Supporting Information for

Metal Carbonyl Clusters of Groups 8 - 10: Synthesis and Catalysis

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Table S1. Structurally characterized homoleptic homometallic Fe carbonyl clusters (including hydrides).

Cluster	**Reference**
$Fe_2(CO)_9$	1
$[Fe_2(CO)_8]^{2-}$	2, 3, 4
$[HFe_2(CO)_8]^-$	5
$Fe_3(CO)_{12}$	6
$[Fe_3(CO)_{11}]^{2-}$	7, 8
$[HFe_3(CO)_{11}]^-$	9
$[Fe_4(CO)_{13}]^{2-}$	10
$[HFe_4(CO)_{13}]^-$	11
$[HFe_4(CO)_{12}]^{3-}$	12
$[H_2Fe_4(CO)_{12}]^{2-}$	13
$[HFe_5(CO)_{14}]^{3-}$	13

Table S2. Structurally characterized oxides and hydroxides of group 8 transition metals.

Cluster	**Reference**
$[Fe_3(CO)_9(\mu_3\text{-}O)]^{2-}$	14
$[\{Fe_3(CO)_9(\mu_3\text{-}O)\}_2H]^{3-}$	15
$[Fe_3(CO)_9(\mu_3\text{-}O)(\mu_3\text{-}AuPPh_3)]^-$	16
$[Fe_3(CO)_9(\mu_3\text{-}O\text{-}CMe_3)]^-$	17
$Fe_3(CO)_9(\mu_3\text{-}O\text{-}CMe_3)(\mu\text{-}AuPPh_3)$	17
$[Fe_3(CO)_9(\mu_3\text{-}O)(\mu_3\text{-}AuPPh_3)(\mu\text{-}AuPPh_3)$	18
$[Fe_3Rh_3(CO)_{12}(\mu_3\text{-}O)]^-$	18
$[Fe_3Mn(CO)_{12}(\mu_4\text{-}O)]^-$	19
$[Fe_3Re(CO)_{12}(\mu_4\text{-}O)]^-$	19
$[Fe_2Ru_3(CO)_{14}(\mu_4\text{-}O)]^-$	20
$FeRu_2(CO)_8(PPh_3)_2(\mu\text{-}OH)_2$	21
$Ru_3(CO)_6(dpAsm)_3(\mu_3\text{-}O)$	22
$Ru_3(CO)_4(dppm)_3(\mu_3\text{-}O)$	23
$[Ru_3(CO)_4(dppm)_3(\mu_3\text{-}OH)]^+$	23
$Ru_4(CO)_8(\mu_3\text{-}OH)_2(COEt)_4(CF_3SO_3)_2$	24

$Ru_4(CO)_{10}(\mu_3\text{-}OH)_2(CCH\text{-}iPr)(\mu\text{-}PPh_2)$	25
$Ru_6Cl_6(CO)_{12}(\mu_3\text{-}OH)_2(COEt)_4$	26
$Ru_6(CO)_{18}(\mu\text{-}OH)_2(\mu_4\text{-}S)$	27
$Os_4(CO)_{12}(\mu_3\text{-}O)_4$	28
$Os_6(CO)_{19}(\mu_3\text{-}O)$	29
$Os_6(CO)_{16}(\mu\text{-}H)(\mu_3\text{-}O)(C_5H_5N)(\mu\text{-}\eta^2\text{-}NC_5H_4)$	30
$Os_3(CO)_8(NMe_3)(\mu\text{-}OH)(\mu\text{-}H)(\mu_3\text{-}S)$	31
$Os_3(CO)_9(L)(\mu\text{-}OH)(\mu\text{-}H)$	32
$Os_3(CO)_9(\mu\text{-}OH)(\mu\text{-}H)(\mu_3\text{-}C_2CPh_2)$	33
$Os_3(CO)_{10}(\mu\text{-}OH)(\mu\text{-}NCMe_2)$	34
$Os_4(CO)_{12}(\mu\text{-}OH)H_3$	35
$[Os_4(CO)_{12}(\mu\text{-}OH)H_4]^+$	36
$Os_6(CO)_{18}(\mu_4\text{-}O)(\mu\text{-}OH)_2$	37
$Os_6(CO)_{18}(\mu\text{-}OH)(\mu\text{-}H)(\mu_4\text{-}S)(\mu_3\text{-}S)$	31

Table S3. Structurally characterized homoleptic homometallic Ru carbonyl clusters (including hydrides).

Cluster	**Reference**
$\{Ru(CO)_4\}_\infty$	38
$[Ru_2(CO)_8]^{2-}$	3, 39
$Ru_3(CO)_{12}$	40, 41
$[Ru_3(CO)_{11}]^{2-}$	42
$[HRu_3(CO)_{11}]^-$	43
$[Ru_4(CO)_{13}]^{2-}$	44
$[HRu_4(CO)_{13}]^-$	45
$H_2Ru_4(CO)_{13}$	46
$[H_2Ru_4(CO)_{12}]^{2-}$	44, 47
$[H_3Ru_4(CO)_{12}]^-$	48
$H_4Ru_4(CO)_{12}$	49
$[Ru_6(CO)_{18}]^{2-}$	8, 50
$[HRu_6(CO)_{18}]^-$	51
$H_2Ru_6(CO)_{18}$	52

$H_2Ru_6(CO)_{17}$	53
$[HRu_7(CO)_{20}]^-$	54
$[H_2Ru_8(CO)_{21}]^{2-}$	55
$[H_2Ru_{10}(CO)_{25}]^{2-}$	56
$[HRu_{11}(CO)_{27}]^{3-}$	56

Table S4. Structurally characterized homoleptic homometallic Os carbonyl clusters (including hydrides).

Cluster	**Reference**
$[Os_2(CO)_8]^{2-}$	39
$Os_3(CO)_{12}$	57, 58
$H_2Os_3(CO)_{11}$	58
$[HOs_3(CO)_{11}]^-$	59
$H_2Os_3(CO)_{10}$	60
$Os_4(CO)_{15}$	61
$Os_4(CO)_{14}$	62
$[HOs_4(CO)_{13}]^-$	63
$H_2Os_4(CO)_{13}$	59
$[H_2Os_4(CO)_{12}]^{2-}$	64
$[H_3Os_4(CO)_{12}]^-$	48
$H_4Os_4(CO)_{12}$	65
$Os_5(CO)_{19}$	66
$Os_5(CO)_{18}$	67
$Os_5(CO)_{16}$	68
$H_2Os_5(CO)_{16}$	69
$[HOs_5(CO)_{15}]^-$	70
$H_2Os_6(CO)_{19}$	71
$Os_6(CO)_{18}$	72
$[Os_6(CO)_{18}]^{2-}$	73
$[HOs_6(CO)_{18}]^-$	74
$H_2Os_6(CO)_{18}$	73, 74
$H_2Os_7(CO)_{22}$	75
$Os_7(CO)_{21}$	76

