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Review

The coordination chemistry of electron-rich alkenes (enetetramines)

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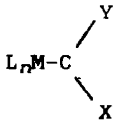
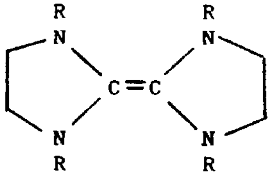
I. Introduction

In 1975 we reviewed for this Journal "The Coordination Chemistry of Bivalent Group IV Donors; Nucleophilic-Carbene and Dialkylstannylene Complexes" [1]. A major topic concerned (nucleophilic) carbenemetal complexes I, where M represents a transition metal and L_n the sum of all the other ligands, except the (nucleophilic) carbene moiety $\ddot{C}XY$ (X and/or Y being a dialkylamino group),

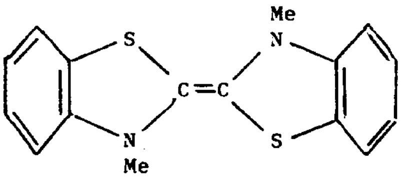


(I)

within the inner coordination sphere of M. The scope was restricted to those compounds I which are accessible directly from an organic precursor (the carbenoid), this having been the pivotal theme of our researches on carbenemetal complexes. Of the various methods for obtaining such complexes I, we had particularly studied those in which the carbenoid is the enetetramine II, or, more rarely, III.



(II) (abbreviated as $L^R{}_2$)



(III) [abbreviated as $(L_S^{Me})_2$]

The principal aim of this article is to bring up to date the story relating to the transition metal coordination chemistry of enetetramines II (and their syntheses, structures, and reactions, especially as reducing agents) and of the related compounds III–IX, VI–IX being optically active. Section II provides a summary of

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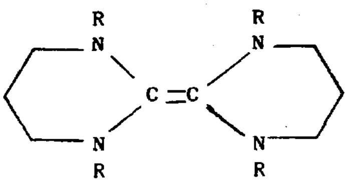
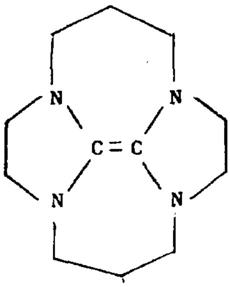
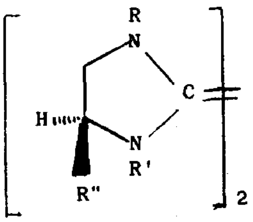


(IV) (abbreviated as L'^{R}_{2})

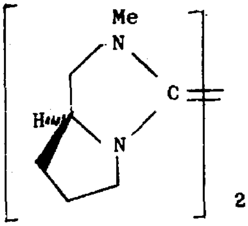


(V) (abbreviated as L^{cyclam}_{2})



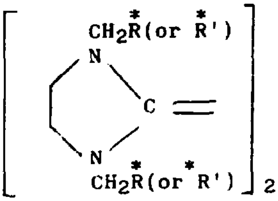
(abbreviated as $[R''\overset{*}{L}{}^{R,R'}]_2$)

(VI)

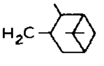


(abbreviated as $[\overset{*}{P}L^{Me}]_2$)

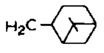
(VII)



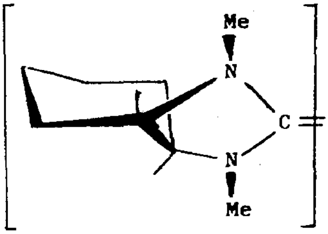
(VIIIa) $CH_2\overset{*}{R}$ = H_2C–



(VIIIb) $CH_2\overset{*}{R}'$ = H_2C–



(abbreviated as $[L^{CH_2\overset{*}{R}}]_2$) or $[L^{CH_2\overset{*}{R}'}]_2$



(IX)

(abbreviated as $[Cy\overset{*}{L}{}^{Me}]_2$

work published between 1975 and mid 1988, while Section III *briefly* outlines some unpublished work from our laboratories. The most recent comprehensive review of carbenemetal chemistry is that of ref. 2.

It is widely held (but see ref. 3) that bonding distinctions can be made between (i) "Fischer-type" complexes, of which the archetype is $[Cr(CO)_5\{C(OMe)Ph\}]$, and (ii) "Schrock-type", exemplified by $[Ta(CH_2Bu^t)_3\{C(Bu^t)H\}]$. This classification is useful, in that it draws attention to the fact that complexes (i) are formally derived from a (soft) nucleophilic carbene, and are susceptible to nucleophilic attack at C_{carb} (e.g., by OMe/NMe_2 exchange); whereas complexes (ii) are formally derived from a

(*Continued on p. 191*)

Table 1

Carbenemetal complexes from electron-rich alkenes

M^n	Complex	Ref.
Cr^0	$[Cr(CO)_5(L^R)]$ (R = Me or Et)	34, 48
	$[Cr(CO)_5(L'^{Me})]$	34
	$[Cr(CO)_4(L)(L^{Me})]$ (L = $AsPh_3$ or C(OMe)Me)	34
	cis- or *trans*-$[Cr(CO)_4(L^R)_2]$ (R = Me or Et)	34
	fac-$[Cr(CO)_3(L_2)(L^{Et})]$ (L_2 = $\{P(OPh)_3\}_2$, dmpe, or dppe)	47
	$[Cr(\eta\text{-}C_6H_6)(CO)_2(L^{Me})]$	34
Cr^I	$[Cr(CO)_4(L^{Et})_2][BF_4]$	47
	$[Cr(CO)_3(L_2)(L^{Et})][BF_4]$ (L_2 = $\{P(OPh)_3\}_2$, dmpe, or dppe)	47
	$[Cr(CO)_3(dmpe)(L^{Et})]Cl$	47
	$[Cr(CO)_3(dmpe)(L^{Et})_2(PPh_3)][BF_4]$	47
	$[Cr(CO)_2(dmpe)(L^{Et})(PPh_3)][BF_4]$	47
	$[Cr(CO)(dmpe)_2(L^{Et})][BF_4]$	47
Mo^0	$[Mo(CO)_5(L^R)]$ (R = Me, Et, Bu, or CH_2Ph)	23, 31, 47
	$[Mo(CO)_5(L'^{Me})]$	29, 31
	cis-$[Mo(CO)_4(L)(L^{Me})]$ (L = py, PPh_3, or C(OMe)Me)	29, 31
	$[Mo(CO)_4(L^{Et})(PCy_3)]$	29, 31
	cis- or *trans*-$[Mo(CO)_4(L^R)_2]$ (R = Me, Et, or CH_2Ph)	23, 29, 31, 54, 66
	fac-$[Mo(CO)_3(L_2)(L^{Et})]$ (L_2 = $\{P(OMe)_3\}_2$ or dppe)	29, 31
	$[MoCp(CO)(L^R)(NO)]$ (R = Me, CH_2Ph, or *p*-Tol)	29, 31
	$[MoCp(CO)(L'^{Me})(NO)]$	31
	$[Mo(I)_2(L^{Me})_2(NO)_2]$	1
Mo^{II}	$[Mo(I)_2(CO)_3(L^{Me})_2]$	29, 32
	$[Mo(X)_2(CO)_2(L^R)_2]$ (X = Cl, Br, or I; R = Me or Et)	29, 32
	$[Mo(OSO_2CF_3)_2(CO)_2(L^{Et})_2]$	10
W^0	$[W(CO)_5(L^R)]$ (R = Me, Et, or CH_2Ph)	32, 47
	$[W(CO)_5(L'^{Me})]$	32
	cis-$[W(CO)_4(L^R)_2]$ (R = Me, Et, or CH_2Ph)	32
	trans-$[W(CO)_4(L^{Me})_2]$	32
	fac-$[W(CO)_3(L^{Me})_3]$	32
	cis-$[W(CO)_4(L)(L^{Me})]$ (L = PBu_3, C(OEt)Me, or C(OEt)Ph)	32
	cis-$[W(CO)_4(L)(L^R)]$ (L, R = PBu_3, Me or PEt_3, Et)	32
	fac-$[W(CO)_3(L)(L^{Me})_2]$ (L = py or $P(OMe)_3$)	32
	fac-$[W(CO)_3(L^{Et})\{P(OR)_3\}]$ (R = Me or Ph)	32
W^{II}	$[W(X)_2(CO)_4(L^{Me})]$ (X = Br or I)	32
	$[W(I)_2(CO)_n(L^R)_2]$ (n = 2 or 3, R = Me or Et)	32
	$[L^{Et}\text{-}H][W(Br)_3(CO)_3(L^{Et})]$	1
Mn^I	$[Mn(\eta\text{-}C_5H_4Me)(CO)_2(L^{Me})]$	35
	fac-$[Mn(Br)(CO)_3(L^{Me})_2]$	35
Fe^{-II}	$[Fe(CO)(L^{Me})(NO)_2]$	35
	$[Fe(L^R)_2(NO)_2]$ (R = Me or CH_2Ph)	35
	$[Fe(L^{Me})(NO)_2(PPh_3)]$	35
Fe^0	$[Fe(CO)_4(L^R)]$ (R = Me, Et, or CH_2Ph)	35, 50, 55
	trans-$[Fe(CO)_3)(L^{Me})_2]$	35, 55
	trans-$[Fe(CO)_3(L)(L^{Me})]$ (L = PEt_3, PPh_3, PEt_2Ph, $PHPh_2$, $P(OPh)_3$, PCy_3, PMe_2Ph, $PMePh_2$, or $AsPh_3$)	35, 55, 65
	trans-$[\{Fe(CO)_3(L^{Me})\}_2(\mu\text{-}dppe)]$	35, 55

continued

Table 1 (continued)

M^n	Complex	Ref.
$\mathrm{Fe^I}$	$\mathrm{[Fe(CO)_3(L^{Me})_2][BF_4]}$	30, 55
	$\mathrm{[Fe(CO)_3(L)(L^{Me})[BF_4]}$ (L = $\mathrm{PEt_3}$, $\mathrm{PEt_2Ph}$, $\mathrm{PPh_3}$, $\mathrm{PHPh_2}$, or $\mathrm{P(OPh)_3}$)	30, 55
	$\mathrm{[Fe(CO)_2(L)(L^{Me})_2][BF_4]}$ (L = $\mathrm{PPh_3}$ or $\mathrm{P(OPh)_3}$)	55
	$\mathrm{[Fe(CO)_2(L)_2(L^{Me})][BF_4]}$ (L = $\mathrm{PEt_3}$, $\mathrm{PPh_3}$, or $\mathrm{P(OPh)_3}$)	30, 55
	$\mathrm{[Fe(CO)_2(L^{Me})(PEt_3)\{P(OPh)_3\}][BF_4]}$	55
	$\mathrm{[Fe(CO)(L^{Me})_2\{P(OPh)_3\}_2][BF_4]}$	55
	$\mathrm{[\{Fe(CO)_3(L^{Me})\}_2(\mu\text{-}dppe)][BF_4]_2}$	30, 55
	$\mathrm{[Fe(L^{Me})_2(NO)_2][BF_4]}$	55
	$\mathrm{[Fe(CN)(CO)_2(L^{Me})(PPh_3)]}$	55
	$\mathrm{[\{FeCp(CO)_3(L^R)\}_2]}$ (R = Me or Et)	35, 55
	$\mathrm{[(CO)_3FeC(L^{Me})C(R)Fe(CO)_3(PPh_2)]}$ (R = $\mathrm{Bu^t}$ or Ph)	42
	$\mathrm{[Fe(CO)_2(L^{Me})(C{\equiv}CBu^t)Fe(CO)_3(PPh_2)]}$	42
$\mathrm{Fe^{II}}$	$\mathrm{[Fe(I)_2(CO)_2(L^{Me})_2]}$	35
	$\mathrm{[Fe(Br)(\eta\text{-}C_3H_5)(CO)_2(L^{Me})]}$	55
$\mathrm{Ru^{-II}}$	$\mathrm{[Ru(L^{Et})(NO)_2(PPh_3)]}$	41
$\mathrm{Ru^0}$	$\mathrm{[Ru_3(CO)_{11}(L^{Et})]}$	35
	$\mathrm{[Ru(L^{Me})_4(NO)]Cl}$	41
	$\mathrm{[Ru(Cl)(L^{CH_2Ph})_2(NO)]}$	41
	$\mathrm{[RuCl(CO)(L^{CH_2Ph})_2(NO)]}$	41
	$\mathrm{[Ru(Cl)(L^{CH_2Ph})_2(NO)_2][BF_4]}$	1
$\mathrm{Ru^{II}}$	*trans*-$\mathrm{[Ru(Cl)_2(L^R)_4]}$ (R = Me, Et, or $\mathrm{CH_2Ph}$)	27, 40, 61
	$\mathrm{[Ru(Cl)_2(L^R)_3]}$ (R = Me or Et)	40
	$\mathrm{[Ru(I)_2(L^{Me})_3]}$	40
	cis-$\mathrm{[Ru(Cl)_2(CO)_2(L^{Me})_2]}$	40
	cis- and *trans*-$\mathrm{[Ru(Cl)_2(CO)(L^{Et})_3]}$	40
	trans-$\mathrm{[Ru(Cl)(CO)(L^{Me})_4]Cl}$	27, 40, 41
	trans-$\mathrm{[Ru(Cl)(L^{Me})_4(PF_3)]X}$ (X = Cl or $\mathrm{[BF_4]}$)	27, 40
	trans-$\mathrm{[Ru(Cl)(CO)(L^{Me})_2(py)_2]Cl}$	40
	$\mathrm{[Ru(Cl)(X)_2(L^{CH_2Ph})_2(NO)]}$ (X = Cl, Br, or I; or $\mathrm{X_2}$ = MeI)	41
	trans-$\mathrm{[Ru(Cl)(L^{Me})_4(NO)]X_2}$ (X = $\mathrm{[BF_4]}$ or $\mathrm{[ClO_4]}$)	41
	$\mathrm{[Ru(Cl)(L^{Tol\text{-}\mathit{p}})(PR_3)_2]}$ (R = Et or Ph)	28, 46, 61
	$\mathrm{[Ru(Cl)L^{Tol\text{-}\mathit{p}})(PPhR_2)_2]}$ (R = H, Et, or $\mathrm{Bu^i}$)	46
	$\mathrm{[Ru(I)(L^{Tol\text{-}\mathit{p}})(PPh_3)_2]}$	46
	$\mathrm{[Ru(Cl)(L^{Ph})(PR_3)_2]}$ R = Et or Ph	46
	$\mathrm{[Ru(Cl)(L^{Ph})(PBu_2Ph)_2]}$	46
	$\mathrm{[Ru(I)L^{Ph})(PPh_3)_2]}$	46
	$\mathrm{[Ru(Cl)(L^{An\text{-}\mathit{p}})(PPh_3)_2]}$	46
	$\mathrm{[Ru(Cl)(L^{Tol\text{-}\mathit{p}})(L^{Et})(PPh_3)]}$	28, 46
	$\mathrm{[Ru(Cl)(L^{Ar})(CO)(PR_3)_2]}$ (Ar = Ph and R = Et, Bu, or Ph; Ar = *p*-Tol and R = Et or Ph; Ar = *p*-An and R = Ph)	28, 46
	$\mathrm{[Ru(Cl)_2(L^{Tol\text{-}\mathit{p}})(NO)(PPh_3)]}$	46
	$\mathrm{[Ru(Cl)(L^{Tol\text{-}\mathit{p}})(NO)(PR_3)_2][PF_6]}$ (R = Et or Ph)	46
	$\mathrm{[Ru(Cl)(L^{Tol\text{-}\mathit{p}})(PF_3)(PR_3)]}$ (R = Et or Ph)	46
	$\mathrm{[Ru(Cl)(L^{Ar})\{P(OMe)_3\}_3]}$ (Ar = Ph or *p*-Tol)	46
	$\mathrm{[Ru(Cl)(L^{Tol\text{-}\mathit{p}})(PPh_3)(dppe)]}$	46
	$\mathrm{[Ru(Cl)_2(CO)(L^H)(PPh_3)_2]}$	69
	$\mathrm{[Ru_2I_3(L^{Me})_6]I}$	27
	$\mathrm{[Ru_2Cl_3(L^{Et})_6]Cl}$	27

