an edge-bridged trigonal-bipyramidal metal core (Scheme 34).

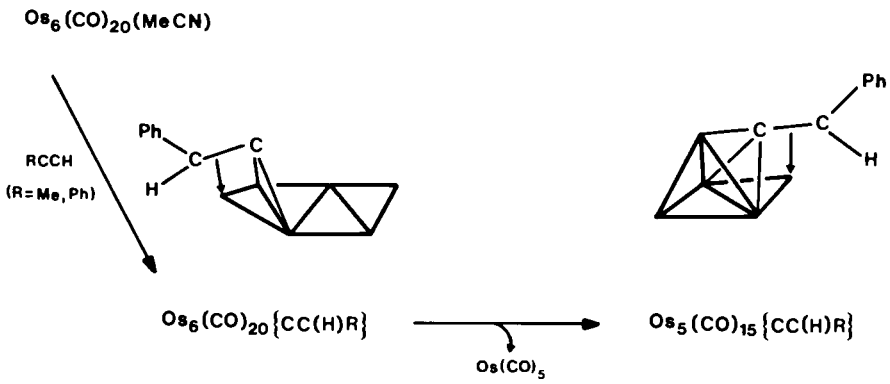
The terminal acetylene derivatives $Os_6(CO)_{16}(RCCH)$ (R = Me, Et, Ph) have been shown to react with CO to give $Os_6(CO)_{17}(RCCH)$, (*89*), in which the acetylene ligand is still intact and sits on the base of the capped pyramidal osmium polyhedron. This compound was found to convert by the action of heat to an isomer in which the proton from the acetylene has been transferred to the metal array. The process is accompanied by an opening up of the metal cluster (Scheme 34).

A different type of C—H bond activation has been observed upon substitution of MeCN in the raft $Os_6(CO)_{20}(MeCN)$ with phenylacetylene (*70*). X-ray analysis of $Os_6(CO)_{20}\{CC(H)Ph\}$ has revealed that a $1 \rightarrow 2$ hydrogen shift has occurred in this system to give a vinylidine ligand with a coordination mode similar to the one exhibited by the CCH_2 fragment on Pt (1:1:1) surfaces (*431*). This process was accompanied by reorganization of the raft Os_6 framework. Ejection of $Os(CO)_5$ from this cluster was found to occur upon heating to afford $Os_5(CO)_{15}\{CC(H)Ph\}$ (*70*) (Scheme 35).

The ligand 1,2-Cyclooctadiene (COD) has also been found to be as good a leaving group in HNCC as it is in $Os_3(CO)_{10}(COD)$. For example, substitution of one COD ligand in $Os_6(CO)_{16}(PtCOD)_2$ has been reported to occur



SCHEME 34. Reactions of $Os_6(CO)_{(18-n)}(MeCN)_n$ ($n = 1, 2$) with acetylenes RCCR′.

