Optically active heterotrimetallic ‘wing-bridged’ butterfly cluster

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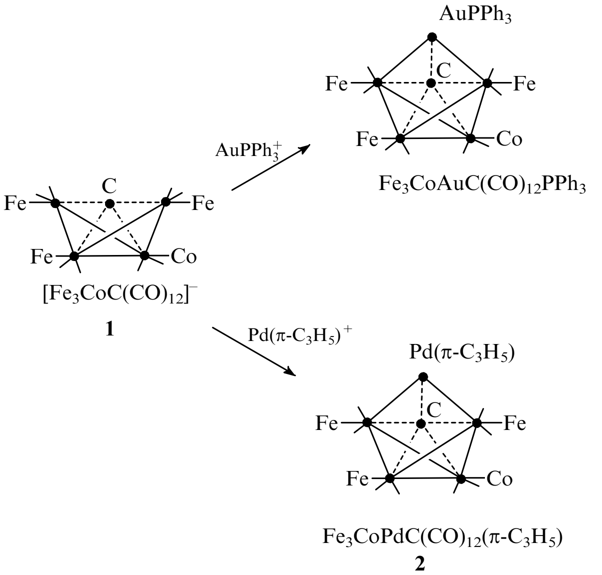
The ‘wing-bridged’ butterfly clusters $Fe_3CoPdC(CO)_{12}(\pi\text{-}C_3H_5)$ 2 and $Fe_3CoPdC(CO)_{12}(\eta^3\text{-}\beta\text{-}C_{10}H_{15})$ 3 have been synthesized; the crystal structure of 2 has been determined, and the absorption and circular dichroism spectra of 3 were investigated and compared with those for the $[Pd(\eta^3\text{-}\beta\text{-}C_{10}H_{15})Cl]_2$ chiral complex 4.

Up to now reports of optically active clusters have been limited to compounds with no more than three atoms in the metal core.[1] It is clear that without consideration of chiroptical properties and electronic structure of more complicated metal cores, the data known are not enough for the theoretical analysis of optical activity of this class of compounds.[2]

Recently we reported that the carbido carbonyl butterfly complex $[Fe_3CoC(CO)_{12}]^-$ **1**[3] reacts with $AuPPh_3^+$ to form a heterotrimetallic $Fe_3CoAuC(CO)_{12}PPh_3$ cluster[4] with a ‘wing-bridged’ butterfly geometry. To extend this cluster series, we have investigated the addition of an $Pd(\pi\text{-}C_3H_5)^+$ group, which is isoelectronic with $AuPPh_3^+$, to the same anion **1** (Scheme 1).



Scheme 1

The reaction leads to the same type of uncharged cluster, namely $Fe_3CoPdC(CO)_{12}(\pi\text{-}C_3H_5)$ **2**.[†] X-ray study of **2**[‡] has shown that the metal cluster moiety has the already known geometry of the ‘wing-tip’ butterfly.[5,6] Three Fe atoms and a Co atom form a tetrahedron with one elongated edge (*i.e.* a butterfly). The wing positions in the butterfly are occupied by Fe atoms, whereas Fe and Co atoms are situated in the central position of the metal framework. The ‘wing’ Fe atoms are

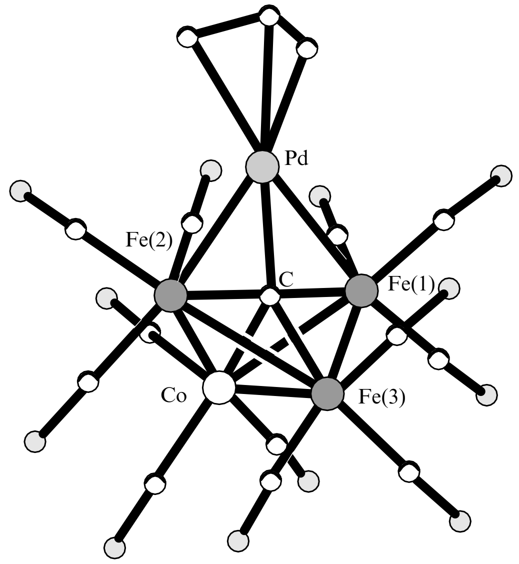


Figure 1 Molecule **2** (H atoms omitted for clarity).

Table 1 Bond distances (d) and angles (φ) of **2**.