Table 1 (continued)

M^n	Complex	Ref.
$\mathrm{Os^{II}}$	*trans*-$[\mathrm{Os(Cl)_2(L^{Me})_4}]$	40
	$[\mathrm{Os(Cl)_2(L^{CH_2Ph})_3(NO)}]\mathrm{Cl}$	41
	$[\mathrm{Os(L^{Me})_4(NO)}]\mathrm{Cl}$	41
	trans-$[\mathrm{Os(Cl)(L^{CH_2Ph})(NO)}]\mathrm{X_2}$ ($\mathrm{X = Cl}$ or $[\mathrm{BF_4}]$)	41
$\mathrm{Co^{-I}}$	$[\mathrm{Co(CO)_2(L^{Me})(NO)}]$	35
	$[\mathrm{Co(CO)(L^R)_2(NO)}]$ ($\mathrm{R = Me}$ or Et)	35
	$[\mathrm{Co(CO)(L)(NO)(PPh_3)}]$ ($\mathrm{L = L^{Et}}$ or $\mathrm{MeL^{\star Me,Me}}$)	35, 63
$\mathrm{Co^{I}}$	$[\mathrm{Co(\eta\text{-}C_5H_5)(CO)(L^{Me})}]$	68
$\mathrm{Co^{II}}$	$[\mathrm{Co(\eta\text{-}C_5H_5)(SPh)(L^{Me})}]$	68
$\mathrm{Co^{III}}$	$[\mathrm{Co(\eta\text{-}C_5H_5)Me(L^{Me})}][\mathrm{BF_4}]$	68
	$[\mathrm{Co(\eta\text{-}C_5H_5)(I)_2(L^{Me})}]$	68
$\mathrm{Rh^{I}}$	*trans*-$[\mathrm{Rh(Cl)(L^R)(PPh_3)_2}]$ ($\mathrm{R = Me, CH_2Ph, Ph}$, *p*-Tol, or *p*-An)	8, 61, 62
	trans-$[\mathrm{Rh(Cl)(L'^{Me})(PPh_3)_2}]$	62
	$[\mathrm{Rh(Br)(L^R)(PPh_3)_2}]$ ($\mathrm{R = Me}$ or *p*-Tol)	62, 74
	$[\mathrm{Rh\{N:C(CF_3)_2\}(L^R)(PPh_3)_2}]$ ($\mathrm{R = Me}$ or *p*-Tol)	12
	trans-$[\mathrm{Rh(Cl)(L^{Me})(AsPh_3)_2}]$	76
	trans-$[\mathrm{Rh(Cl)(CO)(L^R)(PPh_3)}]$ ($\mathrm{R = Me, Et, CH_2Ph}$, *p*-Tol, or *p*-An)	19, 62
	trans-$[\mathrm{Rh(Cl)(CO)(L'^{Me})(PPh_3)}]$	62
	trans-$[\mathrm{Rh(Cl)(CO)(L)(L^{CH_2Ph})}]$ ($\mathrm{L = PEt_3, PMe_2Ph, PMePh_2}$, or $\mathrm{PCy_3}$)	75
	trans-$[\mathrm{Rh(Cl)(CO)(L^R)_2}]$ ($\mathrm{R = Me, Et}$, or $\mathrm{CH_2Ph}$)	19, 38, 61, 75, 78
	trans-$[\mathrm{Rh(Cl)(CO)(L'^{Me})_2}]$	75
	trans-$[\mathrm{Rh(Cl)(CS)(L^{CH_2Ph})_2}]$	75
	cis-$[\mathrm{Rh(Cl)(CO)_2(L^R)}]$ ($\mathrm{R = Me, Et, CH_2Ph, Ph}$, or *o*-An)	19, 62, 75
	$[\mathrm{Rh(X)(CO)(L^{Tol\text{-}\mathit{p}})(PPh_3)}]$ ($\mathrm{X} = [\mathrm{BH_4}]$ or $[\mathrm{ClO_4}]$)	62
	trans-$[\mathrm{Rh(CO)(L^R)(PPh_3)_2}]\mathrm{X}$ ($\mathrm{R = Me}$ and $\mathrm{X = Cl, Br}$, or I; $\mathrm{X = Cl}$ and $\mathrm{R = Et, Ph}$, *p*-Tol, or *p*-An; $\mathrm{R} =$ *p*-Tol and $\mathrm{X} = [\mathrm{ClO_4}]$)	19, 62
	cis-$[\mathrm{Rh(CO)(L^R)_2(PPh_3)}]\mathrm{Cl}$ ($\mathrm{R = Me}$ or Et)	74
	$[\mathrm{Rh(CO)(L^R)_3}]\mathrm{X}$ ($\mathrm{R = Me}$ or Et and $\mathrm{X = Cl}$; $\mathrm{R} =$ *p*-Tol and $\mathrm{X} = [\mathrm{ClO_4}]$)	19, 61
	cis-$[\mathrm{Rh(Cl)(COD)(L^R)}]$ ($\mathrm{R = Me, Et, CH_2Ph, Ph}$, *p*-Tol, *o*-An, or *p*-An)	19, 61, 62, 75
	cis-$[\mathrm{Rh(ClO_4)(COD)(L^R)}]$ ($\mathrm{R} =$ *p*-Tol or *o*-An)	62
	cis-$[\mathrm{Rh(NO_3)(COD)(L^R)}]$ ($\mathrm{R} =$ *p*-Tol, *o*-An, or *p*-An)	62
	cis-$[\mathrm{Rh(COD)(L^{Me})_2}]\mathrm{Cl}$	74
	cis-$[\mathrm{Rh(COD)(L^R)(PPh_3)}][\mathrm{ClO_4}]$ ($\mathrm{R} =$ *p*-Tol or *o*-An)	62
	cis-$[\mathrm{Rh(CH_2SiMe_3)(COD)(L^{Tol\text{-}\mathit{p}})}]$	62
	$[\mathrm{RhCl(L^{Et})_3}]$	61, 77
	$[\mathrm{RhCl(L^{CH_2Ph})_3}]$	61, 78
	cis-$[\mathrm{Rh(Cl)(COD)(L^{\star})}]$ ($\mathrm{L^{\star} = MeL^{\star Me,Me}, Bu^iL^{\star Me,Me}, Bu^iL^{\star Me,Et}, Bu^iL^{\star Et,Et}, PL^{\star Me}}$, or $\mathrm{CyL^{\star Me}}$)	60, 63
	trans-$[\mathrm{Rh(Cl)(L^{\star})(PPh_3)_2}]$ ($\mathrm{L^{\star} = MeL^{\star Me,Me}, Bu^iL^{\star Me,Me}, Bu^iL^{Me,Et}, Bu^iL^{\star Et,Et}, Bu^iL^{\star CH_2Ph,CH_2Ph}, Bu^iL^{\star Me,Tol\text{-}\mathit{p}}, PL^{\star Me}, L^{CH_2R^{\star}}}$ or $\mathrm{L^{CH_2R^{\star\prime}}}$)	56, 60, 63
	$[\mathrm{Rh(Cl)(CO)(Bu^iL^{\star Et,Et})(L)}]$ ($\mathrm{L = Bu^iL^{\star Et,Et}}$ or $\mathrm{PPh_3}$)	56, 60, 63
	$[\mathrm{Rh(COD)(L_2^{cyclam})}][\mathrm{RhCl_2(COD)}]$	53
$\mathrm{Rh^{III}}$	$[\mathrm{Rh(Cl)(I)_2(CO)(L^{CH_2Ph})_2}]$	75
	$[\mathrm{Rh(Cl)_3(CO)(L^{Et})_2}]$	75
	$[\mathrm{Rh(Cl)_3(CO)\{CH(NMe_2)\}(L^{Et})}]$	62

continued

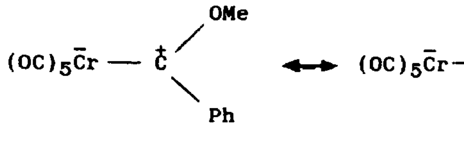
Table 1 (continued)

M^n	Complex	Ref.
Ir$^{\mathrm{I}}$	[Ir(CO)(L$^{\mathrm{Me}}$)$_3$][BF$_4$]	20
	[Ir(CO)(L$^{\mathrm{Me}}$)(PPh$_3$)$_2$][BF$_4$]	20
	[Ir(CO)(L$^{\mathrm{CH_2Ph}}$)$_2$(PPh$_3$)][BF$_4$]	75
	trans-[Ir(X)(CO)(L$^{\mathrm{CH_2Ph}}$)$_2$] (X = Cl or I)	75
	trans-[Ir(Cl)(L$^{\mathrm{CH_2Ph}}$)$_2$(N$_2$)]	75
	trans-[Ir(Me)(CO)(L$^{\mathrm{Me}}$)$_2$]	78
	[Ir(Cl)(L$^{\mathrm{CH_2Ph}}$)$_3$]	78
Ir$^{\mathrm{III}}$	[Ir(Cl)$_2$(X)(CO)(L$^{\mathrm{CH_2Ph}}$)$_2$] (X = Cl, H, HgCl, or TCNE)	75
	[Ir(Cl)(I)(Me)(CO)(L$^{\mathrm{CH_2Ph}}$)$_2$]	75
	[Ir(Cl)$_3$(L$^{\mathrm{H}}$)(PPh$_3$)$_2$]	70
	[Ir(L$^{\mathrm{Ar}}$)$_3$] (Ar = *p*-Tol or *p*-An)	59
	[Ir(L$^{\mathrm{Tol\text{-}}p}$)$_2$(L$^{\mathrm{Tol\text{-}}p}$)]X (X = Cl or [BPh$_4$]	59
Ni^0	[Ni(CO)$_3$(L$^{\mathrm{R}}$)] (R = Me or Et)	35
	[Ni(CO)$_2$(L$^{\mathrm{R}}$)$_2$] (R = Me or Et)	35
	[Ni(CO)$_2$(L$^{\mathrm{Me}}$)(PR$_3$)] (R = Ph or Cy)	35
	[Ni(CO)$_2$(L$^{\mathrm{Et}}$)(PPh$_3$)]	35
	[Ni(Cl)(L$^{\mathrm{Et}}$)$_2$(NO)]	41
	[Ni(Br)(L$^{\mathrm{CH_2Ph}}$)$_2$(NO)]	41
Ni$^{\mathrm{I}}$	[Ni{CH(SiMe$_3$)$_2$}(L$^{\mathrm{R}}$)$_2$] (R = Et or CH$_2$Ph)	79
	[Ni(CH$_2$SiMe$_3$)(L$^{\mathrm{Et}}$)$_2$]	79
	[Ni(CH$_2$SiMe$_3$)(L$^{\mathrm{Me}}$)(PCy$_3$)]	79
	[Ni(η-C$_3$H$_5$)(L$^{\mathrm{Me}}$)$_2$]	79
Ni$^{\mathrm{II}}$	*trans*-[Ni(Cl)(L$^{\mathrm{Me}}$)$_3$][BF$_4$]	20
	cis-[Ni(X)$_2$(L$^{\mathrm{Me}}$)$_2$] (X = Cl, Br, or I)	35
	trans-[Ni(Cl)$_2$(L$^{\mathrm{R}}$)$_2$] (R = Me or CH$_2$Ph)	35
	cis-[Ni(I)$_2$(L$^{\mathrm{Me}}$)(PPh$_3$)]	35
	[Ni(NO$_3$)$_2$(L$^{\mathrm{Me}}$)$_2$]	35
	[Ni(Br)(η-C$_3$H$_5$)(L$^{\mathrm{Me}}$)]	76
	[Ni(η-C$_3$H$_5$)(L$^{\mathrm{Me}}$)$_2$]Br	76
Pd$^{\mathrm{II}}$	*trans*-[Pd(Cl)(L$^{\mathrm{Me}}$)(PEt$_3$)$_2$][BF$_4$]	20
	cis- or *trans*-[Pd(Cl)$_2$(L$^{\mathrm{Ph}}$)(PR$_3$)] (R = Et or Bu)	16, 17, 22
	cis-[Pd(Br)$_2$(L$^{\mathrm{Ph}}$)(PR$_3$)] (R = Et or Bu)	16, 17
	trans-[Pd(Br)$_2$(L$^{\mathrm{Ph}}$)(PEt$_3$)]	16
	cis-[Pd(Cl)$_2$(L$^{\mathrm{Me}}$)(PR$_3$)] (R = Et or Bu)	16, 17, 22
	cis-[Pd(Cl)$_2$(L$_{\mathrm{S}}^{\mathrm{Me}}$)(PR$_3$)] (R = Et or Bu)	16, 17, 22
	cis-[$\overline{\mathrm{Pd(A}}\mathrm{r)}$(X)(L$^{\mathrm{Ph}}$)] (Ar = *o*-C$_6H_4$[C(R)=$\overset{\uparrow}{\mathrm{N}}$OH] (R = Me or Ph) or *o*-C$_6$H$_4$[CH$_2\overset{\uparrow}{\mathrm{N}}Me_2$]	85
	cis-[$\overline{\mathrm{Pd(A}}\mathrm{r)}$(L$^{\mathrm{Ph}}$)(PPh$_3$)][ClO$_4$] (Ar as above)	85
	cis-[{Pd(μ-X)(L$^{\mathrm{Ph}}$)}$_2$] (X = Cl, Br, or OCOMe)	71
	cis-[Pd(X)(L$^{\mathrm{Ph}}$)] (X = acac or Cl, L′ [L′ = 4-MeC$_5$H$_4$N or P(OPr$^{\mathrm{i}}$)$_3$]	71
Pt$^{\mathrm{II}}$	*cis*- or *trans*-[Pt(Cl)$_2$(L)(L$^{\mathrm{R}}$)] (R = Me, CH$_2$Ph, Ph, or L$_{\mathrm{S}}^{\mathrm{Me}}$; L = PEt$_3$, PPr$_3$, PBu$_3$, AsEt$_3$, or PMe$_2$Ph)	16, 17, 18, 22, 72
	cis- or *trans*-[Pt(Br)$_2$(L$^{\mathrm{R}}$)(PEt$_3$)] (R = Me or Ph, or L$^{\mathrm{R}}$ = L$_{\mathrm{S}}^{\mathrm{Me}}$)	16, 17, 18, 22
	trans-[Pt(Me)$_2$(L)(L$^{\mathrm{Me}}$)] (L = PEt$_3$ or AsEt$_3$)	16, 17, 18
	cis-[Pt(Me)$_2$(L)(L$^{\mathrm{Me}}$)] (L = PEt$_3$ or PPh$_3$)	20
	[Pt(X)(L$^{\mathrm{Me}}$)$_3$][BF$_4$] (X = H or Cl)	20
	cis-[Pt(Cl)(L$^{\mathrm{Me}}$)$_2$(PPh$_3$)]X (X = Cl, Br, or I)	20
	[Pt(η^1-C$_3$H$_5$)(Cl)(L$^{\mathrm{Me}}$)(PPh$_3$)]	20
	cis-[Pt(η^1-C$_3$H$_5$)(L$^{\mathrm{Me}}$)$_2$(PPh$_3$)]X (X = Cl or [BF$_4$])	20
	cis-[Pt(R)$_2$(L$^{\mathrm{Et}}$)$_2$] (R = 2-F-C$_6$H$_4$, *m*-Tol, or *p*-Tol)	29
	cis-[Pt(Tol-*p*)$_2$(L$^{\mathrm{Me}}$)$_2$]	76
	cis-[Pt(Cl)$_2$(L$^{\mathrm{CH_2Ph}}$)$_2$]	76

