Syntheses, characterisation and electrochemical properties of C_{70}-metal cluster complexes

Chang Yeon Lee*

Department of Energy and Chemical Engineering, Incheon National University, Incheon 406-772, Korea

The complexes $[Os_3(CO)_9(\mu_3-\eta^2:\eta^2:\eta^2-C_{70})]$ and $[Re_3(\mu-H)_3(CO)_9(\mu_3-\eta^2:\eta^2:\eta^2-C_{70})]$ have been prepared by reaction of C_{70} with $[Os_3(CO)_{10}(NCMe)2]$ or $[Re_3(\mu-H)_3(CO)_{11}(NCMe)]$ and their electrochemical properties studied by cyclic voltammetry in chlorobenzene solutions. The complex $[Re_3(\mu-H)_3(CO)_8(CNCH_2Ph)(\mu_3-\eta^2:\eta^2:\eta^2-C_{70})]$ has also been synthesised by reaction between $[Re_3(\mu-H)_3(CO)_9(\mu_3-\eta^2:\eta^2:\eta^2-C_{70})]$ and $PhCH_2N{=}PPh_3$.

Keywords: C_{70}-metal cluster complexes, Re, Os, carbonyls, electrochemistry

Since the discovery of [60]fullerene and its synthesis in mass quantities,[1] many fullerene derivatives have been synthesised and characterised to develop new nanomaterials and nanodevices.[2–4] Among them, exohedral metallofullerenes have received significant attention concerning the effects of metal coordination on the chemical and physical properties of C_{60}.[5–14] In particular, C_{60}-metal cluster complexes, including a face-capping, cyclohexatriene-like bonding mode between metal-cluster and C_{60}, confer robust thermal and electrochemical stabilities, as well as strong electronic communication between C_{60} and metal cluster centres, to C_{60}-metal cluster complexes.[15–23]

In contrast to the well-defined studies about C_{60}-metal cluster complexes, research on C_{70}-metal cluster complexes has been rarely demonstrated and their electrochemical properties have not been addressed so far. For example, Shapley and coworkers have reported the preparation and structural characterisation of the triruthenium-C_{70} complex, $[Ru_3(CO)_9(\mu_3-\eta^2:\eta^2:\eta^2-C_{70})]$, in which the Ru_3 triangle is coordinated to the near polar C_6 ring in C_{70} (Scheme 1).[24] The same group have published the triphenylphosphine-substituted derivatives of $[Ru_3(CO)_9(\mu_3-\eta^2:\eta^2:\eta^2-C_{70})]$.[25]

In order to investigate more specific characteristics and the electrochemical properties of C_{70}-metal cluster complexes, we now report the synthesis and characterisation of the C_{70}-metal cluster complexes, $[Os_3(CO)_9(\mu_3-\eta^2:\eta^2:\eta^2-C_{70})]$ (**1**), $[Re_3(\mu-H)_3(CO)_9(\mu_3-\eta^2:\eta^2:\eta^2-C_{70})]$ (**2**) and $[Re_3(\mu-H)_3(CO)_8(CNCH_2Ph)(\mu_3-\eta^2:\eta^2:\eta^2-C_{70})]$ (**3**), as summarised in Scheme 2.

