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$[Re_6Te_8(CN)_6][\{Ir(CO)(PPh_3)_2\}_6](OTf)_2$: a new Re_6 cluster-supported iridium(I) compound

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A new hexanuclear rhenium cluster encapsulated by six iridium complexes, $[Re_6Te_8(CN)_6][\{Ir(CO)(PPh_3)_2\}_6](OTf)_2$ (3), which is effective in catalyzing the hydrogenation of *p*-$CH_3C_6H_4C{\equiv}CH$ to *p*-$CH_3C_6H_4CH{=}CH_2$ has been prepared.

Water soluble hexanuclear cluster anions $[Re_6Q_8(CN)_6]^{4-}$ (Q = S, Se or Te) have been used to synthesize 3-D extended solid frameworks.[1–5] In the solid frameworks, metal cations bridge the Re_6 clusters *via* six cyanide groups forming large cubical cavities which can include plenty of small solvent molecules as well as metal ions.[6–13] Recently, we have used metal complexes such as Mn(salen)$^+$ units as a bridging ligand to build 2- or 3-dimensional Re_6 cluster based frameworks.[14–15] These polydimensional compounds can offer the potential capability of serving as molecular sieves utilizing their open pores or as supporting matrices with various chemical reactivities.[16] We also synthesized discrete molecules in preference to polymeric frameworks containing manganese porphyrin complexes, which showed a high catalytic activity in the epoxidation of olefins by iodosylbenzene.[17] These discrete molecules demonstrate that multinuclear metal cyanide clusters are good building blocks for preparation of new heterogeneous catalysts and a new family of supramolecules. We here report the structure of a new spherical molecular compound **3**, which consists of a Re_6 cluster encapsulated by six iridium(I) complexes. The iridium(I) complex has been studied as a catalyst for the hydrogenation of olefins,[18–19] but it is known to have rather low catalytic activity in hydrogenation of simple and inactivated olefins. Here we report a comparison of catalytic activity of compound **3** with the parent iridium(I) complex for hydrogenation of 4-ethynyltoluene.

To prepare compound **3**, an aqueous solution of $Na_4[Re_6Te_8(CN)_6]$ (**1**) was added to a chloroform solution of $[Ir(CH_3CN)(CO)(PPh_3)_2](OTf)$ (**2**), and the mixture was vigorously stirred for 10 h. $[Re_6Te_8(CN)_6]^{4-}$ clusters with red color in water layer were transferred to the chloroform layer. The *n*-pentane was added to the chloroform layer to precipitate out the compound **3**.†

Plate red crystals were obtained from direct diffusion technique in chloroform/ether solvent system. Its crystal structure was determined by X-ray crystallography.‡ An asymmetric cation unit as shown in Fig. 1 contains a Re(CN), one and 1/3 of Te, and an $Ir(PPh_3)_2(CO)$ in rhombohedral unit cell with $Z = 3$. The complete cation is generated by symmetry operations, $(x - y + 2/3, x + 1/3, - z + 1/3)$, $(y - 1/3, - x + y + 1/3, - z + 1/3)$, $(- x + y, - x + 1, z)$, and $(- y + 1, x - y + 1, z)$. The compound **3** represents a new class of compounds consisted of $[Re_6Te_8(CN)_6]^{4-}$ cluster (**1**) encapsulated by six $Ir(CO)(PPh_3)_2$ complexes. Fig. 2 shows the whole symmetry-expended projection of the remarkable spherical cation, $[Re_6Te_8(CN)_6]$ $[\{Ir(CO)(PPh_3)_2\}_6]^{2+}$(**3**, see Fig. 3), which has a three fold rotational axis running through Te1 along the c-axis. The counter-anions OTf $^-(CF_3SO_3^-)$ were not located at the fixed sites, but disordered between cations in the voids of the framework. The Re_6 cluster-supported iridium(I) complex forms a nano-size molecule which the distance between Ir atoms through the Re_6 cluster is 14.38(1) Å. The largest distance between two atoms within the cation is over 2.3 nm. The angles of C–N–Ir, N–Ir–C, and N–C–Re are almost linear with 174.7(9)°, 173.8(5)°, and 178.4(10)°, respectively, suggesting little steric effect of phosphine ligands. In **3**, the six C–N (1.14(1) Å), Re–Te (2.6716(7) ~ 2.7007(7) Å) and Re–Re (2.6960(6) ~ 2.7063(6) Å) are not significantly different from the starting rhenium cluster.[19]

The unsupported mononuclear cation $[Ir(NCCH_3)(CO)(PPh_3)_2]^+$ (**2**) is catalytically active for the hydrogenation of unsaturated