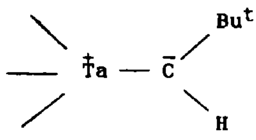
Table 1 (continued)

M^n	Complex	Ref.
Au^I	$[Au(L^{Me})_2]X$ (X = Cl or $[BF_4]$)	20
Hg^{II}	$[Hg(L^{Ph})_2]X$ (X = Cl or $[ClO_4]$)	66, 67

(hard) electrophilic carbene, and behave as C_{carb}-centred nucleophiles (e.g., in Wittig-type reactions). These features may be rationalised in terms of resonance structures such as X and XI. A class (i) complex may be regarded as having either or both of X and Y in I as lone-pair possessing, most typically an amino or alkoxy group, but also including halide or alkanethiolate; the first chlorocarbene-metal complexes were derivatives of Cr^0, Mn^I, or Rh^{III} [24].

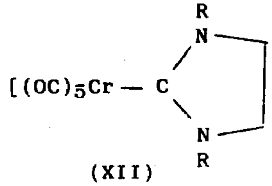


(X)



(XI)

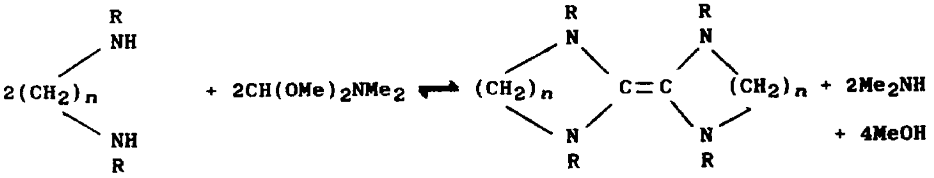
The complex $[Cr(CO)_5(L^{Me})]$ (XII), a typical electron-rich alkene-derived metal complex, could be classified as of type (i), from X-ray and ^{13}C NMR or IR $\nu(CN_2)$ data. However, in their chemical behaviour this and related complexes



(XII)

(Table 1) are quite distinctive, the $M-C_{carb}$ bond being generally extraordinarily inert and rigid (high barrier to rotation about the $M-C_{carb}$ bond [19]). This is attributable to a combination of (a) the chelate effect, (b) steric constraints (e.g., short non-bonding R/CO contacts for XII), making nucleophilic substitution at C_{carb} or L^R displacement at the metal energetically unfavourable, and (c) partial $M \overset{...}{-} C_{carb}$ double-bond character. Thus the complexes of Table 1 form a distinctive class, which we might label (iii) in the context of (i) and (ii) above.

The general synthetic route to electron-rich alkenes such as II involves distilling the appropriate diamine $RNH(CH_2)_nNHR$ (R = primary alkyl or unhindered aryl) with the dimethylacetal of *N,N*-dimethylformamide, eq. 1; the equilibrium is driven to the right by continuous removal by distillation of MeOH and Me_2NH [4]. More recent work (Section III) reveals two intermediates along the pathway to II.

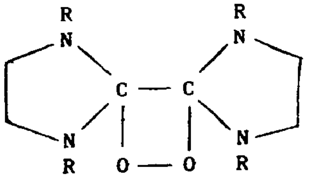


(1)

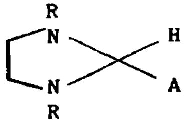
(II) (n = 2)

(IV) (n = 3)

The enetetramines II are electron-rich (first ionisation potential $\leqslant$ 6 eV) [5]. They are generally oxygen- and moisture-sensitive, being chemiluminescent in air due to formation and decay of the dioxetane XIII. They are powerful reducing agents, e.g., abstracting a chlorine atom from a chloroalkane. Electrophiles generally cause scission of the (formal) C=C bond; e.g. a protic reagent HA usually yields the aminal XIV (e.g., A = Cl, OH, or NR'_2). The organic chemistry of electron-rich alkenes was last surveyed in 1972 [6]; this was updated in 1985 [7].



(XIII)



(XIV)

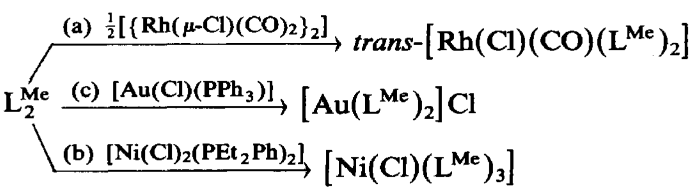
In our earlier review [1], various features relating to electron-rich alkenes II–IV and their role in coordination chemistry were identified. These are summarised in (1)–(5).

(1). The compounds L_2^R (II) were shown not to dissociate thermally or photochemically. However, in the presence of a trace of $[RhCl(PPh_3)_3]$ a facile cross-over reaction, eq. 2, was observed [8]. This provided the first model experiment for

$$L_2^{Ph} + L_2^{Tol\text{-}p} \rightleftharpoons 2L^{Ph}\text{-}L^{Tol\text{-}p} \qquad (2)$$

metal-catalysed alkene metathesis and led (independently of the work of Herrison and Chauvin [9a]) to the explicit proposal that the latter process involves both carbenemetal and also metallacyclic (see also ref. 9b) complexes as intermediates in the catalytic cycle.

(2). The compounds L_2^R (II) were demonstrated to have an extensive carbene-ligand transition metal chemistry, in some ways analogous to that of tertiary phosphines. Stable carbenemetal complexes having 1, 2, 3, or 4 carbene ligands were reported (some from then unpublished work) for Cr^0, Mo^0, Mo^{II}, W^0, W^{II}, Fe^0, Fe^I, Ru^0, Ru^{II}, Rh^I, Rh^{III}, Ir^I, Ni^{II}, Pd^{II}, Pt^{II}, Au^I, and Hg^{II}. The phosphine analogy was elaborated by drawing attention to the fact that such carbenemetal complexes were accessible by: (a) di-μ-halogenodimetal bridge splitting, or (b) displacement of either a neutral (e.g., CO, C_2H_4, or PPh_3) or anionic (e.g., Cl^-) ligand, as exemplified in Scheme 1.



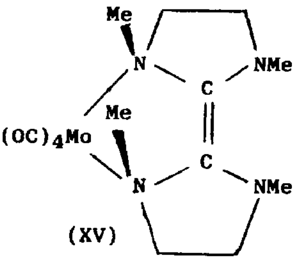
$$L_2^{Me} \xrightarrow{(a)\ \frac{1}{2}[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]} trans\text{-}[Rh(Cl)(CO)(L^{Me})_2]$$

$$L_2^{Me} \xrightarrow{(c)\ [Au(Cl)(PPh_3)]} [Au(L^{Me})_2]Cl$$

$$L_2^{Me} \xrightarrow{(b)\ [Ni(Cl)_2(PEt_2Ph)_2]} [Ni(Cl)(L^{Me})_3]$$

Scheme 1. Some typical reactions of the electron-rich alkene L_2^{Me} (II, R = Me).

(3). In a few instances, the (formal) C=C bond of L_2^R (II) was not cleaved upon reaction with a metal complex, and evidence was presented for the existence of an *N*,*N*″-chelate complex such as XV. In other cases, proton abstraction from solvent or a metal hydride was reported, e.g., in the formation of $[L^{Me}-H][Cr(\eta\text{-}C_5H_5)(CO)_3]$ from L_2^{Me} and either $[\{Cr(\eta\text{-}C_5H_5)(CO)_3)\}_2]$ or $[Cr(H)(\eta\text{-}C_5H_5)(CO)_3]$.



(XV)

(4). X-Ray data on *cis*- and *trans*-$[Pt(Cl)_2(L^{Ph})(PEt_3)]$ [13,16,72] and *trans*-$[Rh(L^{Me})\{N{=}C(CF_3)_2\}(PPh_3)_2]$ [12] showed that (a) the $M-C_{carb}$ bond was not particularly short, indicating that the $M{\overset{...}{-}}C_{carb}$ bond has relatively little π-character, (b) the five-membered L^R ring was almost orthogonal to the d^8 metal plane; and (c) the *trans*-influence in the above Pt^{II} complexes was $L^{Ph} \approx PEt_3 > Cl^-$. It was concluded that the L^R ligand is a good σ-donor but a poor π-acceptor.

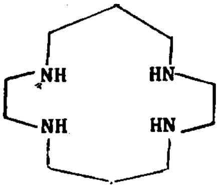
(5). Spectroscopic data of diagnostic value for carbenemetal complexes derived from L_2^R (II) included (a) the $\nu_{asym}(CN_2)$ IR band at 1480–1520 cm^{-1}, and (b) the ^{13}C NMR chemical shift for C_{carb} at ca. 200 ppm (as in a carbenium ion) [18].

Our work on carbenemetal complexes has thus far been published in (i) 35 full papers [10], (ii) 3 reviews [1,11], and (iii) 25 preliminary communications. The 1975 review [1] included references to 9 articles (and an additional paper [12] from another series) of type (i) and 9 of type (iii).

II. Results from publications 1975–1988

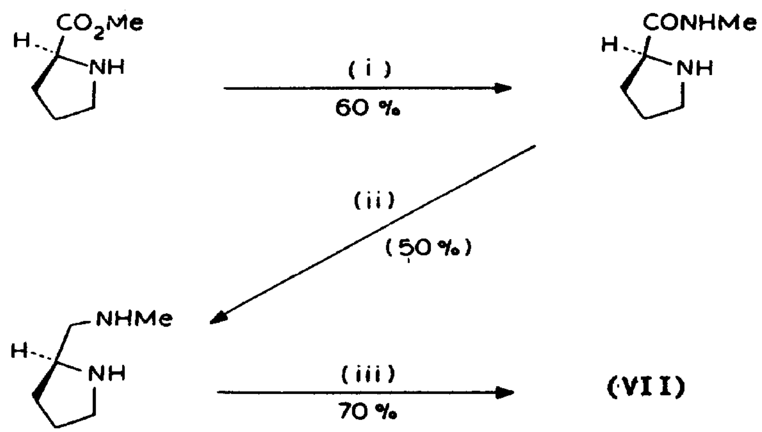
A. Enetetramines: general considerations

As indicated in eq. 1, the exobicyclic electron-rich alkenes L_2^R (II) or $L_2'^R$ (IV) are conveniently prepared from $CH(OMe)_2NMe_2$ and the diamine $RN(H)(CH_2)_nNHR$ ($n = 2$ or 3). Two developments are noteworthy. They relate to the synthesis of analogues in which the new feature is that the alkene is either (i) endotetracyclic (V) [53], or (ii) optically active VI–IX [56,60,63]. As for (i), the polyamine precursor was the nitrogen macrocycle cyclam (XVI).



(XVI)

Regarding (ii), the ultimate chiral starting material was an (*S*)-α-aminoacid (alanine, leucine, or proline), an appropriate terpene ((+)-3-pinanecarboxylic acid (R*COOH, cf. VIIIa) or (−)-*cis*-myrtanylamine (R*′CH_2NH_2, cf. VIIIb)), or (+)- or (−)-*trans*-1,2-diaminocyclohexane. A typical procedure is illustrated in Scheme 2



Scheme 2. Synthetic sequence to the enetetramine $[\mathrm{PL}^{*\mathrm{Me}}]_2$ (VII) from (*S*)-proline methyl ester. Reagents and conditions: (i), $MeNH_2$, EtOH, 20 °C, 7 d; (ii) $Li[AlH_4]$, THF, reflux, 24 h; (iii) $CH(OMe)_2NMe_2$, 90 °C, 1 h, distillation.

[63]; particular care was required to ensure no loss of optical integrity during the step leading to the α-aminocarboxylic acid amide.

The molecular structure of L_2^{Ph} (II, R = Ph) has been solved by single crystal X-ray diffraction, Fig. 1 [73]. The molecule has a non-planar geometry of approximate C_{2h} point-group symmetry. This minimises steric strain between vicinal phenyl rings. There is only a small tetrahedral distortion at the nitrogen and sp^2 carbon atoms. It is caused mainly by (i) rotation about the $N{-}C_{sp^2}$ bond to bring the ring and the phenyl C atoms on opposite sides of the C=C mean plane by equivalent amounts for all four N atoms, and (ii) a rotation about each N–phenyl bond.

