Electron Transfer

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Redox Control of Light-Induced Platinum-Cluster-to-Iron Charge Transfer in a Bis(ferrocenylethynyl)-Substituted Hexanuclear Platinum Derivative**

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Placing equivalent redox-active groups as end-caps in molecular arrays is often used to evaluate whether intramolecular electronic communication occurs through organic[1] or metal-containing fragments.[2–9] To this end, ferrocenyl (Fc = [(η-C_5H_5)Fe(η-C_5H_4)]) pendant groups (often as ferrocenylethynyl termini),[3–5] are commonly used because of their chemical robustness, synthetic versatility, and reversible redox properties. They have been attached to mono-[2,3,6,10] or dinuclear[4,7] organometallic and coordination compounds. However examples of metal clusters capped by equivalent ferrocenyl groups are rare. To our knowledge, structurally characterized examples are limited[8a] to the following compounds: $[Mo_6Cl_8(O_2C{-}Fc)_6]^{2-}$, which contains an octahedral core of Mo^{II} centers $\{Mo_6Cl_8\}^{4+}$,[9a] $[Ru_3(CO)_7(\mu_2\text{-}S\text{-}Fc)_4]$,[9b] $[Cu_3(dppm)_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}C{-}Fc)_2]^+$, (dppm = methylenebis[(diphenyl)phosphine]) with two terminal $(Fc\text{-}C{\equiv}C)^-$ groups bridging the opposite sides of a triangular Cu^I_3 core in an μ_3-η^1 fashion,[5a] $[M_6(\mu\text{-}dppm)_2(\mu_3\text{-}\eta^1\text{-}C{\equiv}C{-}Fc)_4(L)_2]X_2$ (M = Ag, L = CH_3OH, X = BF_4; M = Cu, L = none, X = ClO_4)[5b] and $[Pt_2Au(dppm)_2X(\eta^1\text{-}C{\equiv}C{-}Fc)_2]$.[4a] Electron transfer from, to, or across the cluster-containing spacer, triggered by external stimuli, would make these units promising candidates for the preparation of connector elements in nanoscale switchable molecular devices.[11] Indeed, the utilization of carbonyl

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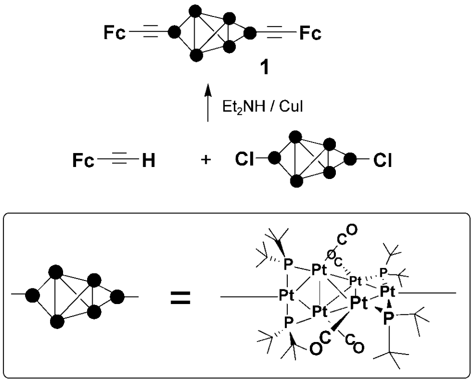
clusters as single-electron tunneling transistors has been reported,[12a] and their employment as molecular capacitors[12b] is also under scrutiny. However, well-documented examples of electron transfer in molecular frameworks containing cluster subunits are exceedingly rare; in all the above-mentioned compounds the metal-cluster spacers do not allow significant electronic communication between the ferrocene units. However, in those derivatives containing one or two ferrocenyl units linked to a hexamolybdate spacer, through π-conjugated arms, a photoinduced charge transfer from the Fc to the polyoxometalate unit was observed,[13] while in a derivative containing a Os_3 core bonded to a viologen-containing acceptor, a photoinduced charge transfer from the triosmium cluster to the acceptor ligand was observed.[11]

Herein, we report the synthesis and structural characterization of $[Pt_6(\mu\text{-}PtBu_2)_4(CO)_4(C{\equiv}C{-}Fc)_2]$ (**1**), in which the hexaplatinum core $[Pt_6(\mu\text{-}PtBu_2)_4(CO)_4]^{2+}$ (hereafter $\{Pt_6\}$) is capped by two ferrocenylethynyl groups, and the results of an electrochemical and spectroelectrochemical study, which shows the presence of photo-electrochemically triggered electron transfer from the $\{Pt_6\}$ core to the peripheral Fc subunits. To our knowledge, this is the first example in which a metallic cluster behaves as electron donor towards a ferrocenium acceptor.