Results and discussion

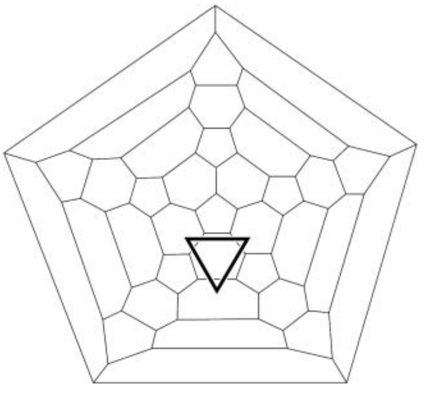
Synthetic procedures for **1**–**3** are summarised in Scheme 2. Compound **1** was prepared in 11% yield from the thermal reaction of $[Os_3(CO)_{10}(NCMe)_2]$ with 1 equiv. of C_{70} in chlorobenzene (CB). Compound **2** can be prepared from the thermal reaction of $[Re_3(\mu-H)_3(CO)_{11}(NCMe)]$ with 0.5 equiv. of C_{70} in CB for 3h in 40% yield. Substitution of **2** with 1.2 equiv. of $PhCH_2N{=}PPh_3$ in CB at room temperature for 12h afforded a regioisomeric mixture (*vide infra*) of compound **3** in 53% yield. The new compounds **1** and **2** are soluble in CS_2 and chlorinated benzene, whereas compound **3** is soluble in various organic solvent such as CS_2, dichloromethane, toluene, and chlorinated benzenes. All the compounds were confirmed by the molecular ion isotope patterns [*m/z* (highest peak): 1668 (**1**); 1656 (**2**); 1889 (**3**)] in the positive ion FAB mass spectra.

The IR spectra of **1** and **2** are identical to those of $[Os_3(CO)_9(\mu_3-\eta^2:\eta^2:\eta^2-C_{60})]$,[17] and $[Re_3(\mu-H)_3(CO)_9(\mu_3-\eta^2:\eta^2:\eta^2-C_{60})]$[20] respectively. Furthermore, the IR spectra of **3** is similar to that of $[Re_3(\mu-H)_3(CO)_8(CNCH_2Ph)(\mu_3-\eta^2:\eta^2:\eta^2-C_{60})]$,[20] in which the benzyl isocyanide ligand occupies an axial position. These results indicate that compounds **1**–**3** are isostructural with their C_{60} analogues.

The ^{13}C NMR spectrum of compound **1** at room temperature is shown in Fig. 1. The carbonyl region in the ^{13}C NMR spectrum of **1** shows two resonances at δ 176.1 and 175.6 in an intensity ratio of 2:1 (Fig. 1a). The separate sets are presumably due to the two different types of $Os(CO)_3$ groups in **1**, assuming rapid local equilibration at each metal centre. On the other hand, the sp^3 carbon region of **1** shows three resonances at δ 58.2, 54.8, and 51.0 with an intensity ratio of 1:1:1, which is assigned to the six coordinated carbons (Fig. 1b). These observations indicate that the triosmium cluster is bound to the near-polar C_6 ring in C_{70} as previously reported in $[Ru_3(CO)_9(\mu_3-\eta^2:\eta^2:\eta^2-C_{70})]$,[24] so that the symmetry of **1** is reduced to C_s (Fig. 1b).

The ^1H NMR spectrum (hydride region) and the ^{13}C NMR spectrum of compound **2** at room temperature are shown in Fig. 2. The NMR data indicate an idealised C_s symmetry for **2** in solution similar to compound **1** and previously reported in $[Ru_3(CO)_8(\mu_3-\eta^2:\eta^2:\eta^2-C_{70})]$.[24] The ^1H NMR spectrum shows two hydridic resonances at δ –16.1 and –16.3 in an intensity ratio of 1:2 due to two different types of hydride in **2** (Fig. 2a). Furthermore, the ^{13}C NMR spectrum (sp^3 carbon region, see Fig. 2c) shows three resonances at δ 58.2, 54.8, and 51.0 with an intensity ratio 1:1:1 as shown in compound **1**. However, the ^{13}C NMR spectrum of compound **2** [carbonyl region see Fig. 2(b)] shows five resonances at δ 184.9, 183.8, 182.6, 182.5, and 182.2 in an intensity ratio of 2:1:2:2:2 for nine carbonyls, which implies the absence of a fast localised 3-fold rotation of three carbonyl groups on each rhenium atom at room temperature. The C_{60} analogue $[Re_3(\mu-H)_3(CO)_9(\mu_3-\eta^2:\eta^2:\eta^2-C_{60})]$,[20] however, has one resonances at δ 183.2 for the nine carbonyl ligands due to the fast localised three-fold rotation of three carbonyl groups on each rhenium centre.