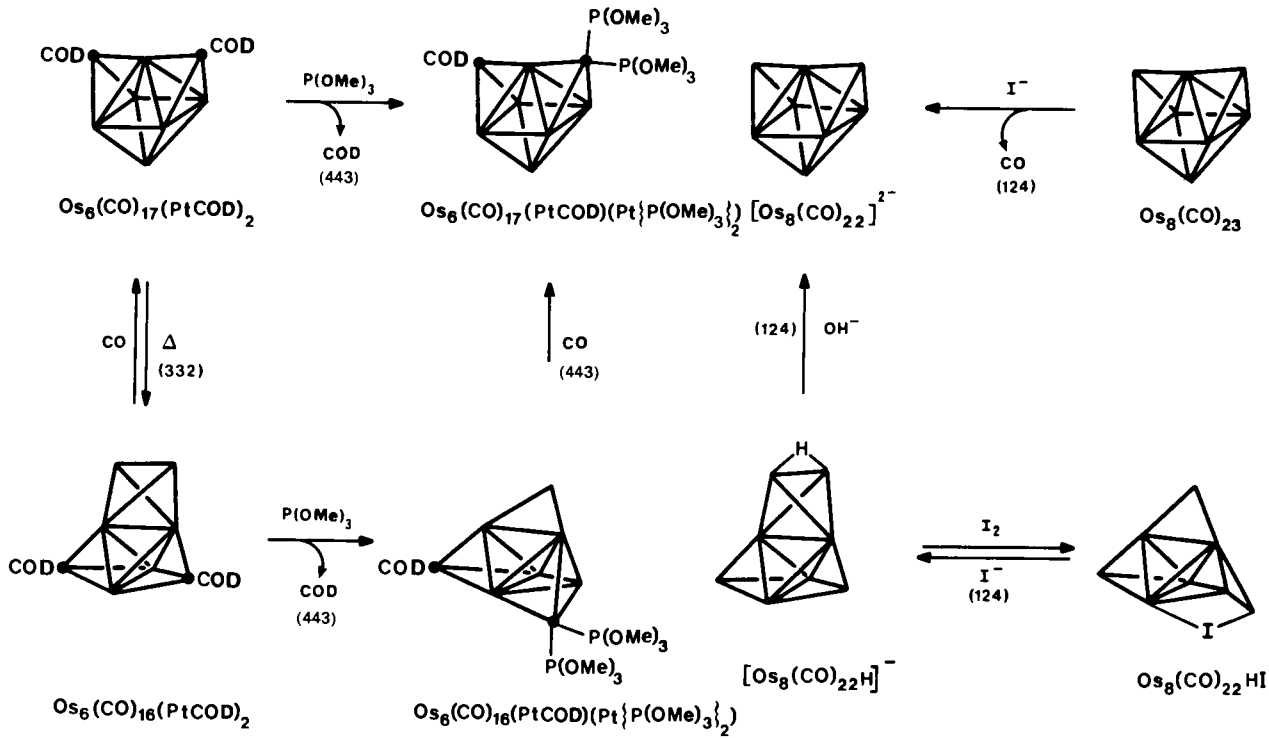


SCHEME 35. Reactions of $Os_6(CO)_{20}(MeCN)$ with RCCH (R = Me, Ph) (*70*).

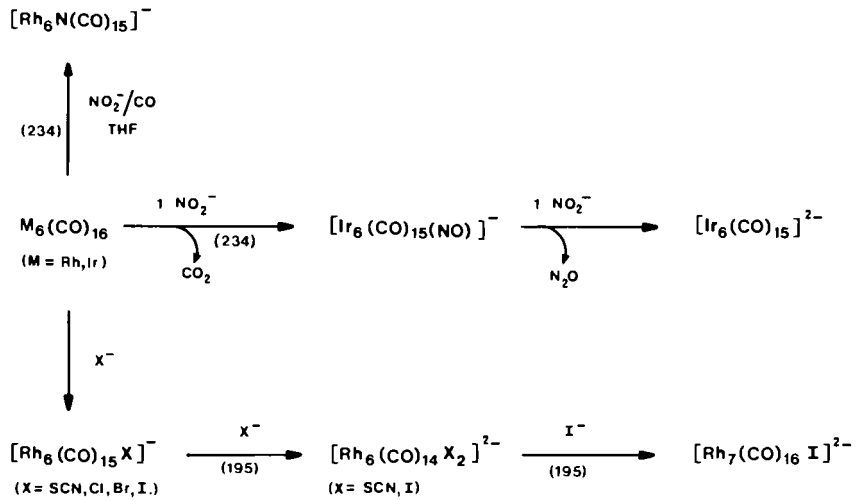
with $P(OMe)_3$, affording $Os_6(CO)_{16}(PtCOD)(Pt\{P(OMe)_3\}_2)$. (*443*). Although this process involves no change in the cluster electron count, it results in a rearrangement of the metal polyhedron (Scheme 36). The two Os_6Pt_2 species react readily with CO to yield $Os_6(CO)_{17}(PtCOD)_2$ and $Os_6(CO)_{17}(PtCOD)(Pt\{P(OMe)_3\}_2)$, respectively. Interestingly, substitution of a COD ligand by two $P(OMe)_3$ groups in $Os_6(CO)_{17}(PtCOD)_2$ is not accompanied by any drastic polyhedral change. As indicated in Scheme 36, the structural flexibility observed in this system is reminiscent of that previously observed in the Os_8 clusters (*124*).