$H_2Os_7(CO)_{21}$	75
$[Os_7(CO)_{20}]^{2-}$	77
$H_2Os_7(CO)_{20}$	78
$Os_8(CO)_{23}$	79
$[Os_8(CO)_{22}]^{2-}$	79
$[HOs_8(CO)_{22}]^{-}$	80
$[Os_9(CO)_{24}]^{2-}$	81
$[HOs_9(CO)_{24}]^{-}$	81
$[Os_{10}(CO)_{26}]^{2-}$	82
$[H_4Os_{10}(CO)_{24}]^{2-}$	83
$[H_5Os_{10}(CO)_{24}]^{-}$	84
$Os_{12}(CO)_{30}$	85
$[Os_{17}(CO)_{36}]^{2-}$	86
$[Os_{20}(CO)_{40}]^{2-}$	86

Table S5. Structurally characterized homoleptic homometallic Co carbonyl clusters (including hydrides).

Cluster	**Reference**
$Co_2(CO)_8$	87, 88
$[Co_3(CO)_{10}]^{-}$	89
$HCo_3(CO)_9$	90
$Co_4(CO)_{12}$	91
$[Co_4(CO)_{11}]^{2-}$	92
$Co_6(CO)_{16}$	93
$[Co_6(CO)_{15}]^{2-}$	8, 93, 94
$[HCo_6(CO)_{15}]^{-}$	95
$[Co_6(CO)_{14}]^{4-}$	93

Table S6. Structurally characterized homoleptic homometallic Rh carbonyl clusters (including hydrides).

Cluster	**Reference**
$Rh_4(CO)_{12}$	96
$[Rh_4(CO)_{11}]^{2-}$	97
$[Rh_5(CO)_{15}]^{-}$	99
$Rh_6(CO)_{16}$	99
$[Rh_7(CO)_{16}]^{3-}$	100
$[Rh_9(CO)_{19}]^{3-}$	101
$[Rh_{10}(CO)_{21}]^{2-}$	102
$[Rh_{11}(CO)_{23}]^{3-}$	8, 103
$[Rh_{12}(CO)_{30}]^{2-}$	104
$H_2Rh_{12}(CO)_{25}$	105
$[H_{5-n}Rh_{13}(CO)_{24}]^{n-}$ (n = 2-4)	106-109
$[Rh_{14}(CO)_{26}]^{2-}$	107, 110
$[H_{4-n}Rh_{14}(CO)_{25}]^{n-}$ (n = 3-4)	111-113
$[Rh_{15}(CO)_{30}]^{3-}$	114
$[Rh_{15}(CO)_{27}]^{3-}$	113, 115
$[Rh_{17}(CO)_{37}]^{3-}$	115
$[Rh_{17}(CO)_{30}]^{3-}$	116
$[Rh_{22}(CO)_{37}]^{4-}$	117
$[H_{8-n}Rh_{22}(CO)_{35}]^{n-}$ (n = 4-5)	118
$[Rh_{33}(CO)_{47}]^{5-}$	119

Table S7. Structurally characterized homoleptic homometallic Ir carbonyl clusters (including hydrides).

Cluster	**Reference**
$Ir_4(CO)_{12}$	120
$[HIr_4(CO)_{11}]^{-}$	121
$[H_2Ir_4(CO)_{10}]^{2-}$	122
$[HIr_5(CO)_{12}]^{2-}$	123
$Ir_6(CO)_{16}$	124
$[Ir_6(CO)_{15}]^{2-}$	125

$[Ir_8(CO)_{22}]^{2-}$	126
$[Ir_8(CO)_{18}]^{2-}$	8
$[Ir_9(CO)_{20}]^{3-}$	127
$[HIr_9(CO)_{19}]^{4-}$	128
$[Ir_{10}(CO)_{21}]^{2-}$	128
$[Ir_{11}(CO)_{23}]^{3-}$	129
$[Ir_{12}(CO)_{26}]^{2-}$	130
$[Ir_{12}(CO)_{24}]^{2-}$	131
$[Ir_{14}(CO)_{27}]^{-}$	132

Table S8. Structurally characterized homoleptic homometallic Ni carbonyl clusters (including hydrides).

Cluster	**Reference**
$[Ni_5(CO)_{12}]^{2-}$	133, 134
$[Ni_6(CO)_{12}]^{2-}$	135
$[Ni_9(CO)_{18}]^{2-}$	136
$[Ni_9(CO)_{16}]^{2-}$	137
$[Ni_{12}(CO)_{21}]^{4-}$	138
$[HNi_{12}(CO)_{21}]^{3-}$	139
$[H_2Ni_{12}(CO)_{21}]^{2-}$	139

Table S9. Structurally characterized high nuclearity heterometallic Ni carbonyl clusters.

Cluster	**Reference**
$[NiRh_{13}(CO)_{25}]^{5-}$	140
$[NiRh_{14}(CO)_{28}]^{4-}$	141
$[Ni_2Rh_{12}(CO)_{25}]^{4-}$	140
$[Ni_5Rh_9(CO)_{25}]^{n-}$ (n = 3, 4)	140
$[Ni_6Rh_5(CO)_{21}]^{3-}$	142
$[Ni_9Rh_3(CO)_{22}]^{3-}$	143
$[Ni_{10}Rh(CO)_{19}]^{3-}$	143
$[Ni_{13}Pd_{13}(CO)_{34}]^{4-}$	144
$[Ni_{16}Pd_{16}(CO)_{40}]^{4-}$	145
$[Ni_{22-x}Pd_{20+x}(CO)_{48}]^{6-}$ (x = 0.62)	146

$[Ni_{26}Pd_{20}(CO)_{54}]^{6-}$	145
$[Ni_{29-x}Pd_{6+x}(CO)_{42}]^{6-}$ (x = 0.09)	146
$[Ni_{29+x}Pd_{6-x}(CO)_{42}]^{6-}$ (x = 0.27)	146
$[Ni_{36}Pd_{8}(CO)_{48}]^{6-}$	147
$[Ni_{14}Pt_{10}(CO)_{30}]^{4-}$	148
$[H_2Ni_{24}Pt_{14}(CO)_{44}]^{4-}$	148
$[H_{6-n}Ni_{24}Pt_{17}(CO)_{47}]^{n-}$	149
$[Ni_{32}Pt_{24}(CO)_{56}]^{6-}$	149
$[Ni_{35}Pt_{9}(CO)_{48}]^{6-}$	147
$[Ni_{36}Pt_{4}(CO)_{45}]^{6-}$	150
$[Ni_{37}Pt_{4}(CO)_{46}]^{6-}$	150
$[H_{6-n}Ni_{38}Pt_{6}(CO)_{48}]^{n-}$ (n = 4-6)	151
$[Ni_{35-x}Cu_{x}(CO)_{40}]^{5-}$ (x = 3 or 5)	152
$[Ni_{12}Au(CO)_{24}]^{3-}$	153
$[Ni_{12}Au_{6}(CO)_{24}]^{3-}$	154
$[Ni_{32}Au_{6}(CO)_{44}]^{6-}$	155

Table S10. Structurally characterized Ni carbide carbonyl clusters.

