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Review

The role of gold in transition metal carbonyl clusters

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ABSTRACT

In this review, the authors describe the role of gold in the chemistry of transition metal carbonyl clusters, a field that has been very active over the past fifty years. Both homo- and heteroleptic Au-containing species of metal carbonyl clusters, fully characterized by X-ray analysis, are discussed across three categories: those which are surface decorated by Au(I) fragments, cluster units connected by naked Au(I) atoms, and Au core–shell species with metallic gold structures embedded in the cluster frameworks.

Contents

1. Introduction

Since the very beginning of our civilization, gold has always been considered a substance of great value, but – perhaps owing to its noble character – in-depth study of the chemistry of gold only took off relatively recently. This started with the first organometallic compounds, followed by molecular clusters [1], colloids and nanoparticles (AuNPs) [2], and most recently atomically precise gold nanoclusters [3]. Once the synthesis of AuNPs was fully elucidated [4], countless papers describing their role in medicine [5], biology [6], catalysis and nanotechnology [7] have been published.

This review focuses on the role of gold in the chemistry of transition-metal carbonyl clusters, an active field that began with the pioneering work of Coffey, Lewis and Nyholm [8] who prepared carbonyl complexes containing M—Au bonds (M = Mn, Fe, Co). Interest in such a topic mainly derives from the potential application of heterometallic clusters in catalysis, where the combined action of different metals may enhance catalytic properties [9], but these clusters can also serve as models of the modifications to the substrate that arise at a molecular level. The first reported bimetallic carbonyl cluster, $[FeCo_3(CO)_{12}]^-$, was synthesized by Chini and co-workers in 1960 [10], and later employed for $[AuL]^+$ addiction reactions (see Table 1).

The authors' ambition is to offer an up-to-date survey of gold-containing transition-metal carbonyl clusters, both homo- and heteroleptic, citing those compounds whose crystal structures have been fully characterized by X-ray analysis, and discussing

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Table 1
Homo- and heteroleptic transition metal carbonyl clusters surface-decorated by Au(I) fragments.