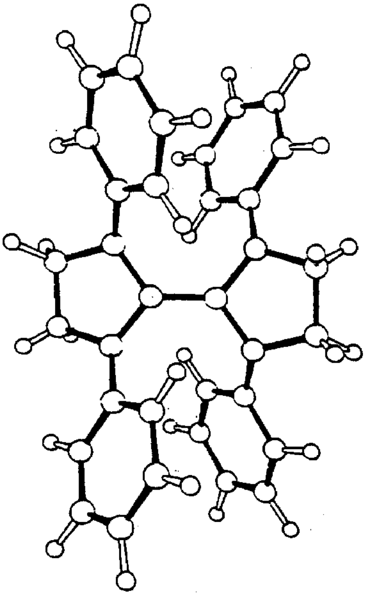
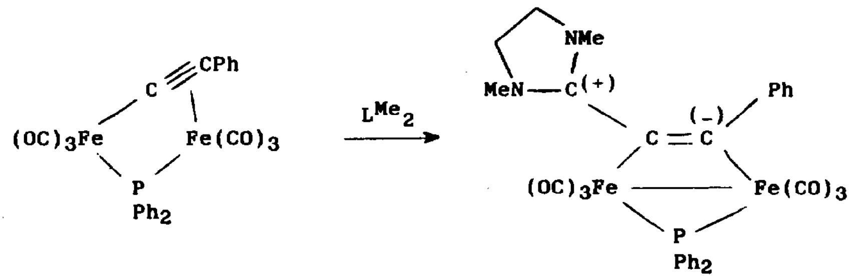
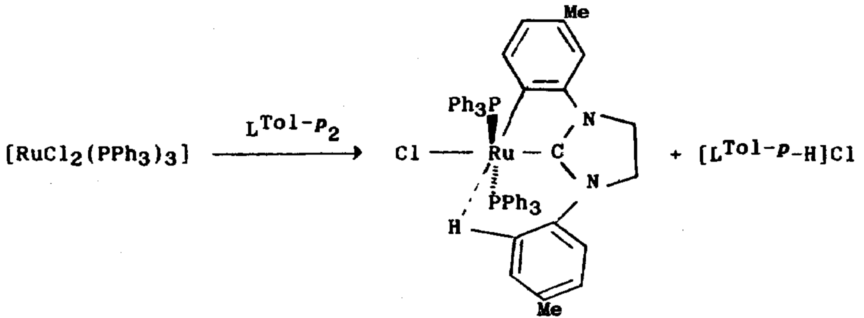


Fig. 1 [73]. Molecular stereochemistry of L_2^{Ph} viewed perpendicular to the main plane of the alkene.



(XVII)

(2)



(XVIII) {abbreviated as $[\mathrm{RuCl(L^{Tol\text{-}\mathit{P}})(PPh_3)_2}]$}

(3)

The enetetramines II–IX have a rich coordination chemistry. Seven types of behaviour have been identified. The most ubiquitous is their ability to generate a wide range of *carbenemetal complexes* (I), Table 1. They are able to function as *bis(heteroatom)-centred ligands* without undergoing C=C bond scission, cf. XV. They can act as *carbenoids*, not only in the context of their organic chemistry (cf. XIV), but also in C_{carb}–C bond-formation involving a metal-coordinated alkyne to yield the X-ray characterised compound XVII, eq. 2 [42]. They have a significant role as *reducing agents*, and sometimes concomitantly behave as *bases*, e.g., in forming $[\mathrm{L^R_2}]\mathrm{Cl_2}$ or $[\mathrm{L^RCl}]\mathrm{Cl}$ with a chlorometal substrate, as in eq. 3. They may participate in an *orthometallation* reaction, e.g., the formation of $[\mathrm{Ru(Cl)(L^{Tol\text{-}\mathit{p}})(PPh_3)_2}]$ (XVIII), eq. (3) [28,46]. Finally, in a formal sense, they may behave as *oxidising agents*, as in the conversion of the iridium(I) precursor $[\{\mathrm{Ir}(\mu\text{-Cl})(\mathrm{COD})\}_2]$ into the $\mathrm{Ir^{III}}$ cyclometallated complex $[\mathrm{Ir(L^{Tol\text{-}\mathit{p}})_3}]$ [59].

B. *Enetetramines as reducing agents for organometallic or coordination compounds*

Irradiation of a bulky Group 14 element halide Y_nMCl in n-hexane or toluene with an electron-rich alkene L_2^{Me}, L_2^{Et}, or $C_2(NMe_2)_4$ provides a convenient method for the generation of the appropriate element-centred radical MY_n, eq. 4 and 5 (e.g., $Y_nMHal = R_3CCl$, R_3SiCl, $(R_2CH)_3GeCl$, or $(R_2CH)_3SnCl$; $R = SiMe_3$) [25]. The advantages of the method are that (i) the yields are quantitative; (ii) separation is easily accomplished, the chloride by-product being the only insoluble component of the reaction mixture; and (iii) the use of one of the above solvents enables the reaction to be carried out at low temperature (e.g., −70 °C) by in situ photolysis in the cavity of an ESR spectrometer, facilitating characterisation of the radical (see also ref. 33). The less electron-rich alkenes L_2^{Ph} or $C_2(SMe)_4$ were ineffective; for L_2^{Ph} this may have been due to its hydrocarbon-insolubility.

$$4Y_nM\text{–}Hal + L_2^R \xrightarrow{h\nu} 4\dot{M}Y_n + 2[L^R\text{–}Hal]Hal\downarrow \qquad (4)$$

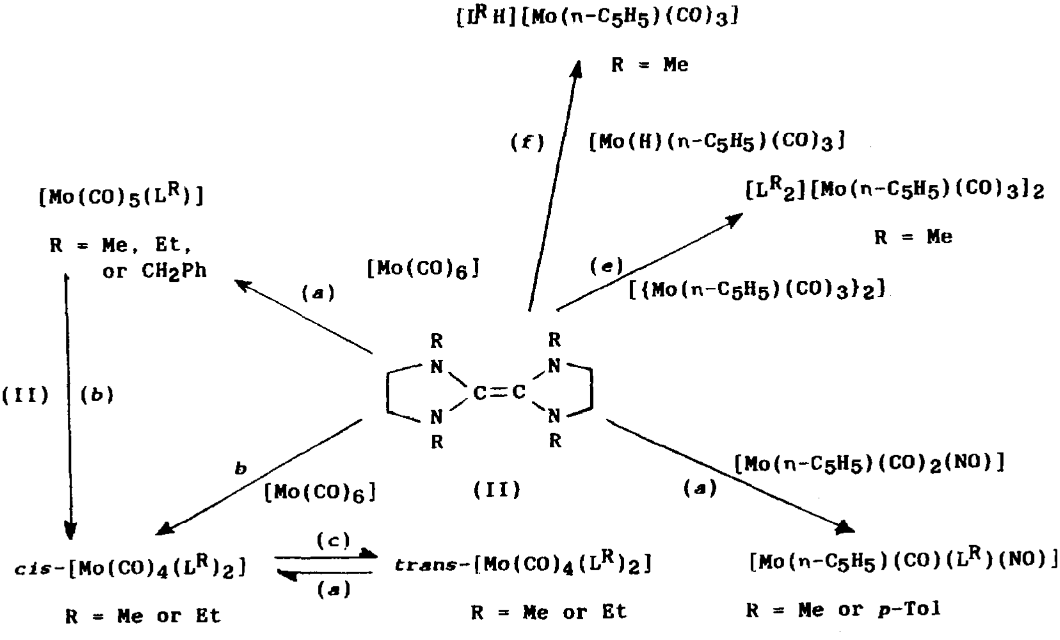
$$2Y_nM\text{–}Hal + C_2(NMe_2)_4 \xrightarrow{h\nu} 2\dot{M}Y_n + [C_2(NMe_2)_4]Hal_2\downarrow \qquad (5)$$

The operative reducing agent may be the triplet alkene. Irradiation of L_2^{Me}, L_2^{Et}, or $C_2(NMe_2)_4$ (but not L_2^{Ph}) in C_6H_{14} or PhMe gave a weak broad ESR signal, g_{av} 2.0033 [25].

The persistent (at 20 °C) radical $\dot{S}n(CHR_2)_3$ ($R = SiMe_3$) was also obtained from $(R_2CH)_2(R')SnX$ ($R'X = Pr^iCl$, Bu^tCl, MeBr, EtBr, Bu^tBr, MeI, Bu^nI, or C_5H_5I), presumably by disproportionation of the transient precursor $\dot{S}n(R')(CHR_2)_2$ [25].

Similar reductions have been carried out on (i) triaryl-silyl, -germyl, or -stannyl chlorides [51], and (ii) dialkyl- or bis(diamido)-phosphorus(III) or -arsenic(III) chlorides [26,52], generating the persistent radicals $\dot{M}Ar_3$ (M = Si, Ge, or Sn; $Ar = C_6H_3Me_2$-2,6 or $C_6H_2Me_3$-2,4,6), $\dot{E}(CHR_2)_2$ or $\dot{E}(NR_2)_2$ (E = P or As, $R = SiMe_3$). Using a less bulky Ge^{IV} chloride, the transient germanium-centred radical could be spin-trapped as the nitroxide $\equiv GeCH(Ph)N(\dot{O})Bu^t$, by carrying out the reductive photolysis in the presence of the nitrone $PhCH{=}N(Bu^t)O$ [39].

Related mild reductions of some other phosphorus(III or V) chlorides have been examined. From R_2PCl and L_2^{Et} without irradiation, the diphosphine $R_2P\text{–}PR_2$ was obtained in high yield for $R = Bu^t$, C_6H_{11}, Ph, or $C_6H_2Bu^t_3$-2,4,6; whereas under



Scheme 3 [31]. Molybdenum(0) complexes derived from an enetetramine (II). (a) $C_6H_{11}Me$, 100 °C. (b) Decalin, 100–120 °C. (c) $h\nu$, Me_2CO, 25 °C. (d) $CHCl_3$, 25 °C. (e) C_6H_6, 25 °C. (f) C_6H_{14}, 25 °C.

similar conditions $RPCl_2$ yielded the cyclopolyphosphine $(PR)_n$ for R = Bu^t ($n = 4$) or Ph ($n = 4$ (55%) and $n = 5$ (45%)) [64]. $ArPCl_2$ gave either $(PArCl)_2$ or *trans*-ArP=PAr (Ar = $C_6H_2Bu^t_3$-2,4,6), depending on the amount of L_2^{Et} employed [64]. Irradiation of ArP(Cl)X and a deficiency of L_2^{Me} in toluene at 25 °C gave $2\dot{P}(Ar)X$ + $[L^{Me}{-}Cl]Cl$; the P^{II} radical was characterized by ESR for X = OBu^t, SPr^n, SBu^t, NR_2, CHR_2, Ph, or OAr (R = $SiMe_3$) [58]. Finally, similar photolysis of $Ar_2P(=O)Cl$ with L_2^{Me} yielded $\dot{P}Ar_2(=O)$ and $\dot{P}Ar_2$, the P^{II} species presumably being formed by L_2^{Me} reduction of the P^{IV} precursor [58].

Facile chlorine atom-abstraction from a transition metal chloride and an enetetramine II has been observed for (i) $[Zr(\eta\text{-}C_5H_5)_2(Cl)(CHR_2)]$ and L_2^{Et} in THF, PhMe, or Et_2O, to yield by photolysis $[Zr(\eta\text{-}C_5H_5)_2(CHR_2)(\eta^2\text{-}N_2)]$ (if carried out under N_2) [37,45]; (ii) $[Ru(Cl)_3(NO)(PPh_3)_2]$ and L_2^R (R = Me, Et, or CH_2Ph), to furnish *trans*-$[Ru(Cl)(NO)_2(PPh_3)]$ [41]; (iii) *mer*-$[Os(Cl)_3(PBu^n_2Ph)_2]$ and L_2^{Me}, to give *trans*-$[Os(Cl)_2(L^{Me})_4]$ via $[Os(Cl)_2(PBu^n_2Ph)_3]$ [40]; and (iv) $[Ru(Cl)_2(NO)(PPh_3)_2]$ and L_2^R, to afford $[Ru(L^{Me})_4(NO)]Cl$ or $[Ru(Cl)(L^{CH_2Ph})_2(NO)_2]$ [41].

Finally, hydrogen atom-abstraction from $[Mo(H)(\eta\text{-}C_5H_5)(CO)_3]$ or electron-transfer from $[\{Mo(\eta\text{-}C_5H_5)(CO)_3\}_2]$ and L_2^{Me} gave the reduction products $[L^{Me}{-}H][Mo(\eta\text{-}C_5H_5)(CO)_3]$ or $[L_2^{Me}][Mo(\eta\text{-}C_5H_5)(CO)_3]_2$, respectively [29,31], Scheme 3.