Cluster	**Reference**
$[Ni_7C(CO)_{12}]^{2-}$	156
$[Ni_8C(CO)_{16}]^{2-}$	157
$[Ni_9C(CO)_{17}]^{2-}$	157
$[Ni_{10}(C_2)(CO)_{16}]^{2-}$	157
$[Ni_{11}(C_2)(CO)_{15}]^{4-}$	156
$[Ni_{12}(C_2)(CO)_{16}]^{4-}$	156
$[Ni_{12}C(CO)_{18}]^{4-}$	159
$[Ni_{16}(C_2)_2(CO)_{23}]^{4-}$	160
$[Ni_{16+x}(C_2)_2(CO)_{23+x}]^{4-}$ (x = 0.12-0.96)	161
$[Ni_{22}(C_2)_4(CO)_{28}Cl]^{3-}$	160
$[Ni_{22}(C_2)_4(CO)_{28}(Et_2S)]^{2-}$	159
$[H_{4-n}Ni_{25}(C_2)_4(CO)_{32}]^{n-}$ (n = 3, 4)	161, 162
$[Ni_{32}C_6(CO)_{36}]^{6-}$	163
$[Ni_{32+x}C_6(CO)_{36+x}]^{6-}$ (x = 0.16)	164

$[HNi_{34}C_4(CO)_{38}]^{5-}$	165
$[Ni_{34+x}C_4(CO)_{38+x}]^{6-}$ (x = 0.09)	166
$[Ni_{35}C_4(CO)_{38}]^{6-}$	167
$[H_{6-n}Ni_{38}C_6(CO)_{42}]^{n-}$ (5, 6)	166
$[Ni_{45}C_{10}(CO)_{46}]^{6-}$	164
$NiFe_4C(CO)_{10}(Cp)_2$	167
$NiFe_4C(CO)_{13}(MeCN)$	168
$NiFe_4C(CO)_{12}(MeCN)_2$	168
$NiFe_5C(CO)_{16}$	1768
$NiFe_5C(CO)_{15}(NH_3)$	168
$NiFe_5C(CO)_{15}(MeCN)$	168
$Ni_2Fe_4C(CO)_{15}$	168
$[Ni_3Ru_3C(CO)_{13}]^{2-}$	169
$NiRu_5C(CO)_{14}(PPh_3)_2$	170
$NiRu_5C(CO)_{16}$	171
$NiRu_5C(CO)_{15}(NH_3)$	171
$NiRu_5C(CO)_{15}(MeCN)$	171
$NiRu_5C(CO)_{13}(C_6H_5R)$ (R = H, Me)	171
$[Ni_4Os_3C(CO)_{15}]^{2-}$	172
$[Ni_2Co_6(C_2)(CO)_{16}]^{2-}$	173
$[Ni_2Co_6(C_2)(CO)_{14}(MeCN)_2]^{2-}$	173
$[Ni_9Co(C_2)(CO)_{16-x}]^{3-}$ (x = 0.58)	174
$[Ni_7Co_3(C_2)(CO)_{16}]^{3-}$	175
$[Ni_{10}Co_2C(CO)_{20}]^{2-}$	176
$[Ni_9Co_3C(CO)_{20}]^{2-}$	176
$[Ni_9Co_3C(CO)_{20}]^{3-}$	177
$[H_{6-n}Ni_{22}Co_6C_6(CO)_{36}]^{n-}$ (n = 4, 6)	174
$[Ni_{36}Co_8C_8(CO)_{48}]^{6-}$	178
$[Ni_{10}Rh_2C(CO)_{20}]^{2-}$	179
$[Ni_9Rh_3C(CO)_{20}]^{3-}$	179
$[Ni_6Rh_8(C_2)_2(CO)_{24}]^{4-}$	179
$[H_2Ni_{30}C_4(CO)_{34}\{Cu(MeCN)\}_2]^{4-}$	180
$[H_2Ni_{29}C_4(CO)_{34}\{Cu(MeCN)\}_2]^{2-}$	180

$[Ni_{38}C_6(CO)_{36}(MeCN)_6\{Cu(MeCN)\}_{2x}]^{2-}$ (x = 0.17)	164
$[HNi_{42}C_8(CO)_{44}(CuCl)]^{7-}$	164
$[HNi_{42+2x}C_8(CO)_{44+2x}(CuCl)_{1-x}]^{7-}$(x = 0.17, 0.30)	181
$[H_2Ni_{43+x}C_8(CO)_{45+2x}(CuCl)_{1-x}]^{6-}$(x = 0.72)	181
$Ni_6C(CO)_9(AuPPh_3)_4$	182
$[Ni_6C(CO)_8(AuPPh_3)_8]^{2+}$	183
$[Ni_{12}(C)(C_2)(CO)_{17}(AuPPh_3)_3]^{-}$	184
$[H_2Ni_{22}(C_2)_4(CO)_{28}(CdBr)_2]^{2-}$	184
$[H_{6-n}Ni_{30}C_4(CO)_{34}(CdX)_2]^{n-}$ (n = 4-6; X = Cl, Br, I)	185, 186
$[H_2Ni_{32-x}C_4(CO)_{36-x}(CdBr)]^{5-}$ (x = 0.22)	186
$[HNi_{33-x}C_4(CO)_{37-x}(CdCl)]^{6-}$ (x = 0.86)	186
$[Ni_{36}C_8(CO)_{36}(Cd_2Cl_3)]^{5-}$	187
$[Ni_{36-x}C_8(CO)_{34-x}(MeCN)_3(Cd_2Cl_3)]^{3-}$(x = 0.61)	187
$[Ni_{42+x}C_8(CO)_{44+x}(CdCl)]^{7-}$(x = 0.19)	187
$[HNi_{42+x}C_8(CO)_{44+x}(CdBr)]^{6-}$(x = 0.19)	187

Table S11. Structurally characterized homoleptic homometallic Pt carbonyl clusters.