3. Reactions with Halides and Nitrides

The reactions of HNCC with the nucleophiles X^- and $[NO_2]^-$ are treated separately because they may either lead to the formation of reduced species, as discussed in Section III,B, or follow the same trends as the reactions with CO and PR_3 discussed above. The outcome of the reaction seems to depend on the nature of the individual cluster considered. For example, simple addition of iodide with opening up of the metal polyhedron has been observed in the formation of $[Os_5C(CO)_{15}I]^-$ and $[Os_5(CO)_{15}H_2I]^-$ (*65*, *76*) from $Os_5C(CO)_{15}$ and $Os_5(CO)_{15}H_2$, respectively. Alternatively, reaction of this nucleophile with $Rh_6(CO)_{16}$ results in the formation of the substituted products $[Rh_6(CO)_{15}I]^-$ and $[Rh_6(CO)_{14}I_2]^{2-}$ (Scheme 37). In contrast, the binary carbonyls $Os_m(CO)_n$ ($m = 6, 7, 8$; $n = 18, 21, 23$) are reduced to their respective dianions (Section II,C,2), while the hydrido clusters $Os_m(CO)_nH_2$ ($m = 6, 7, 8$; $n = 18, 20, 22$) are deprotonated by halides (Section II,B).



SCHEME 36. Structural transformations of the Os_6Pt_2 and Os_8 polyhedra.



SCHEME 37. Reactions of $M_6(CO)_{16}$ (M = Rh, Ir) with NO_2^- and I^-.

Similarly, the reactions of neutral HNCC with $[NO_2]^-$ are complex (*460*). They have often been found to produce nitrosyl-substituted species according to Eq. (39) (*432*).

$$M_m(CO)_n + [NO_2]^- \longrightarrow [M_m(CO)_{(n-2)}(NO)]^- + CO_2 + CO \qquad (39)$$

Substitution of two carbonyls by a linear nitrosyl and a negative charge were observed in the reaction of $Ru_6C(CO)_{17}$ with $[NO_2]^-$, which yields $[Ru_6C(CO)_{15}(NO)]^-$ (*44*). In contrast, the $[NO_2]^-$ reactions of $M_6(CO)_{16}$ (M = Rh, Ir) follow different patterns. The monoanion $[Ir_6(CO)_{15}(NO)]^-$ is the product of the reaction of $Ir_6(CO)_{16}$ with one equivalent of $[NO_2]^-$; it reacts further with more $[NO_2]^-$ to give the reduced species $[Ir_6(CO)_{15}]^{2-}$ (*234*) (Scheme 37). The product of the reaction of $Rh_6(CO)_{16}$ with $[NO_2]^-$ under CO, however, is the nitrido species $[Rh_6N(CO)_{15}]^-$, formed via deoxygenation of NO and expulsion of CO_2 (*234*).

F. Oxidative Addition of the Small Molecules H_2, I_2, and HX

The reactions of HNCC with H_2, I_2, or HX (X = Cl, Br, I, SEt, SH, SeH) to give products of unchanged nuclearity may result in the oxidative addition of these molecules to M—M bonds. For example, the pentanuclear clusters