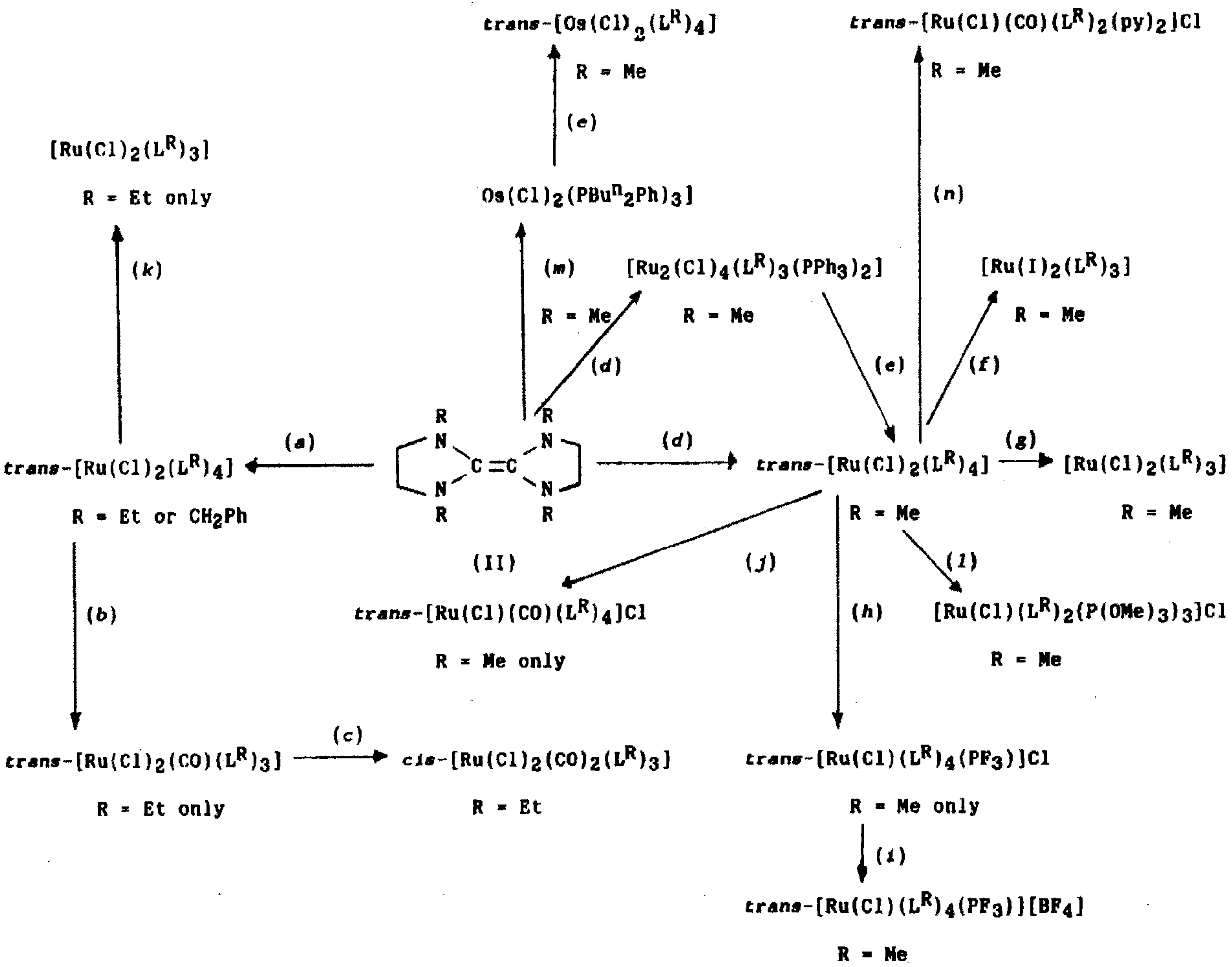
C. Enetetramines as precursors for carbenemetal complexes I

Some typical reactions of the enetetramines II and IV leading to carbenemetal complexes I are illustrated in Schemes 3–6. The reaction types featured include for Scheme 3: nucleophilic displacement at Mo^0 of CO by L^R (denoted as L^R/CO), isomerisation (*cis* ⇌ *trans*), hydrogen atom-abstraction, and electron-transfer [31]; for Scheme 4, the following displacements at Ru^{II} or Os^{II}: L^R/PPh_3, L/L^R [L = CO, py, or $P(OMe)_3$, I^-/Cl^-, Me^-/Cl^-, py/Cl^-, or PF_3/Cl^-], reduction ($Os^{III} \rightarrow Os^{II}$, and L^R addition or elimination reactions [40]; for Scheme 5, the following displacements at Ru^0, Os^0, or Ni^{II}: L^R/PPh_3, CO/NO, or NO/Cl, reduction ($Os^{III} \rightarrow Os^{II}$), oxidation ($Ru^0 \rightarrow Ru^{II}$, or $Os^0 \rightarrow Os^{II}$), and CO addition [41]; and for Scheme 6, di-μ-chlorodirhodium(I) bridge-splitting by L_2^R; the following displacements at Rh^I: X^-/Cl^- (X = CH_2SiMe_3, $[ClO_4]$, or $[NO_3]$), $L/[ClO_4]^-$ (L = CO or PPh_3), $(L)_2/COD$ (L = PPh_3 or CO), or CO/PPh_3; and $Rh^I \rightarrow Rh^{III}$ oxidations with HCl, $[(Me_2N)CHCl]Cl$, or $C_2(CN)_4$ as oxidant [62].

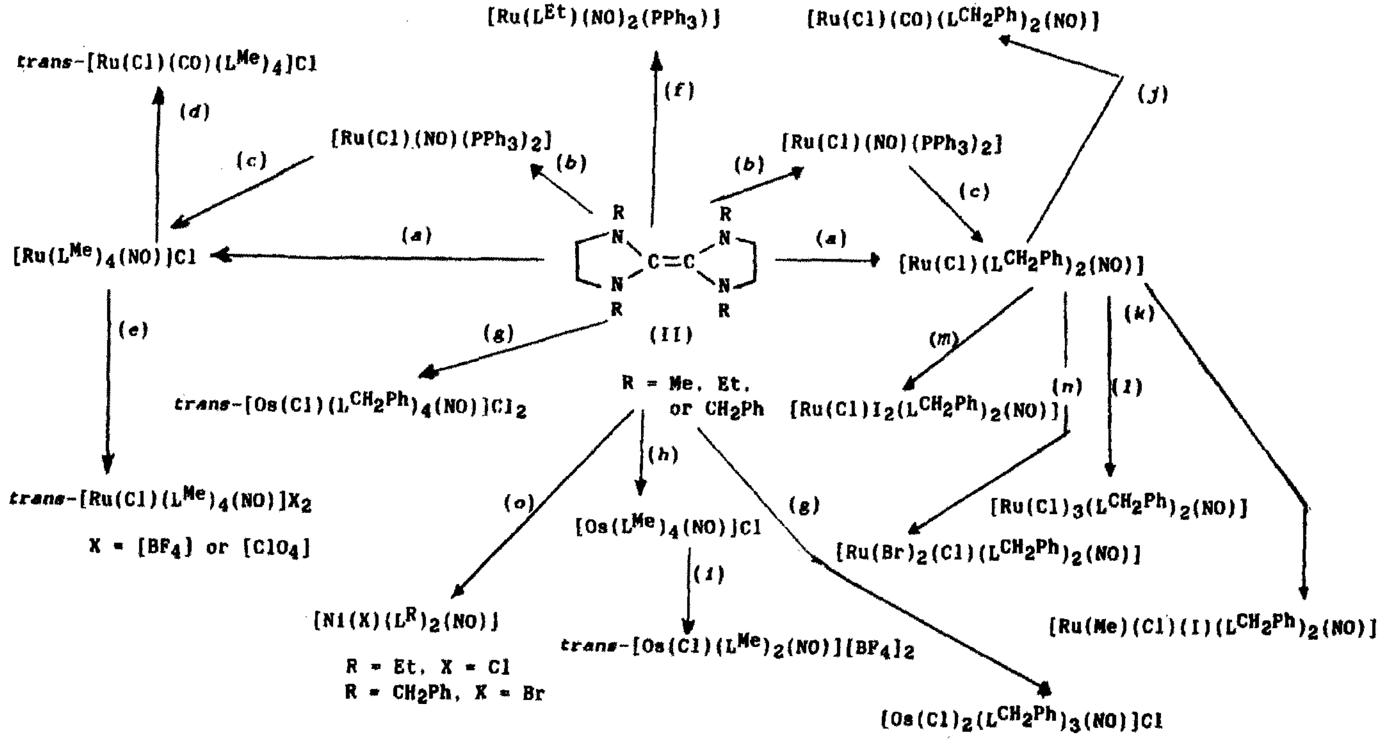
The mechanism of carbenemetal formation from an electron-rich alkene II is unlikely to involve trapping of a free carbene. From *cis*-$[Mo(norbornadiene)(CO)_4]$ and L_2^{Me}, the *N,N″*-metal complex *cis*-$[Mo(CO)_4(L_2^{Me})]$ (XV) has been isolated and X-ray-characterised [23,29,34]. Compound XV was converted into *cis*-$[Mo(CO)_4(L^{Me})_2]$. Using differential scanning calorimetry, this transformation was shown to be smooth at 140 °C in the solid state, obeying a first order rate law [23,34]. Heating XV in toluene at 110 °C for 15 min gave $[Mo(CO)_5(L^{Me})]$. Similar heteroatom complexes to XV, namely *cis*-$[M(CO)_4(LL)_2]$ (M = Cr or Mo) were obtained for LL = $C_2(NMe_2)_4$ [23,44]. $[\overline{S(CH_2)_2SC}]_2$, or $C_2(SEt)_4$ [43], but these did not yield carbenemetal complexes upon heating; $C_2(SEt)_4$ and $[\{Pt(\mu\text{-}Cl)(Cl)(PEt_3)\}_2]$ gave XIX [44].

A plausible mechanism for $[M(CO)_5(L^{Me})]$ formation from $[M(CO)_6]$ and L_2^{Me} (M = Cr, Mo, or W) is shown in Scheme 7 [34].

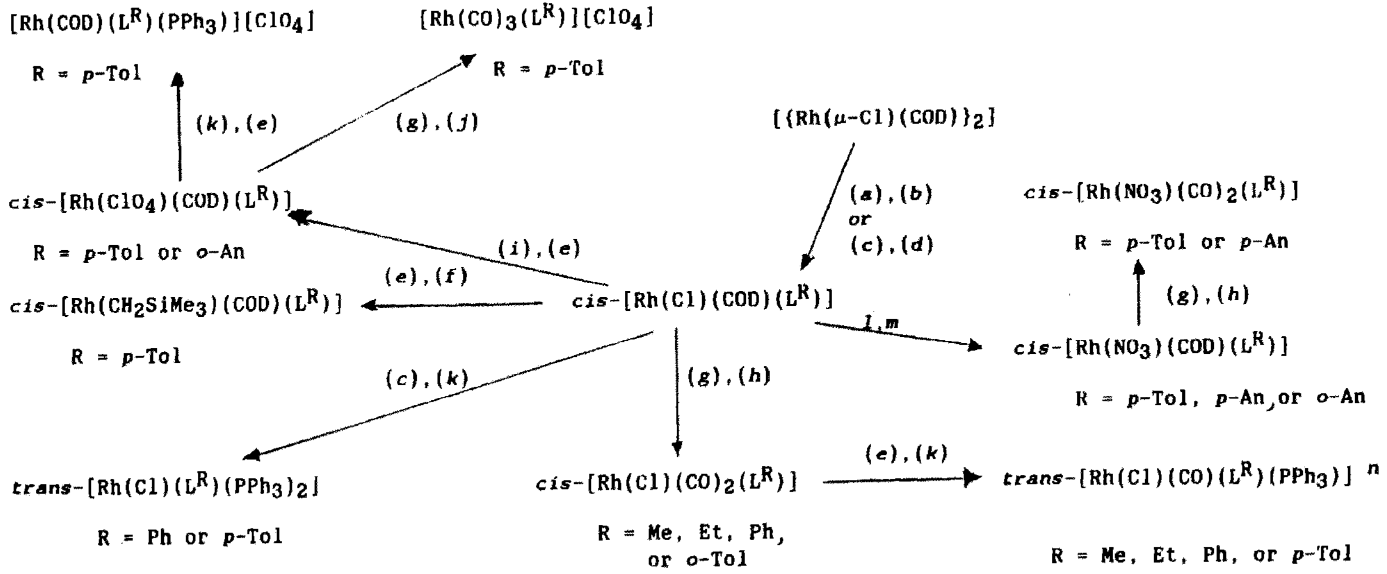
(*Continued on p. 201*)



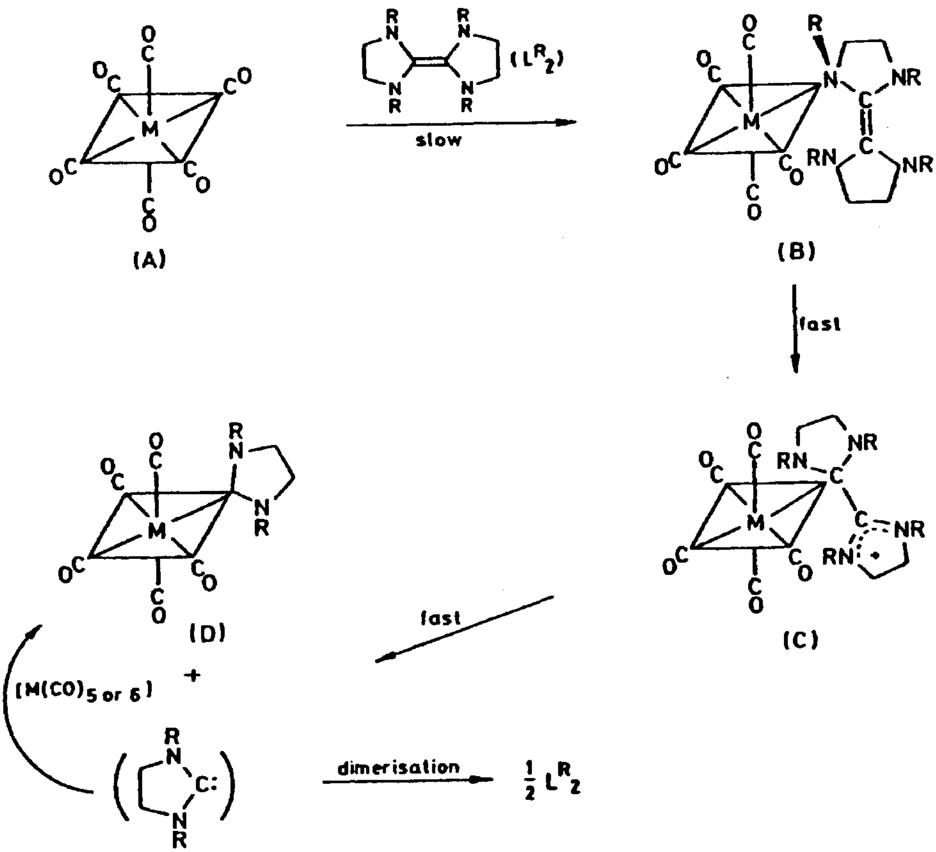
Scheme 4 [40]. Synthesis and reactions of oligocarbeneruthenium(II) complexes and an osmium(II) complex. (a) $[RuCl_2(PPh_3)_3]$, $C_6H_{11}Me$, 100 °C. (b) CO, $C_6H_{11}Me$ or toluene, 100 °C. (c) $CHCl_3$, 25 °C. (d) $[Ru(Cl)_2(PPh_3)_3]$, xylene, 130–140 °C. (e) L_2^{Me}, xylene, 130–140 °C. (f) NaI, Me_2CO, 25 °C. (g) CH_2Cl_2, sealed tube, 60–80 °C. (h) PF_3, $CHCl_3$, 50–55 °C. (i) $Na[BF_4]$, Me_2CO, 25 °C. (j) CO, $CHCl_3$, 50–55 °C; or toluene, 110 °C. (k) CH_2Cl_2, 25 °C. (l) $P(OMe)_3$, $CHCl_3$, 50–55 °C. (m) *mer*-$[Os(Cl)_3(PBu^n{}_2Ph)_3]$, xylene, 25 °C. (n) C_5H_5N, CO, 60 °C, 6 h.