The disubstituted complex **1** was easily prepared from its dichloride precursor $\{Pt_6\}Cl_2$[14] (Scheme 1) and was isolated as a red microcrystalline solid which yielded X-ray quality crystals upon recrystallization from $CHCl_3$ (Figure 1).[15] The structure shows that **1** retains the main structural features which are quite rare for other hexanuclear clusters and that we have found in closely related derivatives.[14,16] The structure consists of a slightly distorted tetrahedral platinum cluster capped, on each of two opposite edges, by a platinum atom linked to a terminally bonded (σ, η^1) ferrocenylethynyl moiety (other possible (π) bonding modes of the alkynyl units are hindered by the bulky phosphido ligands).[16] The ferrocenyl units lie on opposite sides of the plane defined by atoms Pt1, Pt2, Pt3, and Pt6 (Figure 1). Moreover the C_5 ring Cp1–Cp5 is approximately coplanar with the Pt1-Pt2-Pt3 plane (dihedral angle 172(1)°), while the other ethynyl-bound C_5 ring (Cp11–Cp15) is almost perpendicular to the P4-Pt5-Pt6 plane (dihedral angle 102(2)°).



Scheme 1. Synthesis of complex **1**.

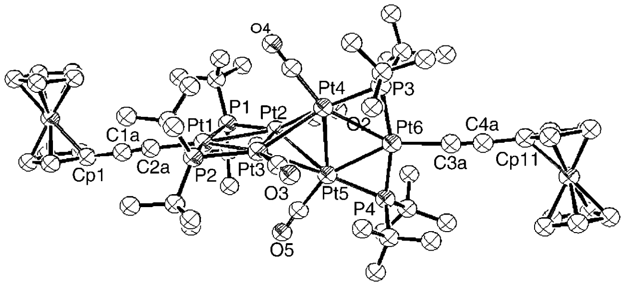


Figure 1. ORTEP view of compound **1**. Thermal ellipsoids set at 50% probability. Selected bond lengths [Å] and angles [°]: Pt1-Pt2 2.7196(5), Pt1-Pt3 2.7196(5), Pt4-Pt6 2.7389(6), Pt5-Pt6 2.7287(5), Pt2-Pt3 2.6875(6), Pt2-Pt5 2.8380(6), Pt2-Pt4 2.8389(5), Pt3-Pt4 2.8421(5), Pt3-Pt5 2.8440(6), Pt4-Pt5 2.6734(5); Pt1-C2a-C1a 178(1), Pt6-C3a-C4a 178(1), C2a-C1a-Cp1 176(1), C3a-C4a-Cp11 173(1).

The structure of **1** is retained in solution, as confirmed by IR and NMR spectra, which show diagnostic signals at the expected positions (IR: $\tilde{\nu} = 2126, 2106$ (ν_{CC}), 2009 (ν_{CO}) cm^{-1}; ^{31}P NMR: $\delta = 333.6$ ppm; ^{195}Pt NMR: $\delta = -4663$ (2 Pt), -2997 ppm (4 Pt)).[14,16]

In CH_2Cl_2 solution the platinum cluster undergoes three reversible, and coulometrically measured, redox processes (Table 1): two slightly separated one-electron reductions ($E^{\circ\prime} = -1.50$ V and -1.64 V versus saturated calomel electrode (SCE)) and one two-electron oxidation ($E^{\circ\prime} = +0.30$ V).[17] A further, apparently irreversible, two-electron oxidation is also present ($E_p = +1.26$ V) (see Supporting Information).

Table 1: Formal electrode potentials (V, vs. SCE) for the redox changes exhibited by $[Pt_6(\mu\text{-}PtBu_2)_4(CO)_4(\eta^1\text{-}C{\equiv}C{-}Fc)_2]$ and related species in CH_2Cl_2.

Compound	$\{Pt_6\}$-centered ox.	Fc-centered ox.	$\{Pt_6\}$-centered red.	
1	$+1.26$[a,b]	$+0.30$[a]	-1.50	-1.64
$[Pt_6(PtBu_2)_4(CO)_4(C_2Ph)_2]$[c]	$+1.05$[a,b]		-1.45	-1.54
Fc-C≡CH[d]		$+0.52$		

[a] Two-electron process. [b] Peak-potential for irreversible processes. [c] Ref. [18]. [d] Ref. [20].

On the basis of the redox behavior of the parent dication $[\{Pt_6\}(CO)_2]^{2+}$ and its substituted product $[\{Pt_6\}(C_2Ph)_2]$[16b,18] both the two one-electron reductions and the irreversible oxidation are assigned as $\{Pt_6\}$ centered. The reversible two-electron removal event can be reliably assigned to the simultaneous one-electron oxidation of each of the two ferrocenyl units. This simultaneous process does not split into two separated one-electron events, even when a very low-coordinating electrolyte (e.g. $[NBu_4][B(C_6F_5)_4]$) is used.[19] This observation confirms that no electronic (through-space or through-bond) communication between the two ferrocenyl units is allowed by the $\{Pt_6\}$ spacer. The more anodic (irreversible) two-electron oxidation takes place at a potential approximately 200 mV more positive than in the parent complex $[Pt_6(\mu\text{-}PtBu_2)_4(CO)_4(C_2Ph)_2]$. At the same time, the ferrocenyl-centered oxidations occur at a potential approximately 200 mV less positive than in free acetylferrocene.[20] These redox shifts suggest that the acetilyde bridging ligands exert cooperative electronic effects inside the molecular frame.[21]