Cluster	**Reference**
$[Pt_6(CO)_{12}]^{2-}$	188
$[Pt_9(CO)_{18}]^{2-}$	188-190
$[Pt_{12}(CO)_{24}]^{2-}$	188, 189, 191-193
$[Pt_{14}(CO)_{18}]^{4-}$	194
$[Pt_{15}(CO)_{30}]^{2-}$	188, 189, 192
$[Pt_{15}(CO)_{19}]^{4-}$	195
$[Pt_{18}(CO)_{36}]^{2-}$	189, 192, 196
$[Pt_{19}(CO)_{22}]^{4-}$	197
$[Pt_{21}(CO)_{42}]^{2-}$	189
$[Pt_{23}(CO)_{27}]^{2-}$	194
$[Pt_{24}(CO)_{48}]^{2-}$	192, 198
$[Pt_{24}(CO)_{30}]^{2-}$	194
$[Pt_{26}(CO)_{32}]^{2-}$	194

$[Pt_{26}(CO)_{32}]^{-}$	194
$[Pt_{33}(CO)_{38}]^{2-}$	196
$[Pt_{36}(CO)_{44}]^{2-}$	194
$[Pt_{38}(CO)_{44}]^{2-}$	191,194, 199
$[Pt_{40}(CO)_{40}]^{6-}$	200
$[Pt_{44}(CO)_{45}]^{n-}$	194

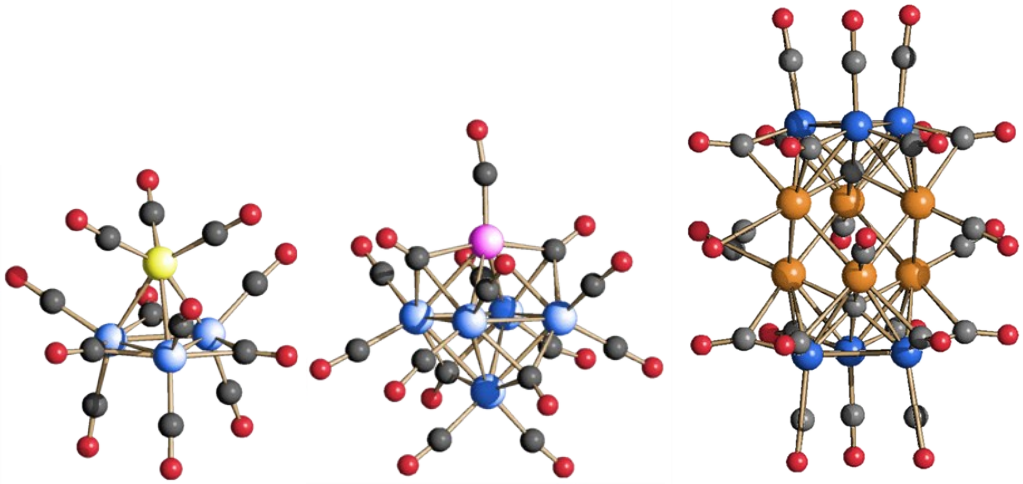


Figure S1. Molecular structures of $[Co_3Fe(CO)_{12}]^-$ (yellow, Fe, blue, Co; grey, C; red, O), $[PtRh_5(CO)_{15}]^-$ (purple, Pt; blue, Rh) and $[Co_8Pt_4C_2(CO)_{24}]^{2-}$ (blue, Co; orange, disordered Pt/Co)

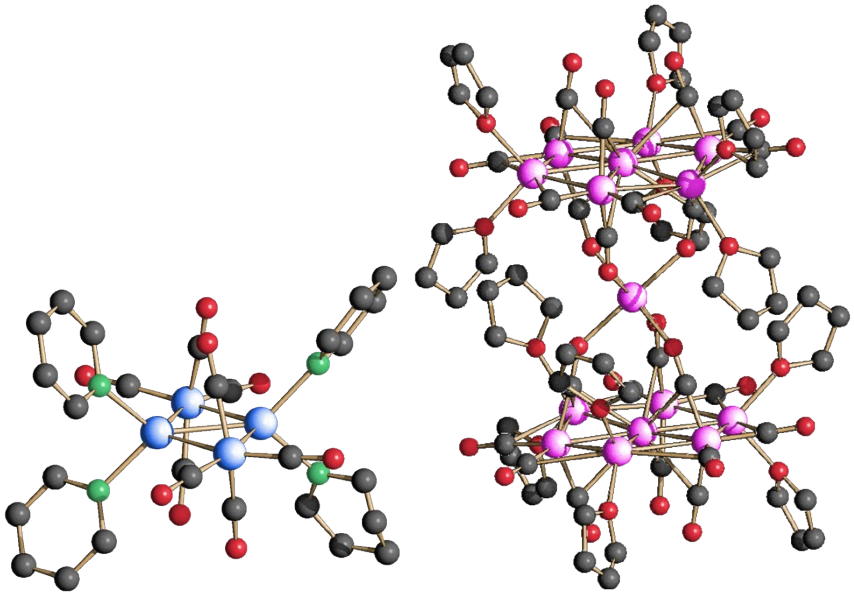


Figure S2. Molecular structures of $Fe_4(CO)_8(py)_4$(blue, Fe; green, N; red, O; grey, C) and $[Mn][Mn_7(thf)_6(CO)_{12}]_2$ (purple, Mn). Hydrogens have been omitted for clarity.

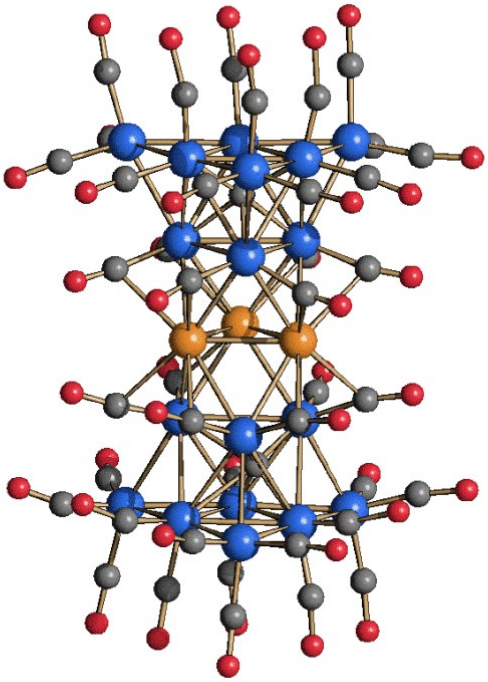


Figure S3. Molecular structure of $[Os_{18}Pd_3C_2(CO)_{42}]^{2-}$ (orange, Pd; blue, Os; red, O; grey, C).