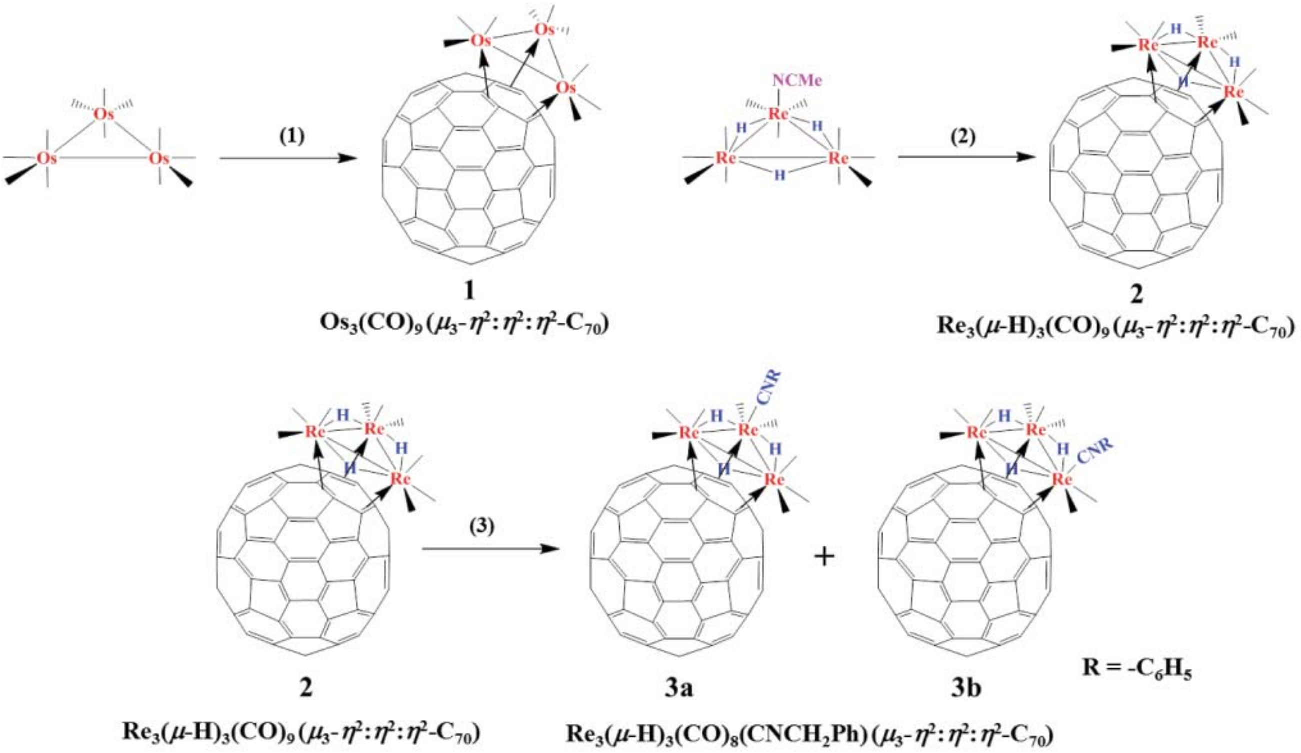
The ^1H NMR and ^{13}C NMR spectra of complex **3** at room temperature are shown in Figs 3 and 4, respectively. ^1H NMR (methylene region and hydride region) data of **3** appear as two sets of resonances in an intensity ratio of 2:1, implying that **3**



Scheme 1 Projection diagram of $[Ru_3(CO)_9(\mu_3-\eta^2:\eta^2:\eta^2-C_{70})]$[24] ($Ru_3$ triangle marked in bold).

---

* Correspondent. E-mail: cylee@incheon.ac.kr



1
$Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{70})$

2
$Re_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{70})$

2
$Re_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{70})$

3a **3b**
$Re_3(\mu\text{-}H)_3(CO)_8(CNCH_2Ph)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{70})$

Scheme 2 (1) Me_3NO(2.2 equiv.)/MeCN, then C_{70}, 132 °C, 2 h; (2) C_{70} (0.5 equiv.), 132 °C, 3 h; (3) $PhCH_2{=}PPh_3$ (1.2 equiv.), 12h (carbonyl ligands are omitted for clarity).