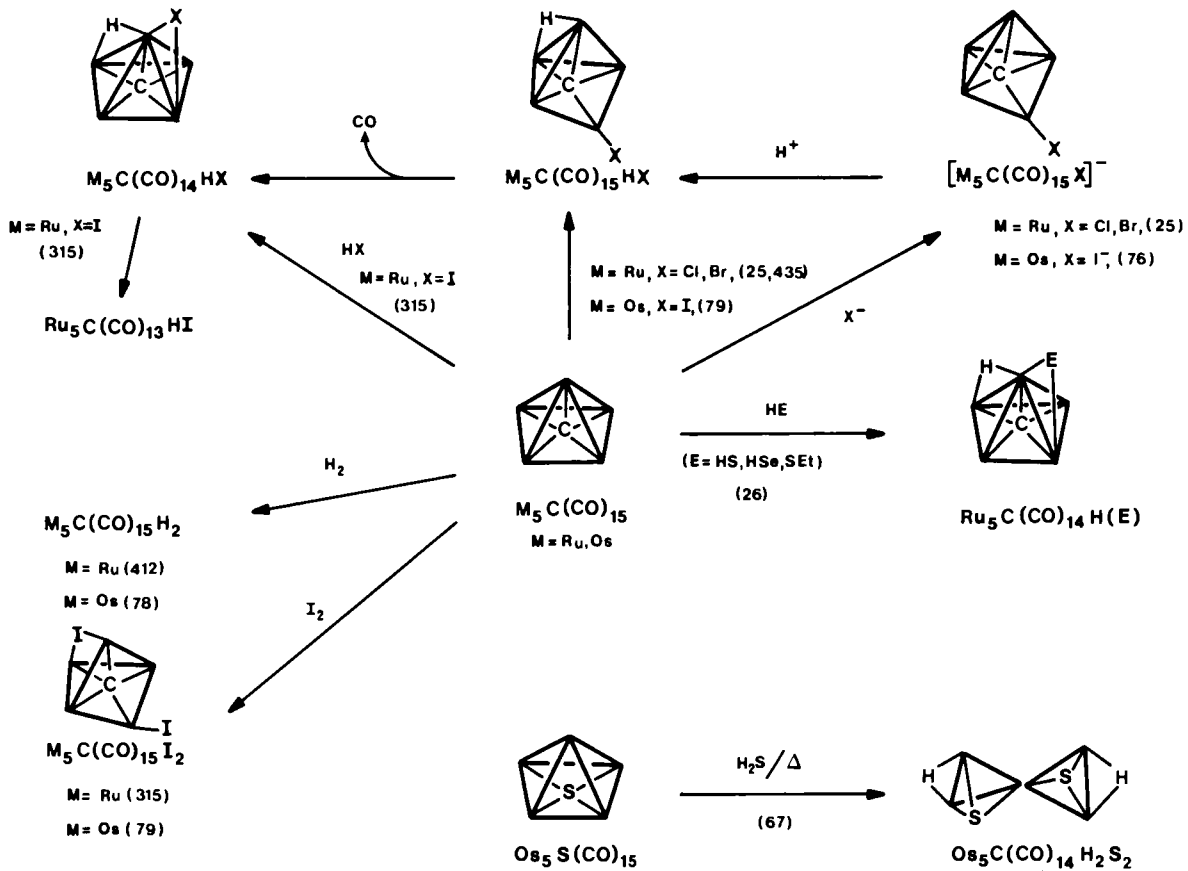
$M_5C(CO)_{15}$ have been shown to react with HX (M = Ru, X = Cl, Br; M = Os, X = I), H_2, and I_2 to yield $M_5C(CO)_{15}HX$, $M_5C(CO)_{15}H_2$, and $M_5C(CO)_{15}I_2$, respectively (Scheme 38). The structures of the $Ru_5C(CO)_{15}HX$ derivatives were elucidated by solid-state infrared spectroscopy (*435*). It has been shown that the metal–carbon stretching modes of carbido clusters give rise to absorptions of high intensity, which reflect the symmetry of the carbido environment (*9*, *149*, *416*, *424*). In this case analysis of the vibrational modes associated with ruthenium–carbido and ruthenium–halogen stretching indicated that the five metal atoms in the compounds $Ru_5C(CO)_{15}HX$ (X = Cl, Br) adopt a bridged butterfly arrangement with a terminally bound halide, analogous to the anion $[Os_5C(CO)_{15}I]^-$, the structure of which has been determined by X-ray crystallography. Furthermore, consideration of the ruthenium–hydrido stretching frequencies in these complexes has led to the suggestion that the hydrogen ligand occupies a μ-bridging position across the shortest Ru—Ru bond in each cluster.

The hydrohalogenated compounds $M_5C(CO)_{15}HX$, which have also been obtained from the reactions of $M_5C(CO)_{15}$ with halides followed by protonation, have been shown to lose CO upon heating to give the species $M_5C(CO)_{14}HX$.