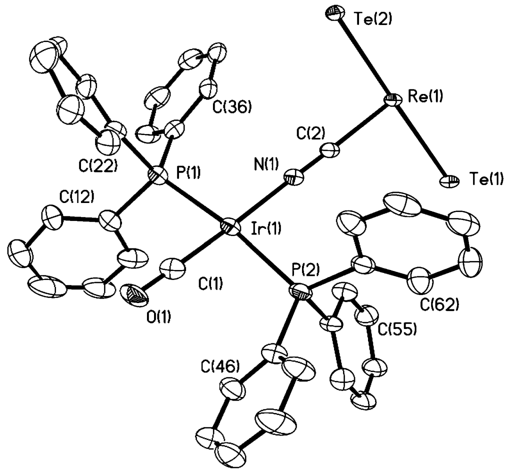

Fig. 1 An asymmetric unit of the title cation. Selected bond distances and angles: Ir1–C1 1.820(13), Ir1–N1 2.050(9), Ir1–P2 2.328(3), Ir1–P1 2.335(3), Re1–C2 2.101(10), O1–C1 1.156(15), N1–C2 1.137(13) Å; C2–N1–Ir1 174.7(9)°, O1–C1–Ir1 178.9(13)°, N1–C2–Re1 178.4(10)°.

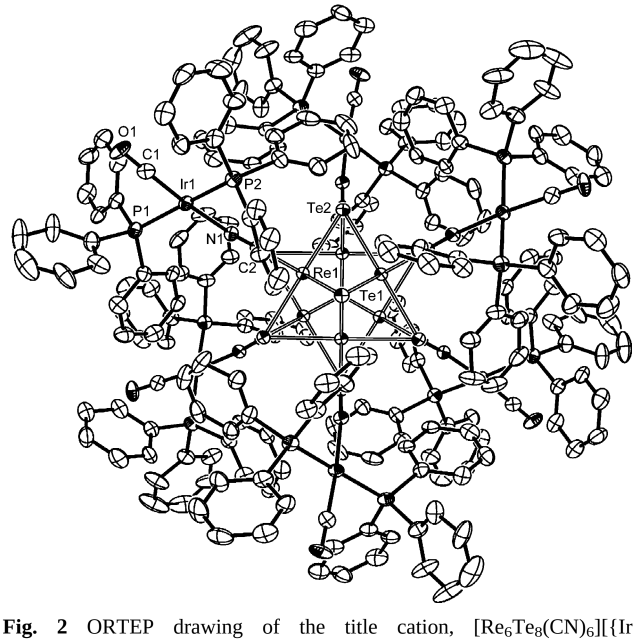

Fig. 2 ORTEP drawing of the title cation, $[Re_6Te_8(CN)_6][\{Ir(CO)(PPh_3)_2\}_6]^{2+}$. All hydrogen atoms are omitted for clarity.

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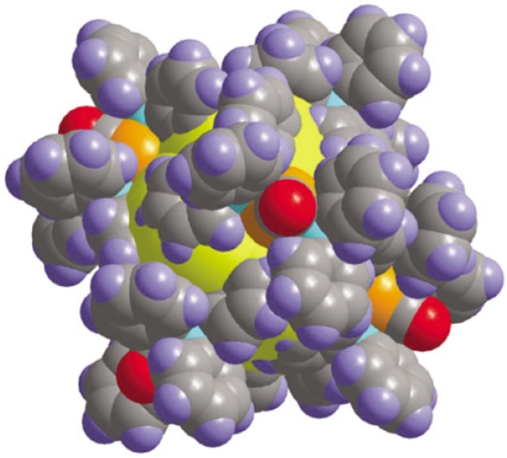

Fig. 3 A space-filling diagram shows the structure of the title compound, $[Re_6Te_8(CN)_6][\{Ir(CO)(PPh_3)_2\}_6](OTf)_2$. The blue, gray, red, orange, and light-blue colored atoms are hydrogen, carbon, oxygen, iridium and phosphine, respectively. A Re_6 cluster molecule is represented in yellow in the center.

nitriles and aldehydes (L)[20] and readily reacts with H_2 and L to give the six-coordinated cation $[Ir(H)_2(L)(CO)(PPh_3)_2]^+$ that yields the hydrogenation products (saturated nitriles and aldehydes) and is regenerated during the catalytic hydrogenation in the presence of excess of L and H_2.