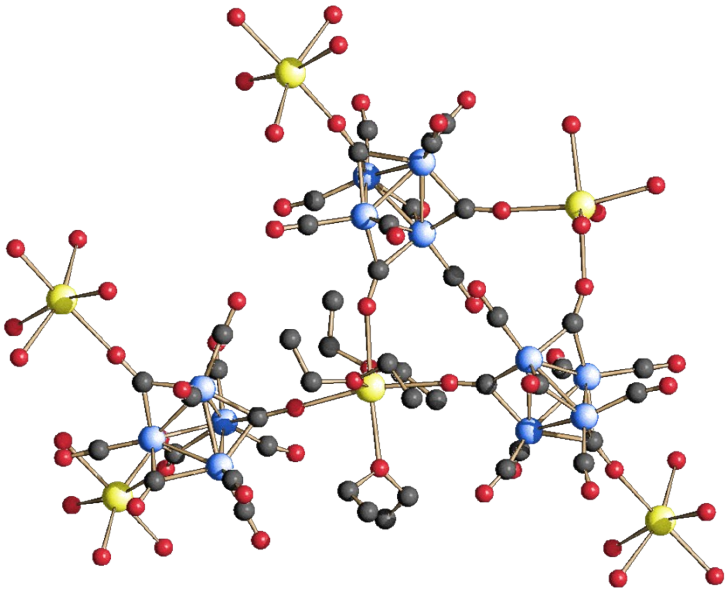


Figure S4. Molecular structure of $[\{(Et_2O)_3Ln[Co_4(CO)_{11}]\}_\infty$ (yellow, Yb or Eu; blue, Co; red, O; grey, C). Hydrogens have been omitted for clarity.

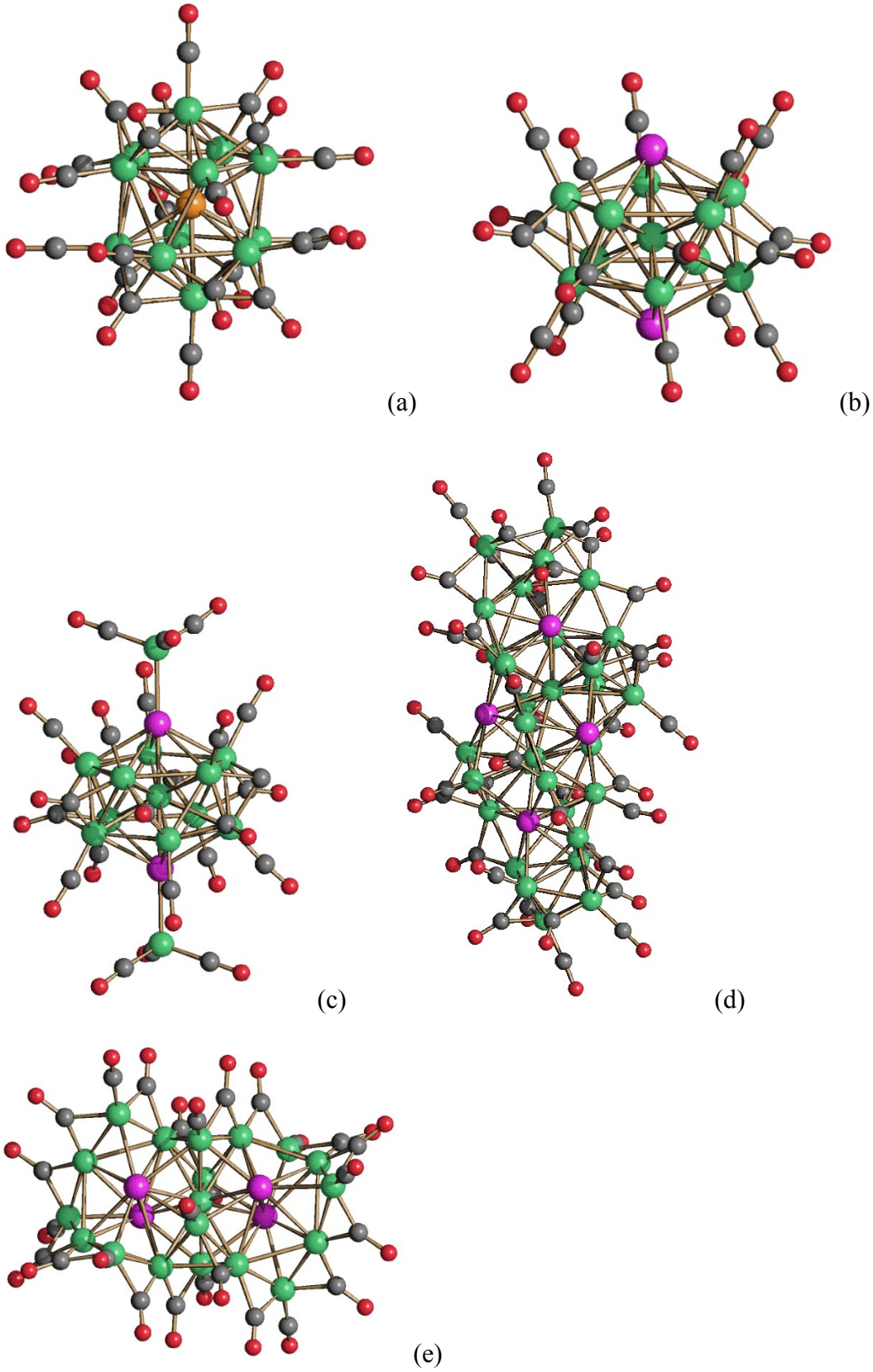


Figure S5. The molecular structures of (a) $[Ni_{12}Ga(CO)_{22}]^{3-}$, (b) $[Ni_{11}Sb_2(CO)_{18}]^{3-}$, (c) $[Ni_{13}Sb_2(CO)_{24}]^{2-}$, (d) $[Ni_{31}Sb_4(CO)_{40}]^{6-}$and (e) $[Ni_{19}Sb_4(CO)_{26}]^{4-}$(green, Ni; orange, Ga; purple, Sb; grey, C; red, O).