As shown in Figure 2, the most significant spectroelectrochemical change upon stepwise two-electron oxidation of complex **1** is the progressive appearance of a broad band in the NIR region ($\lambda = 1025$ nm; $\varepsilon = 2.1 \times 10^3\,\text{M}^{-1}\,\text{cm}^{-1}$). Upon exhaustive two-electron oxidation, the UV/Vis region of the spectrum does not change and does not exhibit the typical blue-to-green ferrocenium absorption ($\lambda = 698$ nm for $[FcCCH]^+$)[20]; the solution remains cherry-red. In the stepwise oxidation, the NIR band keeps growing and does not change position or shape even upon removal of the second electron. Such behavior suggests consecutive metal-to-metal charge transfers (MMCT) from the Pt_6 cluster to the peripheral ferrocenium subunits [Eq. (1) and Eq. (2)]

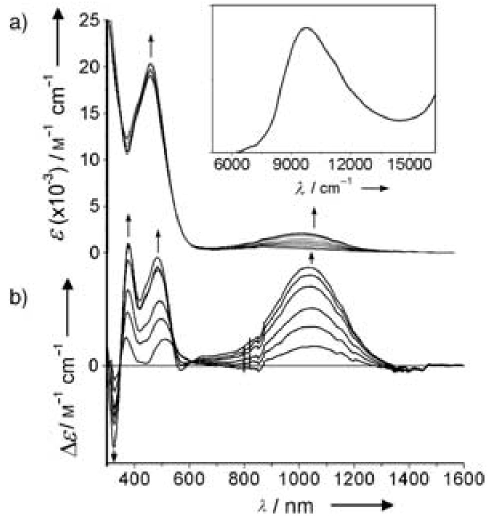


Figure 2. a) UV/Vis/NIR spectra and b) difference spectra recorded upon stepwise oxidation of **1** in an OTTLE cell, $CH_2Cl_2/[NBu_4][PF_6]$ (0.2 mol dm^{-3}) solution. Arrows indicate the change on oxidation. Inset: NIR band in (a) replotted in cm^{-1} to show the asymmetry of this band.

$$\overset{+}{\text{Fc}}\text{-C}\equiv\text{C-}\{\text{Pt}_6\}\text{-C}\equiv\text{C–Fc} \xrightarrow{h\nu} \text{Fc-C}\equiv\text{C-}\{\,\overset{+}{\text{Pt}_6}\,\}\text{-C}\equiv\text{C-Fe} \qquad (1)$$

$$\overset{+}{\text{Fc}}\text{-C}\equiv\text{C-}\{\text{Pt}_6\}\text{-C}\equiv\text{C-}\,\overset{+}{\text{Fc}} \xrightarrow{h\nu} \text{Fc-C}\equiv\text{C-}\{\,\overset{2+}{\text{Pt}_6}\,\}\text{-C}\equiv\text{C–Fc} \qquad (2)$$

Our preliminary observations show that a band at the same position in the NIR develops upon one-electron oxidation of the corresponding monoferrocenyl complex $[\{Pt_6\}(C\equiv C\text{–}Fc)I]$,[22] giving further support to the assumption that this absorption cannot arise from the interaction between the two ferrocene subunits.

We attempted to check the solvent dependence of the NIR band, but our efforts were frustrated by the impossibility of finding different useful solvents and the pertinent supporting electrolytes. Nevertheless, the change of the supporting electrolyte from $[NBu_4][PF_6]$ to the low-coordinating $[NBu_4][B(C_6F_5)_4]$ maintained unchanged the high-energy bands, but causes a red shift ($\lambda = 1108$ nm) of the low-energy band, thus confirming the sensitivity of the actual absorption to the medium, as expected for a MMCT intervalence transfer (IT) absorption.

As can be seen in the inset of Figure 2, when the spectrum is plotted in cm^{-1}, the asymmetry of the MMCT band becomes evident. Indeed, such a cut-off on the low-energy side of IT absorptions is predicted in the case of sizeable electronic coupling between the states involved in the electron transfer (although different factors, such as vibronic progressions or band overlaps, can cause asymmetry of IT bands).[23]

According to the Hush treatment of dinuclear asymmetric derivatives,[24] the limiting value[25] of the bandwidth at half height ($\Delta\bar{\nu}_{1/2}$) for the IT band of a partially delocalized mixed-valent species is theoretically expected to be given by Equation (3) where the free-energy difference between the initial and the final state after the electron transition, $\Delta G°$, is usually approximated as the separation $\Delta E°$ of the redox potentials of the processes centered on the isolated units involved in the electron transfer. Significantly narrower IT absorptions are expected for a completely delocalized mixed-valent species.