Metal	Compound	Cluster Precursor	Au(I) complex	Ref.
Mo, W	$M_3(CO)_9(OEt)_3(AuPPh_3)_3$ (M = Mo, W)	$[M_3(CO)_9(OEt)_3]^{3-}$	$AuPPh_3Cl$	[13]
Re	$Re_2(CO)_8Ph(AuPPh_3)$	$HRe_2(CO)_8(C_2H_2{}^nBu)$	$AuPPh_3Ph$	[14]
	$Re_2(CO)_8(AuPPh_3)_2$	$Re(CO)_5(AuPPh_3)$	–	[15]
	$Re_2(CO)_8(AuNHC)_{2-n}X_n$ (n = 0, 1; X = H, Ph, C_2H_3)	$HRe_2(CO)_8(C_2H_2{}^nBu)$	Au(NHC)Me	[16]
	$[H_3Re_3(CO)_9(AuPPh_3)]^-$	$[H_3Re_3(CO)_{10}]^{2-}$	$AuPPh_3Cl$	[17]
	$[Re_7C(CO)_{21}(AuPPh_3)]^{2-}$	$[Re_7C(CO)_{21}]^{3-}$	$AuPPh_3Cl$	[18]
Fe	$[Fe_2(CO)_8(AuPPh_3)]^-$	$[Fe_2(CO)_8]^{2-}$	$AuPPh_3Cl$	[19]
	$Fe_2(CO)_7(PhC_2PhH)(AuPPh_3)$	$[Fe_2(CO)_7(PhC_2PhH)]^-$	$AuPPh_3Cl$	[20]
	$Fe_2(CO)_7(S^iPr)(AuPPh_3)$	$[Fe_2(CO)_7(S^iPr)]^-$	$AuPPh_3Cl$	[21]
	$Fe_3(C_2Fc)(CO)_9(AuPPh_3)$	$[Fe_3(SC_2Fc)(CO)_9]^-$	$AuPPh_3Cl$	[22]
	$[Fe_4(CO)_{13-n}(COCH_3)_n(AuPEt_3)]^{1-n}$ (n = 0, 1)	$[Fe_4(CO)_{13}]^{2-}$	$AuPEt_3Cl$	[23,24]
	$Fe_4N(CO)_{12}(AuPCy_3)$	$[Fe_4N(CO)_{12}]^-$	$(PCy_3)AuC_2CMe(OH)Et$	[25]
	$[HFe_4(CO)_{12}(AuPPh_3)_{3-n}]^{n-}$ (n = 0, 1)	$[HFe_4(CO)_{12}]^{3-}$	$AuPPh_3Cl$	[26]
	$HFe_4BH(CO)_{12}\{Au(PC_6H_4Me)_3\}$	$[HFe_4(CO)_{12}BH]^-$	$AuP(C_6H_4Me)_3Cl$	[27]
	$HFe_4(CO)_{12}B(AuPR_3)_2$ (R = C_6H_4Me, Et, Ph)	$[HFe_4BH(CO)_{12}]^-$	$AuPR_3Cl$	[28,29]
	$HFe_4B(CO)_{12}(AuAsPh_3)_2$	$[HFe_4BH(CO)_{12}]^-$	$AuAsPh_3Cl$	[30]
	$Fe_4B(CO)_{12}(AuPPh_3)_3$	$[HFe_4BH(CO)_{12}]^-$	$[(AuPPh_3)_3O]BF_4$	[31]
	$Fe_4BH(CO)_{12}(AuPPh_3)_2$	$[HFe_4BH(CO)_{12}]^-$	$AuPPh_3Cl$	[32]
	$HFe_4C(CO)_{12}(AuPPh_3)$	$[Fe_4(CO)_{13}]^{3-}$	$AuPPh_3Cl$	[33]
	$Fe_4C(CO)_{12}(AuPEt_3)_2$	$HFe_4C(CO)_{12}(AuPEt_3)$	–	[33]
	$Fe_4C(CO)_{12}(Au_2dppm)$	$[Fe_6C(CO)_{16}]^{2-}$	$(Au_2dppm)Cl_2$	[34]
	$Fe_5C(CO)_{14}(Au_2dppm)$	$[Fe_5C(CO)_{14}]^{2-}$	$(Au_2dppm)Cl_2$	[35]
	$Fe_5C(CO)_{14}(AuPEt_3)_2$	$[Fe_5C(CO)_{14}]^{2-}$	$AuPEt_3Cl$	[36]
Fe–Co	$Fe_2Co(COCH_3)(CO)_7(C_5H_5)(AuPPh_3)$	$HFe_2Co(COCH_3)(CO)_7(C_5H_5)$	$AuPPh_3Me$	[37]
Fe–Ir	$Fe_2Ir(C_2Ph)(CO)_7(PPh_3)(AuPPh_3)_2$	$Fe_2Ir(C_2Ph)(CO)_8(PPh_3)$	$[(AuPPh_3)_3O]BF_4$	[38]
	$[Fe_2Ir_2(CO)_{12}(AuPPh_3)]^-$	$[Fe_2Ir_2(CO)_{12}]^{2-}$	$AuPPh_3Cl$	[39]
Fe–Rh	$[Fe_2Rh_2(CO)_{12}(AuPPh_3)]^-$	$[Fe_2Rh_2(CO)_{12}]^{2-}$	$AuPPh_3Cl$	[40]
Ru	$HRu_3(CO)_9(PPh)(AuPMe_2Ph)$	$[HRu_3(CO)_9(PPh)]^-$	$AuPMe_2Ph[PF_6]$	[41]
	$H_{1+n}Ru_3(CO)_9(COMe)(AuPPh_3)_{2-n}$ (n = 0, 1)	$H_3Ru_3(COMe)(CO)_9$	$AuPPh_3Me$	[42]
	$HRu_3(CO)_9(COMe)\{Au_2(Ph_2P(CH_2)_nPPh_2)\}$; ($n$ = 1 or 5)	$H_3Ru_3(COMe)(CO)_9$	$[Au_2(Ph_2P(CH_2)_nPPh_2)]Me_2$	[43]
	$Ru_3S(CO)_8PPh_3(AuPPh_3)_2$	$H_2Ru_3S(CO)_9$	$AuPPh_3Me$	[44]