Scheme 5 [41]. Synthetic routes to and reactions of carbenenitrosyl-ruthenium, -osmium, and -nickel complexes. (a) $[Ru(Cl)(NO)(PPh_3)_2]$, toluene, 110 °C. (b) $[Ru(Cl)_3(NO)(PPh_3)_2]$, toluene, 25 °C. (c) Excess of L_2^R toluene, 110 °C. (d) CO, CH_2Cl_2, 25 °C. (e) AgX ($X = [BF_4]$ or $[ClO_4]$), CH_2Cl_2, 25 °C. (f) $[Ru(NO)_2(PPh_3)_2]$, toluene, 110 °C. (g) $[Os(Cl)_3(NO)(PPh_3)_2]$, xylene, 140 °C. (h) $[Os(Cl)(NO)(PPh_3)_2]$, prepared in situ from $[Os(Cl)_3(NO)(PPh_3)_2] + L_2^{Me}$, xylene, 140 °C; and then excess of L_2^{Me}, xylene, 140 °C. (i) $Ag[BF_4]$, CH_2Cl_2, 25 °C. (j) CO, toluene, 25 °C. (k) MeI, toluene, 40 °C. (l) $PhCH_2Cl$, toluene, 25 °C. (m) I_2, CH_2Cl_2, 25 °C. (n) Br_2, CH_2Cl_2, 10 °C. (o) $[Ni(X)(NO)(PPh_3)_2]$, toluene, 100 °C.

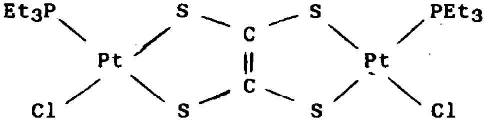


Scheme 6 [62]. Routes to enetetramine-derived monocarbenerhodium(I) complexes from [{Rh(μ-Cl)(COD)}$_2$]. (a) $\frac{1}{2}L_2^R$ (R = alkyl). (b) C_6H_6, 70 °C. (c) Xylene, 140 °C. (d) $\frac{1}{2}L_2^R$ (R = aryl). (e) C_6H_6, 25 °C. (f) Li[CH_2SiMe_3]. (g) CO. (h) $CHCl_3$, 25 °C. (i) Ag[ClO_4]. (j) CH_2Cl_2, 25 °C. (k) PPh_3. (l) Ag[NO_3]. (m) Me_2CO, H_2O, 25 °C. (n) CO *trans* to Cl^-.



Scheme 7 [34]. Proposed pathway to $[M(CO)_5(L^R)]$ (M = Cr, Mo, or W).

The enetetramine $L_2^{\prime Me}$ (IV) was less reactive than the five-membered analogue L_2^{Me} (II); for example $L^{\prime Me}$–Cr^0 complexes, unlike L^{Me}–Cr^0 species, proved to be inaccessible [34]. Reactivity was explained as largely determined by a close Me···Me contact, *d* in XX; assuming reasonable bond lengths and planarity at C_2N_4, *d* is 1.29 Å for $C_2(NMe_2)_4$ or $L_2^{\prime Me}$ but 1.63 Å for L_2^{Me}; hence in the former two, the access by the metal to the sp^2-C is less easy than for L_2^{Me}.



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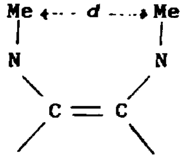

(XX)

Attempts have been made to prepare carbenemetal complexes in situ from a suitable metal substrate and the precursors (eq. 1) of an enetetramine. Thus, from $[Mo(CO)_6]$, $CH(OMe)_2NMe_2$, and $RN(H)(CH_2)_2NHR'$, *cis*-$[Mo(CO)_4(L^R)_2]$ and $[Mo(CO)_5(L^R)]$ were obtained when R = R′ = Me or CH_2Ph; but when R = R′ = Bu^t, the product was *cis*-$[Mo(CO)_4\{Bu^tN(H)(CH_2)_2NHBu^t\}]$ [29]. If either or both of R and R′ was H, then the product was the 2-imidazolinemetal complex $[Mo(CO)_5\{N{=}CHN(R')CH_2CH_2\}]$ (R′ = H or Et) [29].

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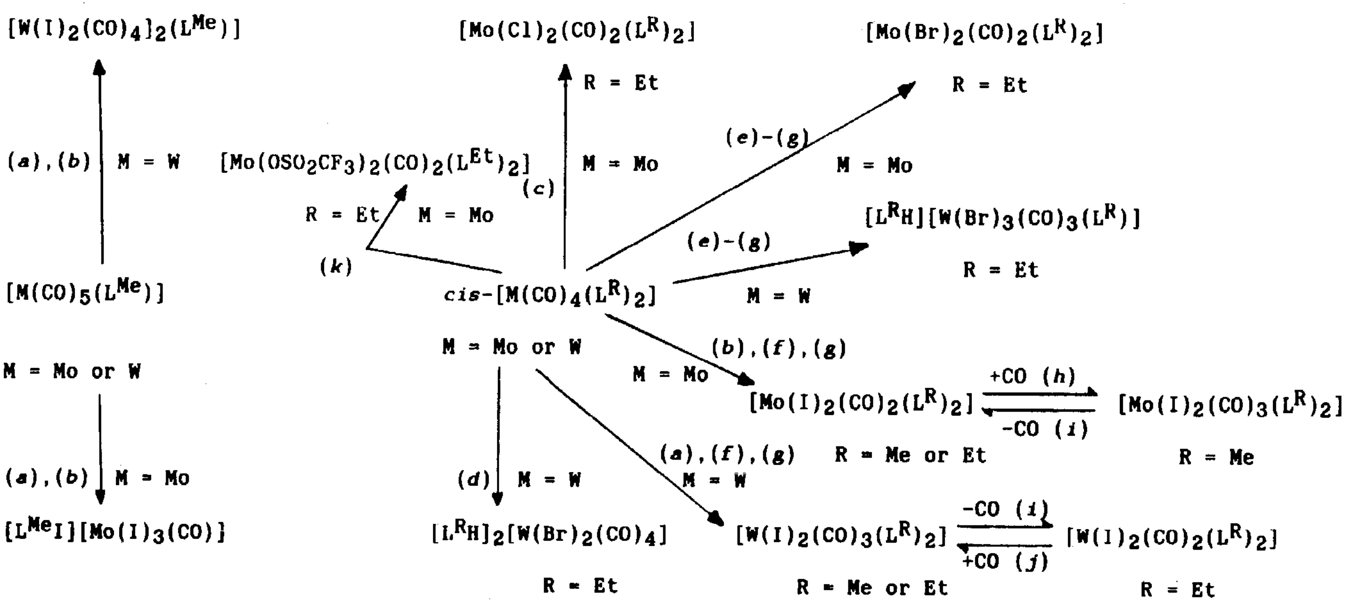
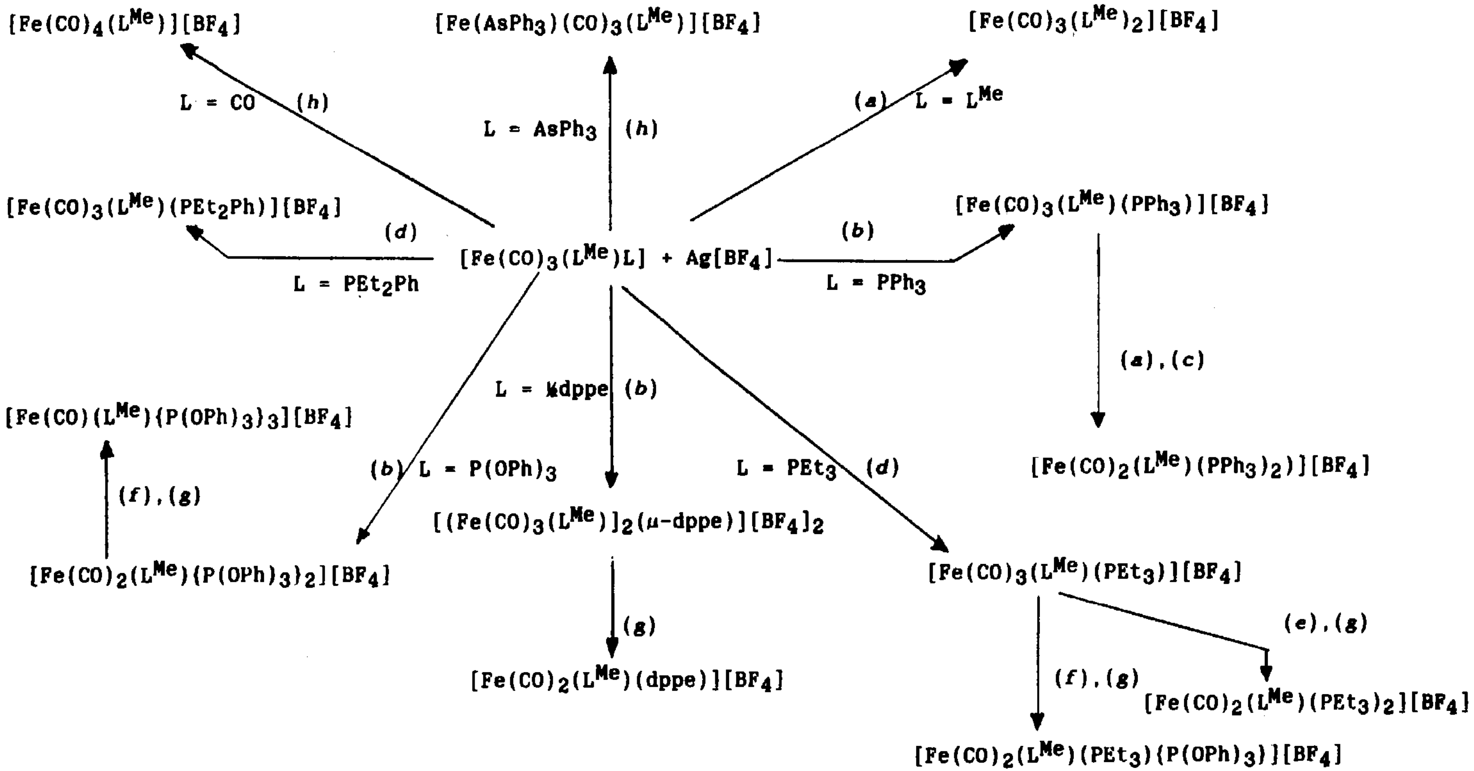


Scheme 8 [32] (for *k*, see [10]). Some reactions of mono- and bis-carbene-molybdenum(0) and -tungsten(0) complexes with dihalogens. (a) Et_2O, −10 °C. (b) I_2. (c) Cl_2, CCl_4, −10 °C. (d) HBr, C_6H_6, 5 °C. (e) Br_2. (f) CH_2Cl_2. (g) −20 °C. (h) < −30 °C. (i) > 30 °C. (j) < 30 °C. (k) $Ag(OSO_2CF_3)$, THF, reflux, 1 h [10].



Scheme 9 [55]. Synthetic routes to paramagnetic carbeneiron(I) complexes. (a) THF, 20 °C. (b) THF, −10 °C. (c) PPh_3. (d) THF, 0 °C. (e) PEt_3. (f) $P(OPh)_3$. (g) CH_2Cl_2, 40 °C. (h) CH_2Cl_2, −50 °C.

Two complexes, $[Ru(Cl)_2(CO)(L^H)(PPh_3)_2]$ [69] and $[Ir(Cl)_3(L^H)(PPh_3)_2]$, [70] having ligated L^H have been obtained from $(H_2NCH_2)_2$ and the appropriate dichlorocarbenemetal precursor.

The telluroureachromium(0) complex $[Cr(CO)_5(TeL^{Et})]$ was a source of $[Cr(CO)_5(L^{Et})]$, by employing a toluene solution in a slow dark reaction at 20 °C or, more quickly, by photolysis or treatment with mercury [48].

D. *Reactions of enetetramine-derived carbenemetal complexes*

In Section II. *C* various types of reactions of carbenemetal complexes derived from electron-rich alkenes L^{R_2} (II) and L'^{R_2} (IV) were identified, see also Schemes 3–6. Some of these require further comment.

The $M^{n+} \rightarrow M^{(n+2)+}$ *oxidation reactions* involved one of the following reagents $Ag[ClO_4]$, $Ag[BF_4]$, MeI, $PhCH_2Cl$, HBr, Br_2, or I_2; further illustrations for $M^0 \rightarrow M^{II}$ (M = Mo or W) conversions are in Scheme 8 [32,66]. Examples of one-electron oxidation are illustrated for the $Fe^0 \rightarrow Fe^I$ system in Scheme 9 [55]. The reaction of $[Co(\eta\text{-}C_5H_5)(CO)(L^{Me})]$ with Ph_2S_2 yielded $[Co(\eta\text{-}C_5H_5)(SPh)(L^{Me})]$ [68].

The carbene-chromium(I) [47] and -iron(I) (low spin d^7) [30,55] (Scheme 9) systems provided the first examples of paramagnetic carbenemetal complexes to be stable at ambient temperature, including $[\{Fe(CO)_3(L^{Me})\}_2(\mu\text{-dppe})][BF_4]_2$ (dppe = $Ph_2PCH_2CH_2PPh_2$) (2 independent low spin d^7 Fe^I centres) [30,55] and *fac*-$[Cr(CO)_3(dmpe)(L^{Et})][BF_4]$ [47]. These were also the first stable Cr^I and Fe^I organometallic compounds. A typical Cr^I synthesis is shown in eq. 6 [47]. ESR spectra gave information on structure (the Fe^I complexes have distorted square pyramidal geometry) and stereochemistry; the *g* values and hyperfine coupling constants indicated that the unpaired electron was only partially metal-centred, with L^{Me} a better π-acceptor of electron-density than PR_3 [55]. Cyclic voltammetry showed that reversible 1-electron-oxidation of $[Fe(CO)_3(L^{Me})(PPh_3)]$ was facile in CH_2Cl_2 using $[NBu^n{}_4][BF_4]$ as supporting electrolyte ($E_{1/2}$ 0.12 V); for $[Fe(CO)_2(L^{Me})(PPh_3)_2][BF_4]$ under similar conditions, the 1-electron-reduction showed that $E_{1/2}$ −0.50 V [55].

The *isomerisations* of eq. 7 [29,31,32,54] and 8 [40] have been studied (M = Mo or W and R = Me or Et). Using diethyl phthalate as solvent (chosen for its involatility), differential scanning calorimetry showed that the thermal *trans*- to *cis*-isomerisation of eq. 7 (M = Mo) was first order with a large negative entropy of activation, indicating an associative transition state (possibly involving the solvent) [54].