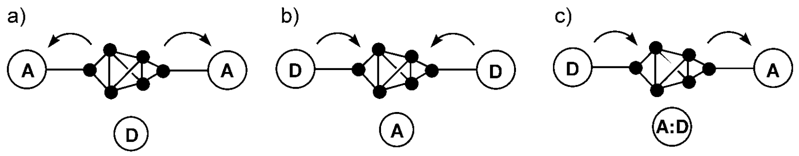
$$\Delta\bar{\nu}_{1/2} = 48\,(\bar{\nu}_{\max} - \Delta G^{o})^{1/2} \qquad (3)$$

On placing the values in Equation (3) it follows that $\Delta\bar{\nu}_{1/2}$ in the present case is given by Equation (4) where $\Delta G° \approx \Delta E° = 4195\ \text{cm}^{-1}$ has been calculated on the basis of the formal electrode potentials of $[\{Pt_6\}(C\equiv C\text{-}Ph)_2]^{2+/0}$ and $[HC\equiv C\text{–}Fc]^{+/0}$.[18,20]

$$\Delta\bar{\nu}_{1/2\,\text{theoretical}} = 48(9760-4195)^{1/2} = 3580\ \text{cm}^{-1} \qquad (4)$$

The experimental bandwidth, taken as twice the difference between the band maximum and the half-height point on the high-energy side, is $\Delta\bar{\nu}_{1/2\,\text{experimental}} = 4470\ \text{cm}^{-1}$, which is much larger than the theoretical limiting value of 3580 cm^{-1}. This result suggests that both the singly and doubly oxidized species (the monocation and the dication) can be regarded as valence-trapped systems.

As a final consideration, we underline that compounds that can absorb light in the NIR region may, in principle, be used in optical data-storage devices that are able to read and write through proper diode lasers (that is, operating in the NIR region of the spectrum),[26] in particular when the NIR absorption can be triggered by external perturbations. Even though the intensity of the present NIR transition is too weak[26] for practical applications in data-storage devices, these compounds offer the appealing possibility of easily tuning both the redox capacity of the attached ferrocenyl units and the resulting MMCT NIR absorption. Moreover, the ability of the $\{Pt_6\}$ unit to be both oxidized and reduced[14a] suggests the possibility of building systems in which, based on the proper calibration of redox potentials of the end-cap



Scheme 2. Electron transfer from (a), to (b), or across (c) the {Pt_6} cluster unit. See text for details.

donor (D) and/or acceptor (A) units, the electron transfer might be driven through the different paths illustrated in Scheme 2.

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[15] Crystal data for **1**·(0.5 $CHCl_3$): $C_{56.5}H_{90.5}Cl_{1.5}Fe_2O_4P_4Pt_6$, $M_r = 2293.08$. Monoclinic, space group $C2/c$, $a = 24.424(2)$, $b = 17.604(1)$, $c = 33.489(2)$ Å, $\beta = 105.250(2)°$, $V = 13892(2)$ Å^3, $Z = 8$, $\rho_{calcd} = 2.193\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 126.10\ cm^{-1}$, dimensions $0.4 \times 0.4 \times 0.3\ mm^3$. 63429 reflections were collected, at 120 K (on a Bruker SMART CCD diffractometer), of which 13675 were unique ($R_{int} = 0.0875$). An empirical absorption correction was applied using the program SADABS (transmission factors in the range 1.000–0.522). Structure solution was by direct and Fourier methods and refinement by full-matrix least squares on F^2 (programs WinGx vs. 1.70 and SHELX-PC). Isotropic displacement parameters were used for the carbon atoms of the C_5 rings of the Fc units and of the ethynyl moieties; the Pt, Fe, and P atoms, and the remaining carbon atoms were refined using anisotropic displacement parameters. From the difference Fourier maps a solvent molecule (CH_2Cl_2) was found, disordered across a crystallographic inversion center, and its contribution was taken into account. Final agreement factors were $R_1 = 0.0403$, $R_{w2} = 0.0890$ for 9178 observed reflections [$I \geq 2\sigma(I)$] and 582 refined parameters; GOF = 1.011. CCDC-272174 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[22] [{Pt_6}($C\equiv C$–Fc)I] was prepared by coupling the unsymmetrical dihalide [{Pt_6}(Cl)I] with one equivalent of Fc-$C\equiv CH$ (see

Supporting Information) and it exhibits spectroelectrochemical intervalence transfer (IT) absorptions nearly identical to those given by complex **1**. Full details of the synthesis, and the cyclic voltammetric and spectroelectrochemical characterization will be given elsewhere.

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