Bond	d/ A	Angle	φ/°
Pd–Fe(1)	2.694(1)	Fe(1)–C(1)–Pd	89.5(2)
Pd–Fe(2)	2.686(1)	Fe(1)–C(1)–Fe(3)	92.0(2)
Fe(1)–Fe(3)	2.658(2)	Fe(1)–C(1)–Co	89.7(2)
Fe(1)–Co	2.655(2)	Fe(2)–C(1)–Pd	88.2(2)
Fe(2)–Fe(3)	2.653(2)	Fe(2)–C(1)–Fe(3)	90.8(2)
Fe(2)–Co	2.653(2)	Pd–C(1)–Fe(3)	142.4(2)
Fe(3)–Co	2.521(2)	Pd–C(1)–Co	134.7(2)
Pd–C(1)	2.014(6)	Fe(3)–C(1)–Co	82.9(2)
Fe(1)–C(1)	1.808(7)	Fe(1)–C(1)–Fe(2)	177.2(2)
Fe(2)–C(1)	1.840(7)		
Fe(3)–C(1)	1.886(8)		
Co–C(1)	1.921(7)		
Pd–C(allyl)	2.14–2.16		
Fe–C(CO)	1.77–1.82		
Co–C(CO)	1.78–1.82		
Co···Pd	3.631(1)		
Fe(3)···Pd	3.692(1)		

[†] *Preparation of* **2**: $[Fe_3CoC(CO)_{12}](Me_4N)$ (0.1 g, 0.15 mmol) was dissolved in CH_2Cl_2 (10 ml) at 25 °C. Excess $[Pd(C_3H_5)Cl]_2$ was added and the suspension was stirred at room temperature for 5 min until the initially deep red solution turned brown. The solvent was removed and the residual solid extracted with pentane. Filtration followed by evaporation of the solution to dryness yielded $Fe_3CoPdC(CO)_{12}(C_3H_5)$ (0.09 g, 0.12 mmol, 80%). After recrystallization from pentane (– 5 °C) a black crystalline compound was obtained. IR (pentane) ν_{CO}/cm^{-1}: 2080 m, 2039 s, 2018 m, 2004 w, 1991 w, 1963 w, 1974 w. IR (Nujol) ν_{M-O}/cm^{-1}: 778, 757, 750; (Found: C 26.91; H 0.65. Calc. for **2**: C 26.59, H 0.69%).

[‡] *Crystal data for* **2**: Single crystal X-ray study of the cluster **2** was carried out in the Centre of X-ray studies. Single crystal X-ray data were collected on a Syntex P2$_1$ diffractometer at –100 °C (λMo Kα, $\theta/2\theta$ scan, 3676 independent reflections up to $2\theta = 54$, space group *Pbca*, $a = 10.878$ A, $b = 13.191$ A, $c = 30.214$ A, $V = 4336$ A^3, $Z = 8$). The structure was solved by direct methods and refined in full-matrix least squares in anisotropic approximation to $R = 0.038$ using the PC version of the SHELXTL programme package. The position of H atoms and of the Co atom in the metal cluster framework were revealed by the X-ray data. Details of the X-ray study and a complete discussion of the cluster structure will be published elsewhere.

Table 2 Absorption (AB) and circular dichroism (CD) spectra of the [$Fe_3CoC\{Pd(\eta^3\text{-}C_{10}H_{15})\}(CO)_{12}$] cluster and [$(\eta^3\text{-}C_{10}H_{15}\}PdCl]_2$ dimer complex in CH_2Cl_2 solution.

[$Fe_3CoC\{Pd(\eta^3\text{-}C_{10}H_{15})\}(CO)_{12}$]				[$(\eta^3\text{-}C_{10}H_{15})PdCl]_2$			
Absorption		CD		Absorption		CD	
ν/kK[a]	ε	ν/kK	$\Delta\varepsilon$	ν/kK	ε	ν/kK	$\Delta\varepsilon$
17.50 infl	2210	15.50	+2.96				
		18.18 sh	+4.50				
20.0 sh	3316	18.59	+6.00	18.50 sh	5	17.86 sh	–0.002
		22.12	–9.13			23.81	–0.060
31.0 sh	21056	28.57	+24.65	29.50	1903	26.88	+0.527
						29.94	+1.0
36.5 sh	29215	>32.26	–CE	>37.0	>3000	34.96	–0.064
						>35.7	+CE

[a] 1kK = 10^3 cm^{-1}.

restricted by the bridging Pd atom (see Figure 1). The interstitial carbide, C(1), atom is in a distorted trigonal bipyramidal environment. Each Fe and Co atom also has three terminal CO ligands, and the Pd atom is coordinated by an η^3-allyl ligand. The main bond distances and angles are shown in Table 1.

It is apparent that the bond lengths and angles for the (π-C_3H_5)Pd fragment in **2**, in essence, do not differ from the appropriate values for the initial dimer [$(\pi\text{-}C_3H_5)PdCl]_2$.[7] In other words, the fragment π-allyl-Pd transfers to the cluster's core without substantial changes to its structure.