Dehydrochlorinative cyclometallation reactions (or orthometallations) (Section II.A), as in eq. 3, have been observed for Ru^{II} [28,41,46], Ir^{III} [59], and Pd^{II} [71] systems. In a single example, the *retroreaction*, eq. (9), has also been observed [59].

$$fac\text{-}[Cr(CO)_3(L^{Et})(dmpe)] \xrightarrow{Ag[BF_4],\ CH_2Cl_2,\ -20\,°C} fac\text{-}[Cr(CO)_3(L^{Et})(dmpe)][BF_4] \qquad (6)$$

$$cis\text{-}[M(CO)_4(L^R)_2] \underset{\text{heat}}{\overset{h\nu}{\rightleftharpoons}} trans\text{-}[M(CO)_4(L^R)_2] \qquad (7)$$

$$trans\text{-}[Ru(Cl)_2(CO)(L^{Et})_3] \xrightarrow{\text{heat}} cis\text{-}[Ru(Cl)_2(CO)(L^{Et})_3] \qquad (8)$$

$$[Ir(L^{Tol\text{-}p})_3] + HCl \rightarrow [Ir(L^{Tol\text{-}p})_2(L^{Tol\text{-}p})]Cl \qquad (9)$$

E. Physical properties and structures of enetetramine-derived carbenemetal complexes

The asymmetric CN_2 stretching mode is a useful diagnostic guide as to the nature of the bonding in an L^R-derived metal complex. For example in carbenepoly(carbonyl)molybdenum(0) complexes or W^0 analogues, such as $[M(CO)_5(L^R)]$ or *cis*- or *trans*-$[M(CO)_4(L^R)_2]$, it was found at 1480–1510 cm^{-1} [31,32]. In related M^{II} complexes, such as $[Mo(X)_2(CO)_2(L^{Me})_2]$ (X = Cl, Br or I) or $[W(X)_2(CO)_4(L^{Me})]$ (X = Br or I), it was at 1500–1530 cm^{-1} [29,32]; and in amidinium metallate(0)s, the $[L^R{-}H]^+$ or $[L_2^R]^{2+}$ moiety displayed a characteristic band at 1640–1710 cm^{-1} [29]. Heteroatom donor complexes, such as *cis*-$[Mo(CO)_4(L_2^{Me}\text{-}N,N'')]$ (XV), did not absorb in the 1450–1700 cm^{-1} range [29].

Corresponding ^{13}C NMR chemical shift data showed $\delta(C_{carb})$ at 210–230 ppm for $M^{0\text{ or }II}(L^R)_n$ complexes (M = Mo or W) [29,31], with $^1J(^{183}W{-}^{13}C)$ at 90–130 Hz [32]. The corresponding $\delta(^{13}C_{carb})$ in metallate(0)s having the $[L^{Me}{-}H]^+$ or $[L_2^{Me}]^{2+}$ cation was at 185 and 149 ppm, respectively [29]. In XV it was found at 134 ppm [29].

He(I) Photoelectron spectroscopy (PES) has revealed that the first ionisation potentials of $[M(CO)_5(L^{Et})]$ [47] and $[Fe(CO)_4(L^{Me})]$ [50] corresponded to 7.12 (Cr), 6.90 (Mo), 7.02 (W), and 7.3 (Fe) eV; the value for *fac*-$[Cr(CO)_3(dmpe)(L^{Et})]$ was 6.70 eV [47]. PES Data for the series $[Fe(CO)_4(L)]$ (L = L^{Me}, $CN(Me)CH{=}CHNMe$, or $COCMe_2CMe_2O$) were recorded; the first six bands for each complex were assigned with the aid of molecular orbital calculations [50], and confirmed the view [31] that each of the carbene ligands is a good σ-donor but weak π-acceptor.

ESR Spectroscopic data on carbeneiron(I) cations led to the proposal that L^{Me} is a better π-acceptor than PR_3 [55].

Although L^R ligands are generally firmly bound to soft metal centres, as in Mo^0, Ru^{II}, or Rh^I complexes, displacement of L^R can be achieved (e.g., see Schemes 4 and 6) if the metal environment is crowded in the substrate, as in $[Ru(Cl)_2(L^{Et})_4]$ [40]. The L^{CH_2Ph} ligand is more labile than L^{Et}, exemplified by reactions of $[Rh(Cl)(L^R)_3]$ with CO in CH_2Cl_2 leading to *trans*-$[Rh(Cl)(CO)(L^{CH_2Ph})_2]$ [61,78] or $[Rh(CO)(L^{Et})_3]Cl$ [61].

Variable temperature ^1H NMR data on a number of carbenemetal complexes have shown that, in general, there is restricted rotation about the $M \nleftarrow C_{carb}$ bond, first noted for some Rh^I complexes in 1974 [19]. Activation free energies for such processes were subsequently evaluated for *cis*-$[M(CO)_4(L^R)_2]$ (40–46 kJ mol^{-1} for R = Me, Et, or CH_2Ph; M = Cr [31], Mo [31], or W [32]; with Cr the highest) and $[W(I)_2(CO)_4(L^R)]$ (56 kJ mol^{-1}). For the bis(carbene)metal complexes, the behaviour may be due to concerted motions of the two carbene ligands. For the tri- or tetra-carbenemetal complexes *trans*-$[Ru(Cl)_2(CO)(L^{Et})_3]$, *trans*-$[Ru(Cl)(CO)(L^{Me})_4]Cl$, and *trans*-$[Ru(Cl)(L^{Me})_4]X$ (X = Cl or $[BF_4]$), NMR distinguished the *N*- and *N'*-methyl (or ethyl) signals, each almost planar imidazolidine ring being at an angle of ca. 45° to the RuC_4 equatorial plane in a propeller arrangement (as shown by X-ray data); the barrier to rotation was beyond the NMR range [27,40].

Other structures of stereochemical interest included $[Ni(NO_3)_2(L^{Me})_2]$, the only diamagnetic Ni^{II} nitrate [35], and the stereochemically rigid five-coordinate Ru complexes: $[Ru(Cl)(L^{Tol\text{-}p})(PEt_3)_2]$, XXI, an analogue of XVIII [28,46] (see eq. 3) (which has an agostic *o*-H ··· Ru contact) and $[Ru(L^{Me})_4(NO)]Cl$ (which appears to have a square pyramidal geometry with the bent NO ligand in the apical position) [41].

Single crystal X-ray data have been determined for the following compounds: *cis*- [31] and [54] *trans*-$[Mo(CO)_4(L^{Me})_2]$, $[Mo\{(OS(O_2)CF_3)_2$-*cis*$\}\{(CO)_2$-*cis*$\}\{(L^{Et})_2$-*trans*$\}]$ [66], *trans*-$[Fe(CO)_3(L^{Me})(PEt_3)]$ [65], $[Ru(Cl)(L^{Tol\text{-}p})(PEt_3)_2]$ (XXI, an analogue of XVIII) [28,46], $[Ru(Cl)(CO)(L^{Tol\text{-}p})(PEt_3)_2]$ (XXII) [46], *trans*-$[Ru(Cl)_2(L^{Et})_4]$ [40], $[Co(CO)(MeL^{\star Me,Me})(NO)(PPh_3)]$ [56,60,63], $[Co(\eta\text{-}C_5H_5)(SPh)(L^{Me})]$ [68], *cis*-$[Rh(Cl)(COD)(L^{\star})]$ ($L^{\star} = CyL^{Me}$ or $PL^{\star Me,Me}$) [56,60,63], *trans*-$[Rh(Cl)(Bu^iL^{\star Me,Me})(PPh_3)_2]$ [63], [*cis*-$Rh(COD)(L_2^{cyclam})][Rh(Cl)_2(CO)_2$-*cis*] [53], $[Ir(L^{Tol\text{-}p})_3]$ (Fig. 1) [59], and $[Ir(L^{Tol\text{-}p})_2(L^{Tol\text{-}p})]Cl$ [59]. In addition to the structural features described above, a number of further comments are in order. (i) For the complexes $[Mo(CO)_4(L^{Me})_2]$, the Mo–C_{carb} distance was shorter for the *trans*- (2.232(2) Å) [54] than the *cis*-complex (2.293(3) Å) [31], reflecting the poorer π-acceptor character of L^{Me} compared with CO [54]. (ii) In bis(carbene)metal complexes, the two imidazolidine rings are parallel, rather than perpendicular (this would correspond to a 2-metallaallene arrangement), contrary to MO predictions [31,54,76]. (iii) The bond length data for the trigonal bipyramidal complex *trans*-$[Fe(CO)_3(L^{Me})(PEt_3)]$ and a number of analogues *trans*-$[Fe(CO)_3(L)(PR_3)]$ show that the *trans*-influence of the ligand L falls in the sequence $L = CO > PR_3 > L^{Me}$ [65]. (iv) The two cyclometallated Ru^{II} complexes XXI and XXII have virtually identical structures (cf. XVIII), the agostic *o*-H (2.23 Å for Ru ··· H) of XXI being replaced by a CO ligand in XXII [28,46]. (v) Data on the complexes XXI and XXII allow comparisons to be made between Ru^{II}–C_{sp^2}(aryl) and Ru^{II}–C_{sp^2}(carbene) within the same molecules, the respective distances being 2.006(8) and 1.908(5) Å for XXI and 2.125(5) and 1.989(6) Å for XXII [46]; thus, there is clearly some $Ru \overset{\cdots}{-} C_{carb}$ double-bond character. (vi) The two cyclometallated Ir^{III} complexes have different conformations: *fac* for $[Ir(L^{Tol\text{-}p})_3]$ (Fig. 3) but *mer* for $[Ir(L^{Tol\text{-}p})_2(L^{Tol\text{-}p})]$ [59]; in the latter, there is an unexpectedly close Ir ··· C(*o*-aryl) contact (2.52 Å)

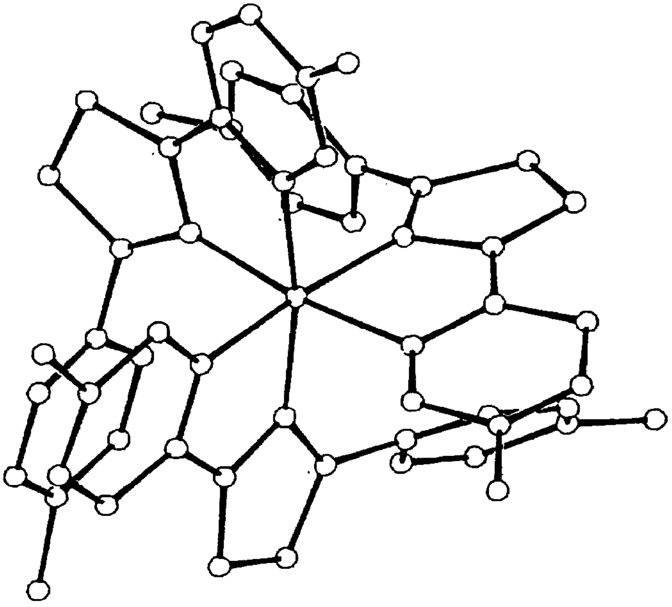


Fig. 2 [59]. The molecular structure of *fac*-$[Ir\{CN(C_6H_4Me\text{-}p)(CH_2)_2NC_6H_3Me\text{-}p\}_3]$ {abbreviated as $[Ir(L^{Tol\text{-}p})_3]$}.

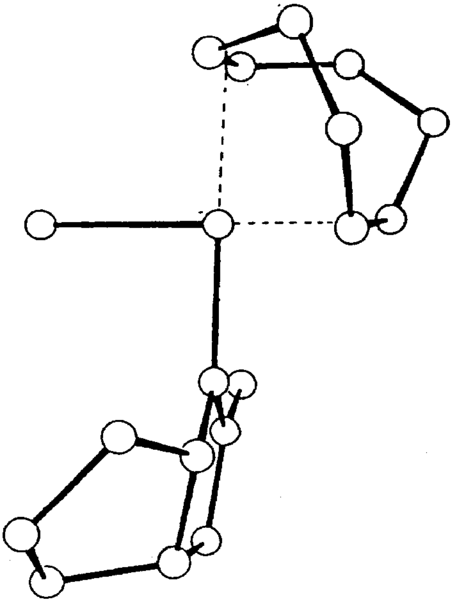


Fig. 3 [56,60,63]. The molecular structure of *cis*-[RhCl(COD)(PL$^{\star\mathrm{Me}}$)].

involving the "free" L$^{\mathrm{Tol}\text{-}p}$. (vii) The cobalt complex [Co(CO)(MeL$^{\star\mathrm{Me,Me}}$)(NO)(PPh$_3$)] is a very rare case of a chiral tetrahedral transition metal complex; however, there was disorder between the CO/NO positions [63]. (viii) The complex *cis*-[Rh(Cl)(COD)(PL$^{\star\mathrm{Me,Me}}$)] crystallised as a single conformer in which, because of hindered rotation about the $\mathrm{Rh}\nleftarrow\mathrm{C}_{\mathrm{carb}}$ bond, the carbene ligand was *anti* rather than *syn* to the COD ligand [63] (Fig. 3); this is a rare case of diastereoselectivity in the realm of transition metal chemistry. (ix) The only case of a chelating bis(carbene) ligand is illustrated in Fig. 4 [53].