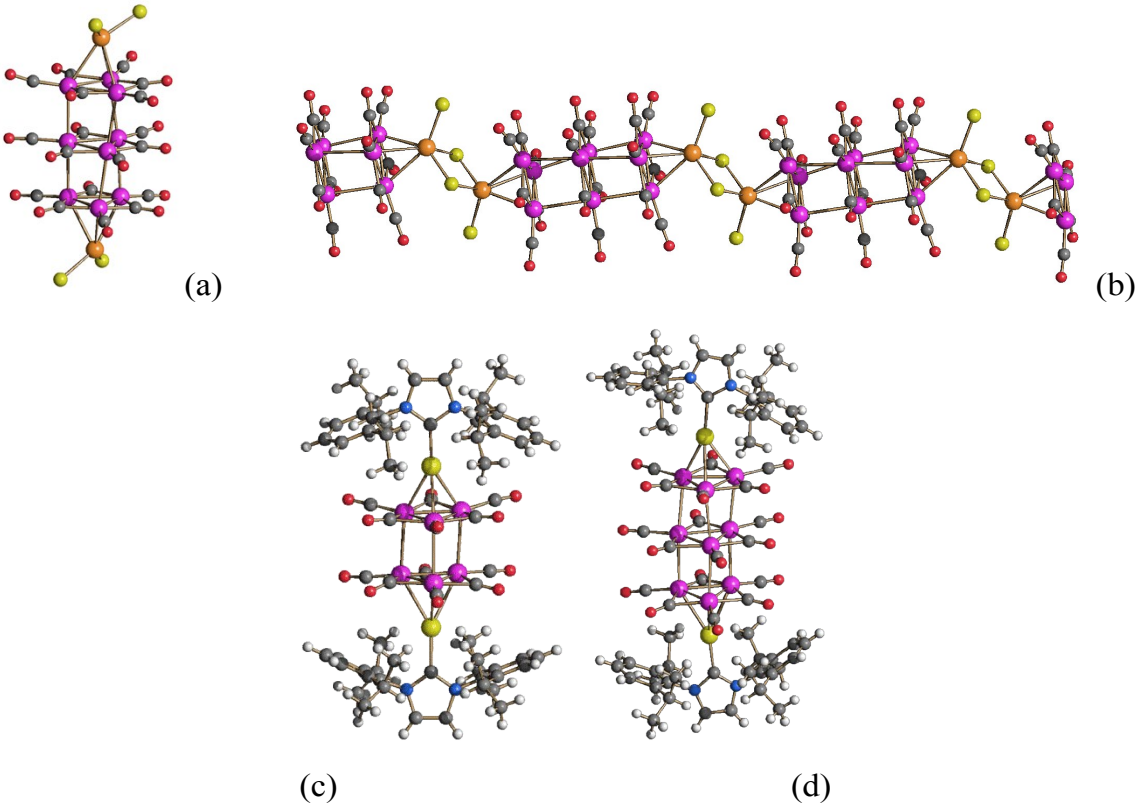


Figure S6. Formation of Lewis acid-base adducts of Chini clusters: (a) The molecular structure of $[Pt_9(CO)_{18}(\mu_3\text{-}CdCl_2)_2]^{2-}$ and (b) a chunk of the 1-D $\{[Pt_9(CO)_{18}(\mu_3\text{-}CdCl_2)_2]^{2-}\}_\infty$ superwire (purple, Pt; orange, Cd; yellow, Cl; red, O; grey, C). The molecular structure of (c) $[Pt_6(CO)_{12}(AgIPr)_2]$ and (d) $[Pt_9(CO)_{18}(AgIPr)_2]$ (purple, Pt; yellow, Ag; blue, N; red, O; grey, C; white, H).

$$nPd(OAc)_2 + (x+n)CO + yPR_3 + nH_2O \longrightarrow Pd_n(CO)_x(PR_3)_y + nCO_2 + 2nHOAc$$

Scheme S1. Synthesis of Pd-CO-PR_3 clusters.

Synthesis of $[HFe_3(CO)_{11}]^-$

$$NEt_3 + H_2O \rightleftharpoons [NEt_3H]^+ + OH^-$$

$$Fe(CO)_5 + 3OH^- \rightleftharpoons [Fe(CO)_4]^{2-} + HCO_3^- + H_2O$$

$$[Fe(CO)_4]^{2-} + H_2O \rightleftharpoons [HFe(CO)_4]^- + OH^-$$

$$[HFe(CO)_4]^- + Fe(CO)_5 \rightleftharpoons [HFe_2(CO)_8]^- + CO$$

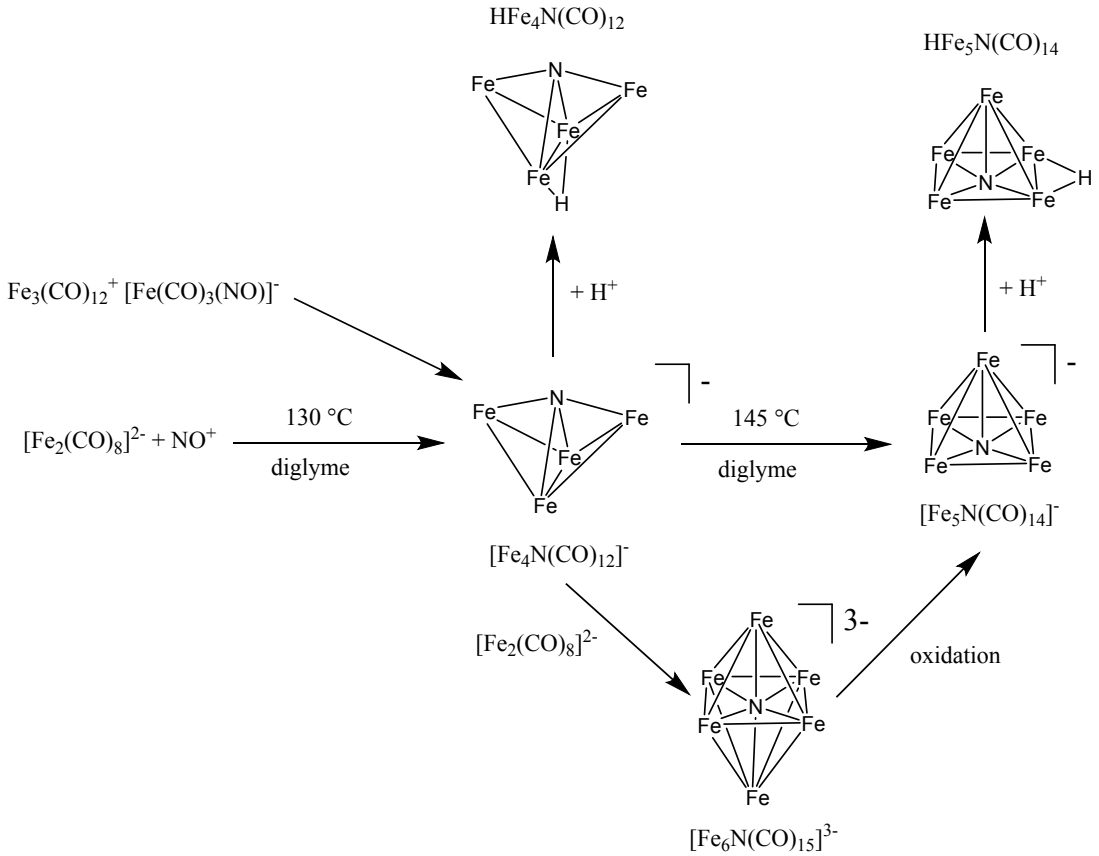
$$[HFe_2(CO)_8]^- + Fe(CO)_5 \rightleftharpoons [HFe_3(CO)_{11}]^- + 2CO$$