The obtained results allow one to hope that other π-allylic complexes of Pd will behave in the same way. The interaction of butterfly **1** with the known optically active complex of Pd containing a β-pinenyl ligand[8–10] was examined. As a result, a cluster $Fe_3CoPdC(CO)_{12}(\eta^3\text{-}\beta\text{-}C_{10}H_{15})$ **3**[§] was produced that was similar to **2** in its properties and spectral characteristics.

The absorption (AB) and circular dichroism (CD) spectra of **3** were studied (Figure 2 and Table 2) and compared with those for the [Pd(β-pinenyl)Cl]$_2$ chiral complex **4** used in preparing **3**. The optical activity of **3** is due to the planar chirality of the allyl fragment at the Pd atom and the C asymmetric atoms of the (−)-(1*S*,5*S*)-η^3-β-pinenyl ligand.[¶] However, the energy and high intensity of the Cotton effects (CEs) in the CD spectrum of **3** compared with those for **4** (Table 2 and refs. 9,11) show undoubtedly that the CEs induced by the electronic transitions of the cluster metallo-chromophore are caused by the strong interactions with the chiral π-ligand.

As far as we know, this phenomenon is observed for the first time; however, more detailed data are needed about the electronic structure of these heterometallic clusters for the theoretical analysis of their chiroptical properties.

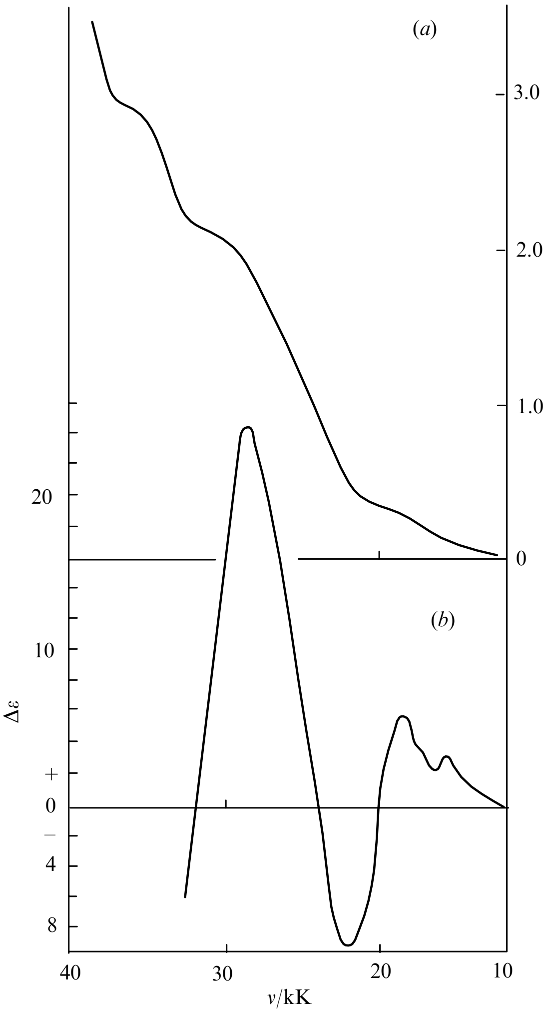


Figure 2 AB (*a*) and CD (*b*) spectra of **3** in CH_2Cl_2.

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[§] *Preparation of* **3**: Compound **3** was obtained in the same way as **2** (0.1 g, 0.12 mmol, 80%). IR (pentane) ν_{CO}/cm^{-1}: 2075 m, 2030 s, 2013 m, 2005 m sh, 1986 w, 1970 w, 1956 w; *m*/*z* = 816 [M^+, calc. for $Fe_3CoPdC(CO)_{12}(\eta^3\text{-}\beta\text{-}C_{10}H_{15})$ 816].

[$(\eta^3$-β-pinenyl)PdCl]$_2$ was obtained by the method reported in ref. 10.

[¶] The absolute configuration of the cluster **3** is (+)-[{(1*R*,2*S*,3*S*,5*R*)-η^3-$C_{10}H_{15}$}$PdCCoFe_3(CO)_{12}$] following the Cahn–Ingold–Prelog nomenclature[12] or (+)-[{(1*R*,5*R*,*R*p$_l$)-η^3-$C_{10}H_{15}$}$PdCCoFe_3(CO)_{12}$] according to the Schlogl–Ugi system.[13,14] The apparent inversion of the absolute configuration of the β-pinenyl asymmetric C atoms is due to the change of the substituent seniority at their asymmetric atoms upon Pd coordination.

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