	$Ru_3S(CO)_9(Au_2dppm)$	$[Ru_3S(CO)_9]^{2-}$	$(Au_2dppm)Cl_2$	[45]
	$Ru_3(CO)_8(CCHCPh_2OCO)(AuPPh_3)_3$	$HRu_3(CO)_9(C_2CPh_2OH)$	$AuPPh_3Cl$	[46]
	$Ru_3(CO)_9(C_2{}^tBu)(AuPPh_3)$	$[Ru_3(CO)_9(C_2{}^tBu)]^-$	$AuPPh_3Cl$	[47]
	$Ru_3(COMe)(CO)_{10}(AuPPh_3)$	$HRu_3(COMe)(CO)_{10}$	$AuPPh_3Me$	[48]
	$H_{3-n}Ru_3(COMe)(CO)_9(AuPPh_3)_n$ (n = 1, 3)	$H_3Ru_3(COMe)(CO)_9$	$AuPPh_3Me$	[48]
	$Ru_3(C_{12}H_{15})(CO)_8(AuPPh_3)_3$	$[Ru_3(C_{12}H_{15})(CO)_9]^-$	$[(AuPPh_3)_3O]BF_4$	[49]
	$Ru_3(CMeCHCMe)(CO)_8(AuPPh_3)_3$ (R = CMeCHCMe, C_2Ph)	$HRu_3(CMeCHCMe)(CO)_9$	$[(AuPPh_3)_3O]BF_4$	[50]
	$HRu_4(CO)_{12}(AuPPh_3)_3$	$[H_3Ru_4(CO)_{12}]^-$	$[(AuPPh_3)_3O]BF_4$	[51]
	$HRu_4(CO)_{12}(AuPPh_3)_3$	$H_4Ru_4(CO)_{12}$	$AuPPh_3Me$	[52]
	$HRu_4(CO)_{12}(AuPPh_3)(Au_2dppm)$	$HRu_4(CO)_{12}(AuPPh_3)_3$	$(Au_2dppm)Cl_2$	[53]
	$Ru_4C(CO)_{12}(AuPMe_2Ph)_2$	$[Ru_5C(CO)_{14}]^{2-}$	$AuPMe_2Ph[ClO_4]$	[54]
	$Ru_4C(CO)_{12}X(AuPR_3)$ (X = I, R = Et; X = H, R = Ph)	$[Ru_4C(CO)_{12}(AuPR_3)_2]$ + I_2/HI	–	[54]
	$H_2Ru_4(CO)_{12}(Au_2dppm)$	$[H_3Ru_4(CO)_{12}]^-$	$(Au_2dppm)Cl_2$	[55]
	$H_2Ru_4(CO)_{12}(AuPPh_3)_2$	$[H_2Ru_4(CO)_{12}]^{2-}$	$AuPPh_3Cl$	[56]
	$H_2Ru_4(CO)_{12}\{Au_2(Ph_2AsCH_2PPh_2\}$	$[H_2Ru_4(CO)_{12}]^{2-}$	$Au_2(Ph_2AsCH_2PPh_2)Cl_2$	[57]
	$H_2Ru_4(CO)_{12}\{Au_2(Ph_2P(CH_2)_nPPh_2)\}$ (n = 1 or 2)	$[H_2Ru_4(CO)_{12}]^{2-}$	$[Au_2(Ph_2P(CH_2)_nPPh_2)]Cl_2$	[58]
	$H_3Ru_4(CO)_{12}(AuPPh_3)$	$[H_3Ru_4(CO)_{12}]^-$	$AuPPh_3Cl$	[59,60]
	$Ru_5C(CO)_{15}Cl(AuPPh_3)$	$Ru_5C(CO)_{15}$	$AuPPh_3Cl$	[61]
	$Ru_5C(CO)_{14}Br(AuPPh_3)$	$Ru_5C(CO)_{15}$	$AuPPh_3Br$	[62]
	$Ru_5C(CO)_{13}(C_5H_5)(AuPPh_3)$	$Ru_5C(CO)_{15}$ + $Na(C_5H_5)$	$AuPPh_3[ClO_4]$	[62]
	$Ru_5C(CO)_{14}(MeCO)(AuPPh_3)$	$Ru_5C(CO)_{15}$ + LiMe	$AuPPh_3Cl$	[62]
	$Ru_5C(CO)_{14}(Au_2dppe)$	$[Ru_5C(CO)_{14}]^{2-}$	$Au_2(dppe)Cl_2$	[63]
	$Ru_5C(CO)_{13}(NO)(AuEt_3)$	$[Ru_5C(CO)_{13}(NO)]^-$	$AuPEt_3Cl$	[64]
	$Ru_6C(CO)_{14}Ph(AuNHC)$	$Ru_6C(CO)_{17}$	Au(NHC)Ph	[65]
	$Ru_5C(CO)_{13+n}Ph(AuNHC)$ (n = 0, 1)	$Ru_5C(CO)_{15}$	Au(NHC)Ph	[65]
	$Ru_5(CO)_{15}(Au_2dppm)$	$[Ru_6(CO)_{18}]^{2-}$	$Au_2(dppm)Cl_2$	[66]
	$Ru_6C(CO)_{16}(Au_2dppm)$	$[Ru_6C(CO)_{16}]^{2-}$	$Au_2(dppm)Cl_2$	[66]
	$Ru_6C(CO)_{16}\{AuP(MePh_2)\}_2$	$[Ru_6C(CO)_{16}]^{2-}$	$AuP(MePh_2)Cl$	[67]
	$Ru_6B(CO)_{17}\{AuP(C_6H_4Me)_3\}$	$[Ru_6B(CO)_{17}]^-$	$AuP(C_6H_4Me)_3Cl$	[68]
	$H_{1-n}Ru_6B(CO)_{16}\{Au(PPh_3)\}_{2+n}$ (n = 0, 1)	$[H_2Ru_6B(CO)_{18}]^-$	$AuPPh_3Cl$	[68]
	$Ru_6C(CO)_{15}(NO)(AuPPh_3)$	$[Ru_6C(CO)_{15}(NO)]^-$	$AuPPh_3Cl$	[69]

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