Synthesis of $[Fe_4(CO)_{13}]^{2-}$

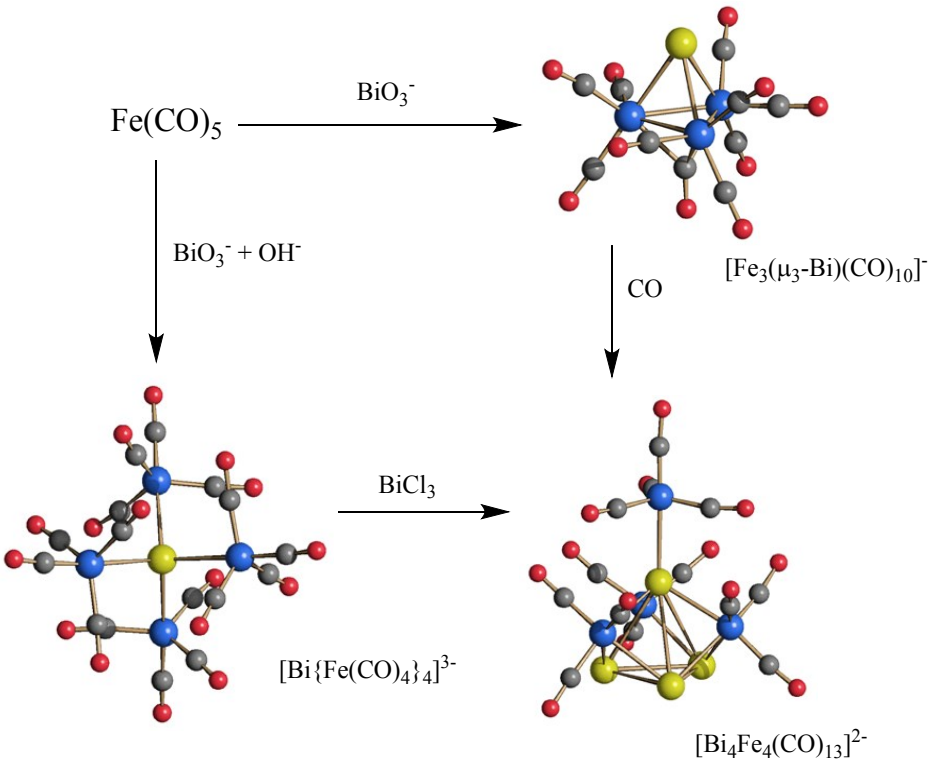
$$5Fe(CO)_5 + 6solv \xrightarrow{100\ °C} [Fe_4(CO)_{13}]^{2-} + [Fe(solv)_6]^{2+}$$

solv = DMF or pyridine

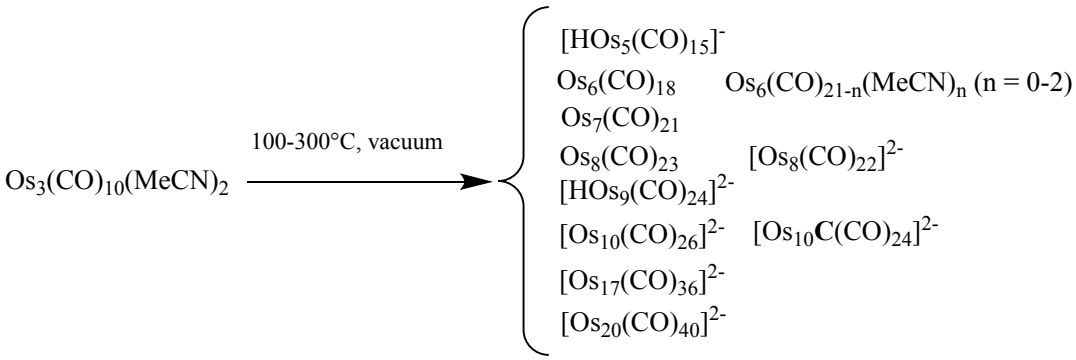
Scheme S2. Synthesis of $[HFe_3(CO)_{11}]^-$ and $[Fe_4(CO)_{13}]^{2-}$.



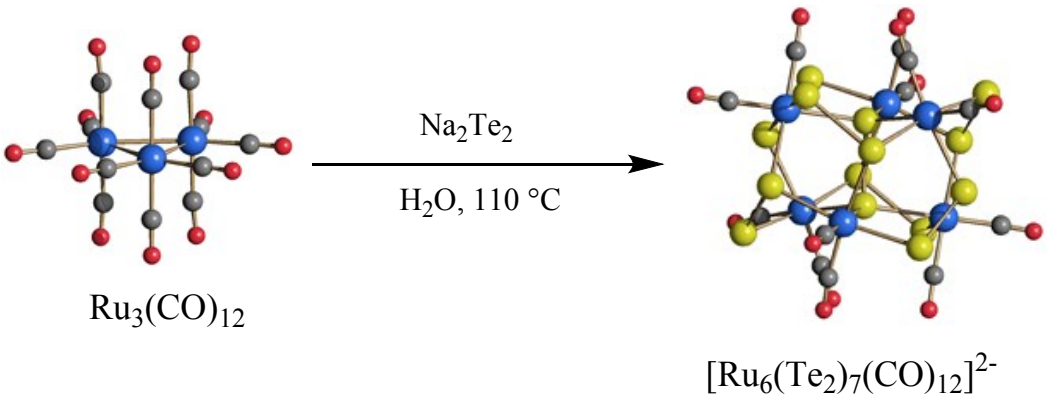
Scheme S3. Synthesis of Fe nitride carbonyl clusters.CO ligands have been omitted for clarity.



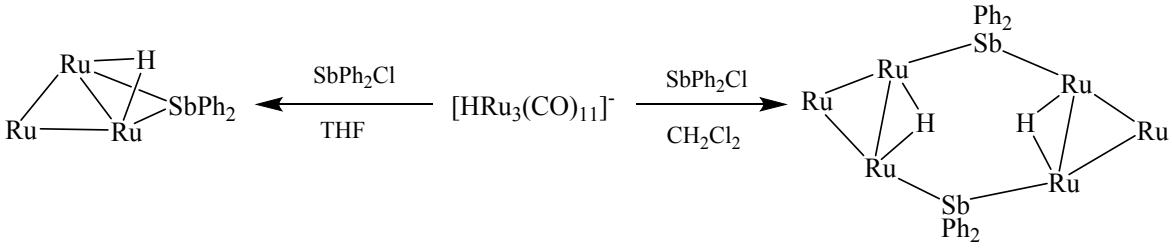
Scheme S4. Synthesis of some Fe-Bi carbonyl clusters (yellow, Bi; blue, Fe; red, O; grey, C).