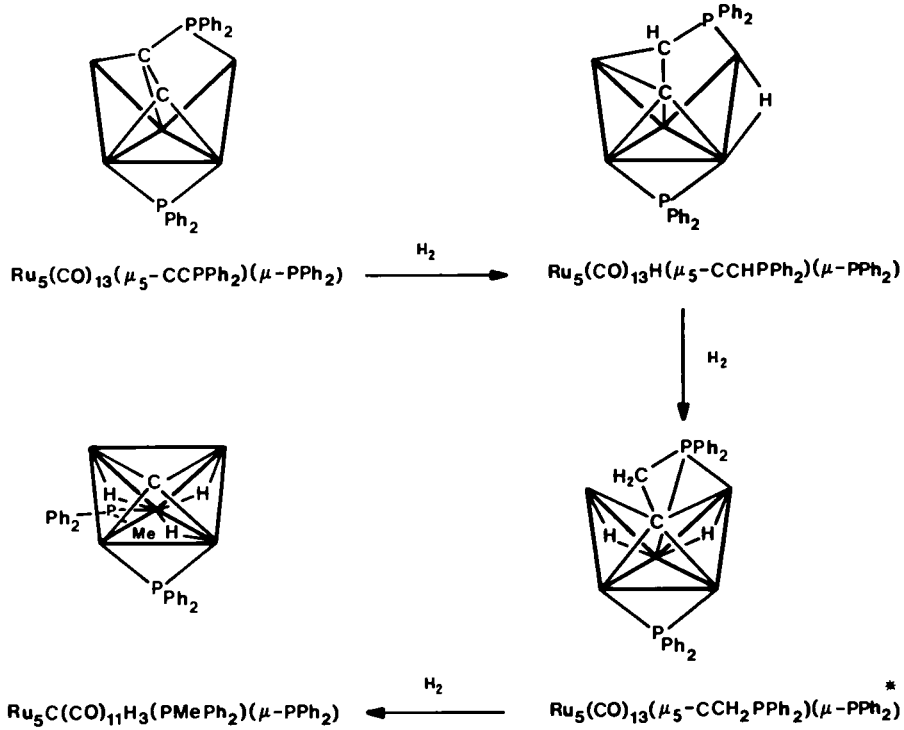
In the reactions of $M_5C(CO)_{15}$ with HX (M = Ru, X = SEt, SH, and SeH; M = Os, X = SH), the adduct $M_5C(CO)_{15}HX$ was isolated for M = Os. Upon heating $Os_5C(CO)_{15}H(SH)$, dissociation of a CO ligand was found to occur to give $Os_5C(CO)_{14}H(SH)$, a compound analogous to $Ru_5C(CO)_{14}HX$ (X = SEt, SH, SeH), the first-formed products in the reactions of $Ru_5C(CO)_{15}$. As shown in Scheme 38, ejection of CO is accompanied by the formation of a sulfur or selenium bridge (*26*).

In contrast, reaction of the sulfido cluster $Os_5S(CO)_{15}$ with H_2S gave the bisulfido compound $Os_5(CO)_{14}H_2S_2$ with a "bow tie" metal atom arrangement capped by sulfur atoms. Hydrogen transfer from the SH group to the metal atoms is probably a result of the forcing conditions employed for this reaction (*67*).

Reaction may also occur at a ligand. For example, hydrogenation of an acetylide ligand on a ruthenium cluster surface has also been reported (*19*). The reaction of $Ru_5(CO)_{13}(\mu_5\text{-}CCPPh_2)(\mu\text{-}PPh_2)$ with H_2 (1 atm) proceeds stepwise with absorption of three molecules of H_2 and successive formation of pentanuclear cluster complexes containing μ_5-vinylidene, -methylidene, and -carbide ligands (Scheme 39). Thus, the net reaction is the unusual conversion of the μ_5-$CCPPh_2$ ligand into carbon and $MePPh_2$. Under more forcing conditions (10 atm H_2), breakdown of $Ru_5(CO)_{13}(\mu_5\text{-}CCPPh_2)(\mu\text{-}PPh_2)$ to $Ru_4(CO)_{10}H_3(\mu_4\text{-}CCPPh_2)(\mu\text{-}PPh_2)$ has been observed (*436*).



SCHEME 38. Reactions of $M_5C(CO)_{15}$ (M = Ru, Os) and $Os_5S(CO)_{15}$ with HX (X = Cl, Br, I, SH, SEt, SeH).



SCHEME 39. Stepwise hydrogenation of $Ru_5(CO)_{13}(\mu_5\text{-}CCPPh_2)(\mu\text{-}PPh_2)$ (*19*). Asterisk indicates structures proposed on the basis of NMR spectroscopy.

IV. Concluding Remarks

The potential that HNCC offer is beginning to be realized. It is clear that they have properties and exhibit reaction patterns that differ markedly from their mononuclear counterparts and even low-nuclearity clusters. It is also apparent that their reactivity patterns may be rationalized in simplistic terms and thereby extended to other systems. However, much work remains to be done, particularly in designed synthesis and studies of reaction mechanisms. The ability of these clusters to combine with important small substrates such as CO and H_2 need also to be explored in much more detail. The study of the reactivity of large mixed-metal systems, which, as expected, exhibit enhanced and modified reactivities, equally requires more detailed investigation. In fact it would be useful to have available HNCC, which contain early and late transition metal elements, in order to combine both Lewis basic and Lewis

acidic properties in the same molecule. To date few examples of such systems have been reported.

In summary, despite the enormous effort that has been devoted to the synthesis and characterization of HNCC, there is a serious deficit in data related to their reactivity. Given the remarkable reactions that they are known to exhibit, efforts in this area are still needed and desirable.

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