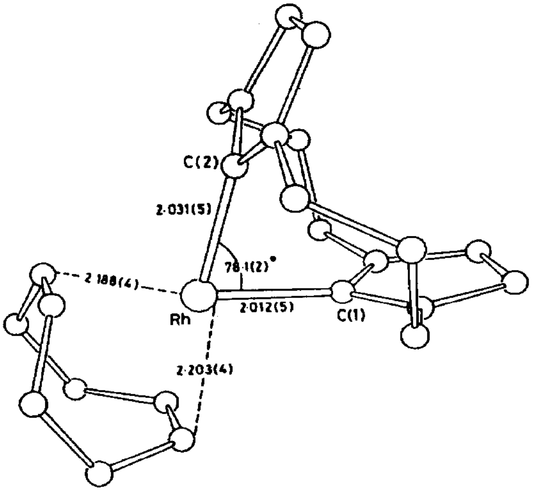
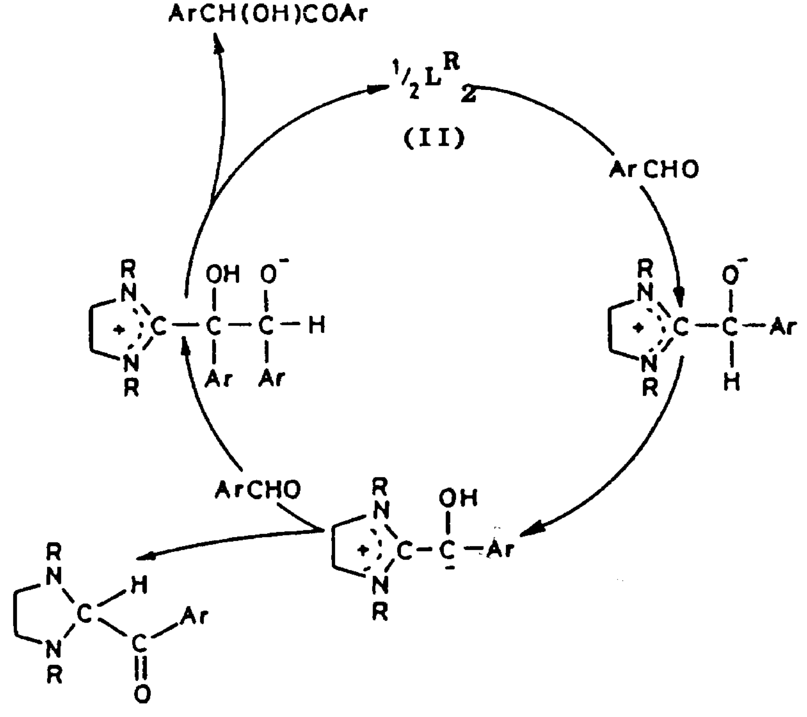


Fig. 4 [53]. Molecular structure of the cation of [*cis*-Rh(COD)(L$_2^{\mathrm{cyclam}}$)][Rh(Cl)$_2$(CO)$_2$-*cis*], showing important lengths (Å) and an angle.

F. Enetetramines and derived metal complexes as homogeneous catalysts

Carbenemetal complexes have catalytic activity comparable to that of related tertiary phosphinemetal analogues. Systems which have been investigated include (i) the *hydrogenation* of an *N*-acylamido acrylic ester (the dehydro precursor of an α-amino acid) [56], e.g., using XVIII or $[Ru(Cl)_2(L^{Me})(PPh_3)_2]$ as catalyst; (ii) the *hydrosilylation* of alkenes [56,61,83], alkynes [61], or ketones [56,61], e.g., using *cis*-$[Rh(Cl)(COD)(L^{Me})]$ or *trans*-$[Rh(Cl)(L^{Me})(PPh_3)_2]$, $[Rh(Cl)(L^R)_3]$ ($R = Et$ or CH_2Ph), (XVIII), or *trans*-$[Ru(Cl)_2(L^{Me})_4]$, (iii) the *cis*- to *trans-isomerisation* of $PhCH{=}CHSiEt_3$ using *trans*-$[Rh(Cl)(L^{Me})(PPh_3)_2]$, (iv) *Si–Si coupling*, e.g., from Ph_2SiH_2 to $[Ph_2Si(H)]_2$ using *cis*-$[Rh(Cl)(COD)(L^{Me})]$ [61] (cf. ref. 84); (v) the *metathesis* of octa-1,7-diene to cyclohexene and ethene using $[Mo(CO)_5(L^{Me})]$ in presence of $(EtAlCl_2)_2/[NBu^n_4]Cl$ [86]; and (vi) the *polymerisation* of methyl methacrylate using *cis*-$[M(CO)_4(L^{Me})_2]$ ($M = Cr$, Mo, or W) in conjunction with CCl_4 [86] (cf., ref. 87).

Regarding hydrosilylation, the following points are noteworthy [61]. (i) The addition of Et_3SiH to $PhC{\equiv}CH$ or $PhC{\equiv}CPh$ catalysed, by a carbenerhodium(I) complex, proceeded stereoselectively via *trans*-addition. (ii) The conversion of PhCOMe into $PhCH(Me)OSiEt_3$ was markedly dependent upon the nature of the *N*-substituents on the carbene ligand; thus *trans*-$[Rh(Cl)(L^{Me})(PPh_3)_2]$ gave an almost quantitative yield after 4 h at 100 °C, whereas the L^{CH_2Ph} analogue yielded only 23% after 4 h at 120 °C. (iii) Ph_2SiH_2 was very much more reactive than Ph_3SiH in the hydrosilylation of ketones, but in some cases the dehydrogenated product, e.g., $PhC({=}CH_2)OSiHPh_2$ from PhCOMe, was a significant byproduct. (iv)



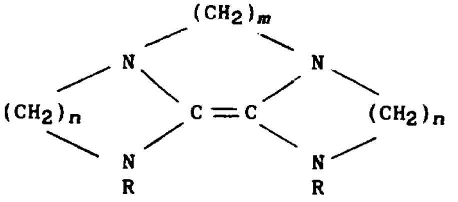
Scheme 10 [57]. A catalytic cycle for the enetetramine-catalysed benzoin condensation.

The addition of Et_3SiH to $PhC{\equiv}CH$ in presence of *cis*-$[Rh(Cl)(COD)(L^{Me})]$ was significantly photocalalysed (cf., ref. 88).

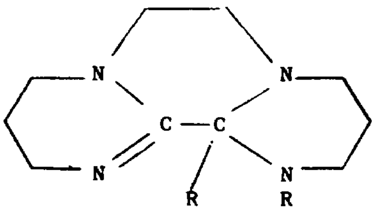
The enetetramine L_2^R ($R = Me$, Et, or CH_2Ph) was shown to be an effective catalyst (at < 1 molar% concentration) for the benzoin condensation in aprotic non-polar media [57]. When a stoicheiometric amount of L_2^{Ph} or $L_2^{o\text{-}An}$ (*o*-An = *o*-anisyl) was used in high dilution, the appropriate 2-aroylimidazolidine was obtained. The results were interpreted in terms of the cycle of Scheme 10; the catalytic activity was crucially dependent on the nature of the *N*-substituent on L_2^R ($R = Me \approx Et > CH_2Ph \gg Ar$), and for L_2^{Me} or L_2^{Et} compared favourably with those claimed for other catalysts such as thiamine (vitamin B_1) pyrophosphate.

III. A brief account of some unpublished data

The *synthesis* of (i) four endotricyclic enetetramines (XXIII) (n, m, $R = 2$, 2, CH_2Ph; 2, 3, CH_2Ph; 3, 2, CH_2Ph; and 2, 2, Me) [7] and (ii) three *N*-functionalised enetetramines II L_2^R ($R = CH_2CH_2CH_2PPh_2$, $CH_2CH{=}CHMe$, or $CH_2CH_2CH{=}CH_2$) [81] has been carried out. The precursors for (i) were either the appropriate tetramine $HN(R)(CH_2)_nNH(CH_2)_mNH(CH_2)_nNRH$ and $CH(OMe)_2NMe_2$, or (for XXIII, $n = m = 2$ and $R = Me$) $H_2N(CH_2)_2NH_2 + 2ClCH_2COCl$; whereas for (ii), the procedure of eq. 1 was employed.



(XXIII)



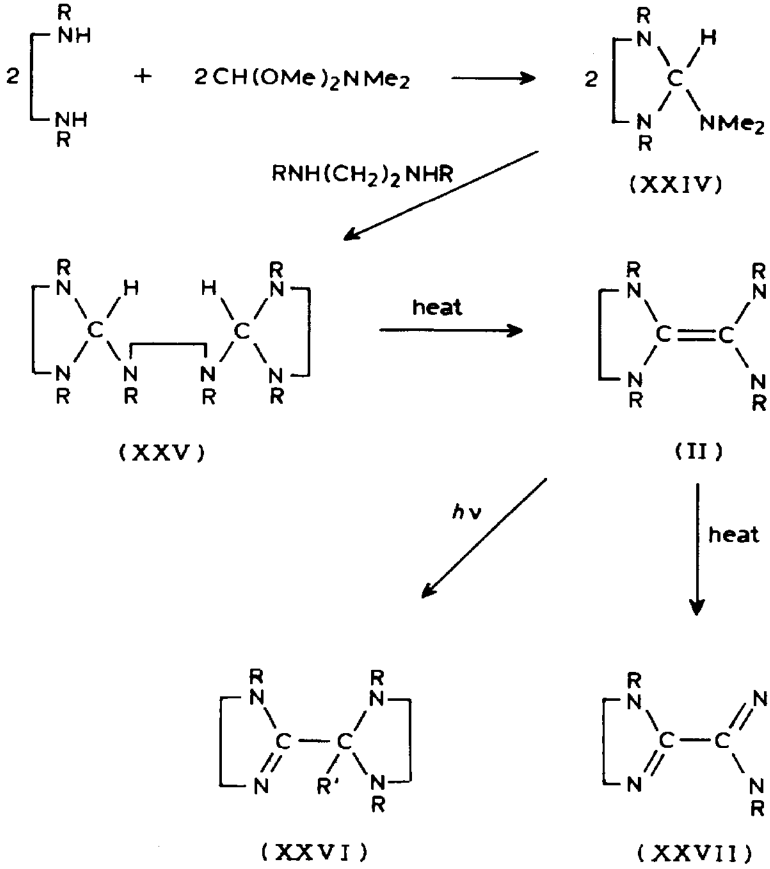
(XXVIII, R = CH2Ph)

Two *intermediates in the synthetic pathway* were isolated, XXIV and XXV [81,90], each X-ray characterised [81], Scheme 11.

X-*Ray structural data* on $L_2^{CH_2Ph}$ [82] and compound XXIII ($n = 2$, $m = 3$, $R = CH_2Ph$) [89], showed that the nitrogen environments are pyramidal rather than planar (in contrast to the situation for L_2^{Ph} [93]). A *gas electron diffraction* study of L_2^{Me} [91] revealed a molecule of D_2 symmetry with a similar geometry about the nitrogen atoms to that found for $L_2^{CH_2Ph}$ in the solid state.

Quantitative *cyclic voltammetry data*, in THF with $[NBu^n_4][ClO_4]$ as supporting electrolyte, on a series of enetetramines II, IV ($R = Me$), V, XXIII (the 4 compound mentioned above) [90,92], and L_2^R ($R = (CH_2)_3PPh_2$, $CH_2CH{=}CHMe$, or $(CH_2)_2CH{=}CH_2$) [81] showed that, in general, there are reversible one-electron oxidations [90]. In situ controlled potential electrolysis in the cavity of an ESR spectrometer enabled the *radical cations* to be fully ESR-characterised [81,92]. The unpaired electron interacted with four equivalent nitrogens for L_2^R (II) but only with those protons which are attached to the carbon atoms adjacent to these nitrogen atoms.

New reactions, not involving metals, of the enetetramines L_2^R (II) have been (i) their oxidation to *chalcogeno-ureas* $L^R = E$ (E = S, Se, or Te; R = Et [7] or CH_2Ph [90]) and (ii) their *thermolysis* or *photolysis*. X-Ray data for the $L^{Et} = E$ series



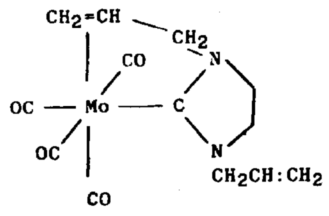
Scheme 11. Intermediates, XXIV and XXV, in the synthetic pathway to the enetetramine L_2^R, and products of thermolysis or photolysis of L_2^R (II, R = CH_2Ph).

indicated that the $C_{carb}\overset{\cdot\cdot}{-}E$ double-bond character decreased in the sequence S > Se > Te [82]. Cyclic voltammetry showed that each chalogenourea underwent an oxidation process in the range 0.2 to +1.0 V [90.92].

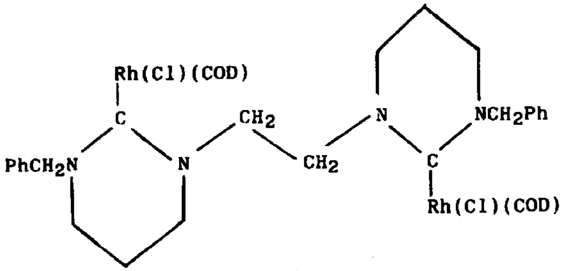
As for (ii), two of the compounds L_2^R underwent a [3,3]-*sigmatropic rearrangement* upon photolysis ($L_2^{CH_2Ph}$ [82,90]) or heating ($L_2^{CH_2CH=CHMe}$ [81]) to yield the isomer XXVI ($R = CH_2Ph = R'$; or $R = CH_2CH{=}CHMe$, $R' = CH(Me)CH{=}CH_2$, respectively). Similar benzylic sigmatropic rearrangements were observed for some of the endotricyclic enetetramines (XXIII: $n = 2 = m$; $n = 2$, $m = 3$; or $n = 3$, $m = 2$) [7] and one of them (XXVIII) [89], as well as XXVI ($R = CH_2Ph$) [82], have been crystallographically characterised. Heating $L_2^{CH_2Ph}$ caused *debenzylation* to occur to give XXVII, Scheme 11, [82,90].

New noteworthy *carbenemetal complexes*, with X-ray data, include [Ru(η^2-BH_4)($L^{Tol\text{-}p}$)(PPh_3)$_2$] [76,93], [Rh{SnCl(NR_2)$_2$}(COD)(L^{Me})] ($R = SiMe_3$) [94], [Rh(Cl)($L_3^{CH_2Ph}$)$_3$] and *trans*-[Rh(Cl)(CO)(L^{CH_2Ph})$_2$] [78], *trans*-[Pd(Cl)$_2$-($L^{CH_2CH=CH_2}$)$_2$] (XXIX) [81,82], XXX [81,89], and XXXI [7,89]. Treatment of [Rh(Cl)(L^{CH_2Ph})$_3$] with CO gave [Rh(Cl)(CO)(L^{CH_2Ph})$_3$] which upon heating yielded *trans*-[Rh(Cl)(CO)(L^{CH_2Ph})$_2$], whereas reaction with O_2 furnished [Rh(Cl)(O_2)-(L^{CH_2Ph})$_2$] [78]. An interesting feature about compounds XXIX and XXX is that they were made by an in situ procedure from $RNH(CH_2)_2NHR$ (R =

$CH_2CH{=}CH_2$), $CH(OMe)_2NMe_2$ and either $[Mo(CO)_6]$ or $[Pd(Cl)_2(NCPh)_2]$, respectively; attempts to make $L^{CH_2CH=CH_2}{}_2$ according to eq. 1 failed, the product being the isomer XXVI ($R = CH_2CH{=}CH_2$) [81]. Compound XXX is significant as a rare example of a metal complex having both an alkene and a carbene ligand, a species postulated as implicated in alkene metathesis.



(XXX)



(XXXI)

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