Scheme S5. Synthesis of Os carbonyl clusters by pyrolysis of $Os_3(CO)_{10}(MeCN)_2$.



Scheme S6. Synthesis of $[Ru_6(Te_2)_7(CO)_{12}]^{2-}$ (blue, Os; yellow, Te; red, O; grey, C).



Scheme S7. The reaction of $[HRu_3(CO)_{11}]^-$ with $SbPh_2Cl$.CO ligands have been omitted for clarity.

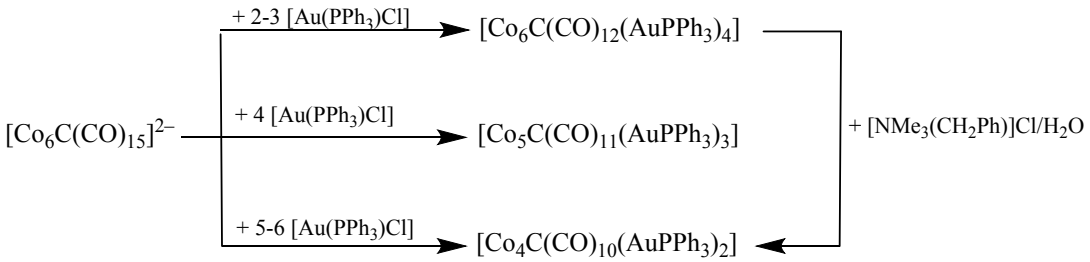
$3Co_2(CO)_8 + 12solv \rightarrow 2[Co(solv)_6][Co(CO)_4]_2 + 8CO$

$7[Co(solv)_6][Co(CO)_4]_2 \rightarrow 3[Co(solv)_6][Co_6(CO)_{15}] + 11CO$

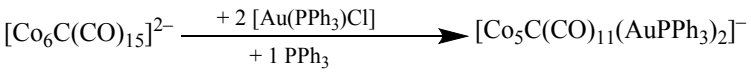
$7Co_2(CO)_8 + 8py \rightarrow 2[Co(py)_4][Co_3(CO)_{10}]_2 + 16CO$

Scheme S8. Disproportionation of $Co_2(CO)_8$.

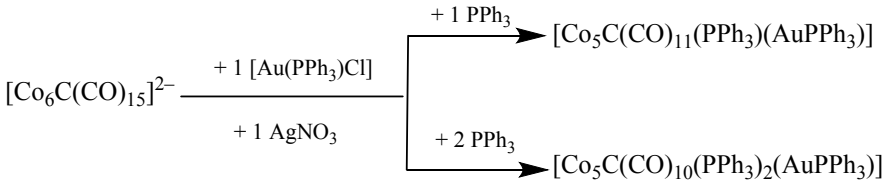
1) Amount of $[Au(PPh_3)Cl]$



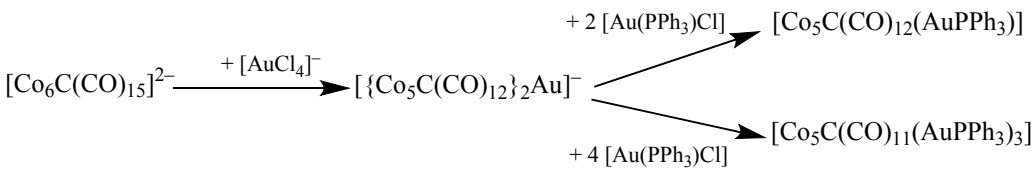
2) With free PPh_3



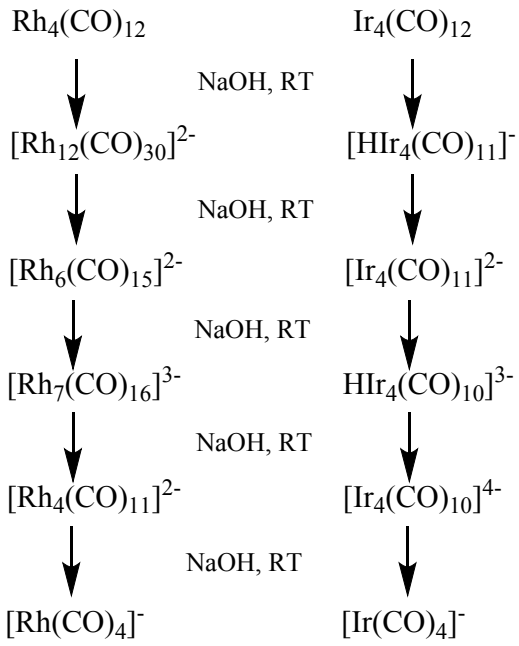
3) Silver salts



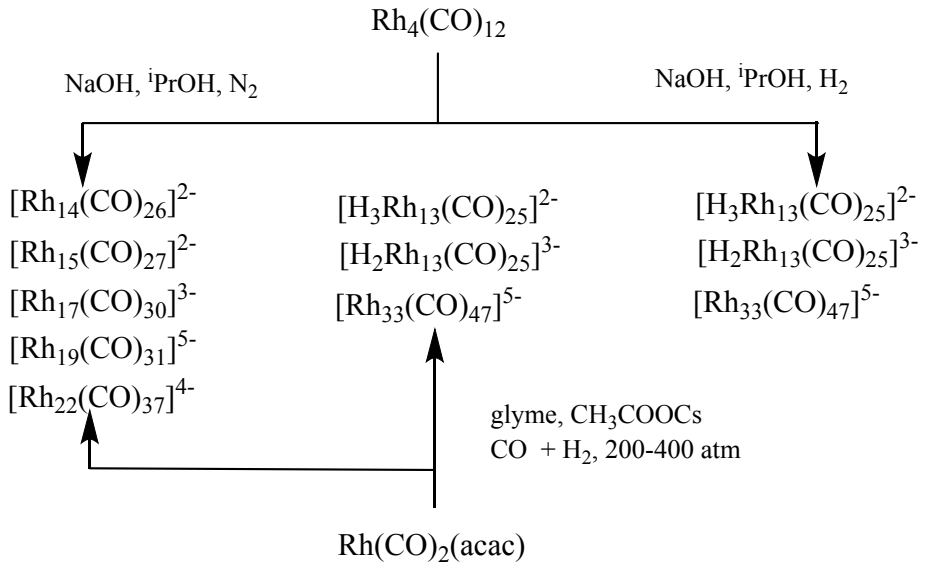
4) Other methods



Scheme S9. Synthesis of Co-carbide carbonyl clusters decorated by $AuPPh_3$ fragments.



Scheme S10. Reduction of $M_4(CO)_{12}$ (M = Rh, Ir) with NaOH.



Scheme S11. Thermolysis of $Rh_4(CO)_{12}$.

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