Compound **3** reacts with H_2 to give the six-coordinated dihydrido-iridium(III) complex, $[Re_6Te_8(CN)_6][\{Ir(CO)(H)_2(PPh_3)_2\}_6](OTf)_2$ (**3(H)₂**)§ and shows catalytic activity for the hydrogenation of alkynes to olefins. Since the cluster cation $[Re_6Te_8(CN)_6]^{4-}$ is known to be non-active for the hydrogenation, it is likely that the hydrogenation occurs at the iridium site although we may not completely exclude the possibility of the some role of the Re in **3** for the hydrogenation. It is interesting to observe the hydrogenation of $p\text{-}CH_3C_6H_4C{\equiv}CH$ to $p\text{-}CH_3C_6H_4CH{=}CH_2$ being significantly faster with **3** than with **2**.¶ The initial product, $p\text{-}CH_3C_6H_4CH{=}CH_2$, is further hydrogenated to give $p\text{-}CH_3C_6H_4CH_2CH_3$. It should also be mentioned that the complex **3(H)₂** is recovered in high yield after the catalytic hydrogenation.‖

In summary, we have synthesized a new compound, Re_6 cluster-supported iridium(I) compound, with multicatalytic sites. The compound **3** shows catalytic activity for the hydrogenation of 4-ethynyltoluene suggesting dissociation of "$Ir(CO)(PPh_3)_2$" groups from **3** during the hydrogenation. This new compound suggests the potential of the soluble Re_6 cluster as a supporting building unit by combining with various metal complexes for new types of catalysts.

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Notes and references

† ^1H NMR (acetone-d^6, ppm) for compound **3**: δ 6.8–7.5 (m, Ir-P(C_6H_5)). ^{31}P NMR: δ 24.9 (s, Ir-*P*Ph$_3$). IR (KBr, cm^{-1}): 2090.4 (s, $\nu_{C\equiv N}$), 1984.2(s, $\nu_{C\equiv O}$), 1273.1, 1148.6, 1031.5 (due to uncoordinated OTf). ^1H NMR (acetone-d^6, ppm) for $[Ir(CO)(PPh_3)_2(CH_3CN)](OTf)$: δ 1.69 (s, Ir-NCC*H*$_3$).

‡ The diffraction data were collected on a Nonius Kappa-CCD diffractometer using Mo Kα (λ = 0.71073 Å).[21] The crystals were mounted on glass fibers under epoxy resin. The CCD data were integrated and scaled using the DENZO-SMN software package,[22] and the structures were solved and refined by using SHEXTL V5.0.[23] The OTf anion was not located in the system because of disorder. PLATON checks show a void of some 5047 Å^3 centered at the origin and presumably this is where the disordered OTf anion is located. All non-hydrogen atoms were located in the calculated positions.

Crystal Data for compound **3**: $C_{230}H_{180}F_6Ir_6N_6O_{12}P_{12}Re_6S_2Te_8$, M = 7060.76, Rhombohedral, a = 21.6325(3), c = 48.8453(12) Å, V = 19795.5(6) Å^3, T = 150(1) K, space group $R\bar{3}$, Z = 3, μ(MoKa) = 6.760 mm^{-1}, 36896 reflections collected, 10080 unique (R_{int} = 0.0593). Final $GooF$ = 1.371, R_1 = 0.0591 (ωR_2 = 0.1839) with reflections having intensities greater than 2σ (refinement on F^2), 409 parameters, 0 restraints. CCDC 233539 for compound **3**. See http://www.rsc.org/suppdata/cc/b4/b403995e/ for crystallographic data in .cif or other electronic format.

§ ^1H NMR (acetone-d^6, ppm) for compound **3(H)₂**: δ −7.71 (td, Ir-*H*), –18.32 (td, Ir-*H*). ^{31}P NMR: δ 6.07 (s, Ir-*P*Ph$_3$). IR (KBr, cm^{-1}): 2114.3 (s, $\nu_{C\equiv N}$), 2000.3 (s, $\nu_{C\equiv O}$), 1270.7, 1145.6, 1031.4 (due to uncoordinated OTf). ^{31}P NMR of $Ir(CO)(PPh_3)_2(OTf)$: δ 28.6. ^{31}P NMR of $Ir(H)_2(CO)(PPh_3)_2(OTf)$: δ 15.9.

¶ A 74% of $p\text{-}CH_3C_6H_4C{\equiv}CH$ (**S**) for S/Ir = 50 is hydrogenated to give $p\text{-}CH_3\text{–}C_6H_4CH{=}CH_2$ (**P**) in the presence of **3** while only a 20 % of **S** is converted to **P** with **2** under the same conditions. Catalytic reaction was followed by ^1H-NMR measurements.

‖ The recovered solid after the hydrogenation has been unambiguously identified as the hydrido compound **3(H)₂** by the detailed NMR data (^1H and ^{31}P, chemical shifts and multiplicity)

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