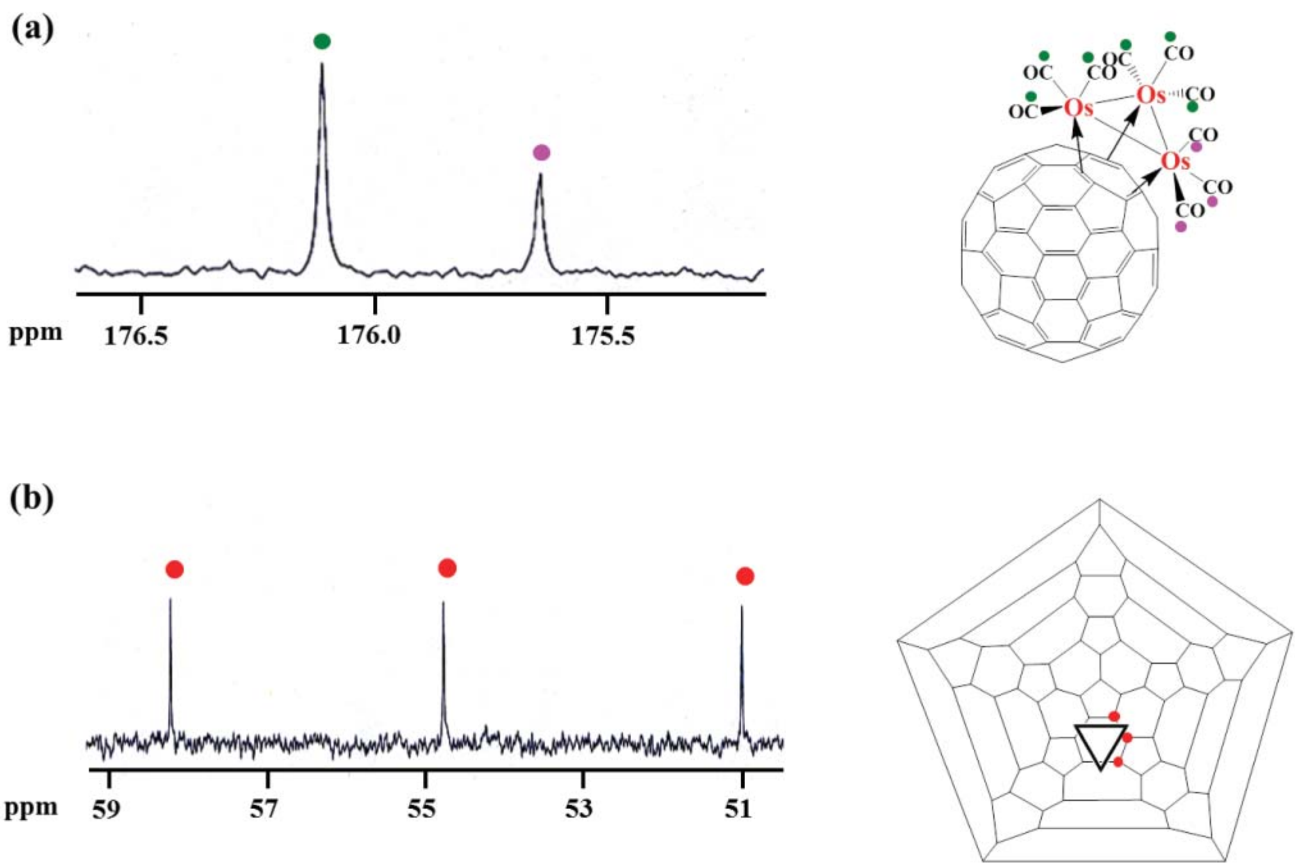


Fig. 1 ^{13}C NMR spectrum (100 MHz, *o*-ODCB-d_4, 298 K) of **1**. (a) Carbonyl region (b) sp^3 carbon region.

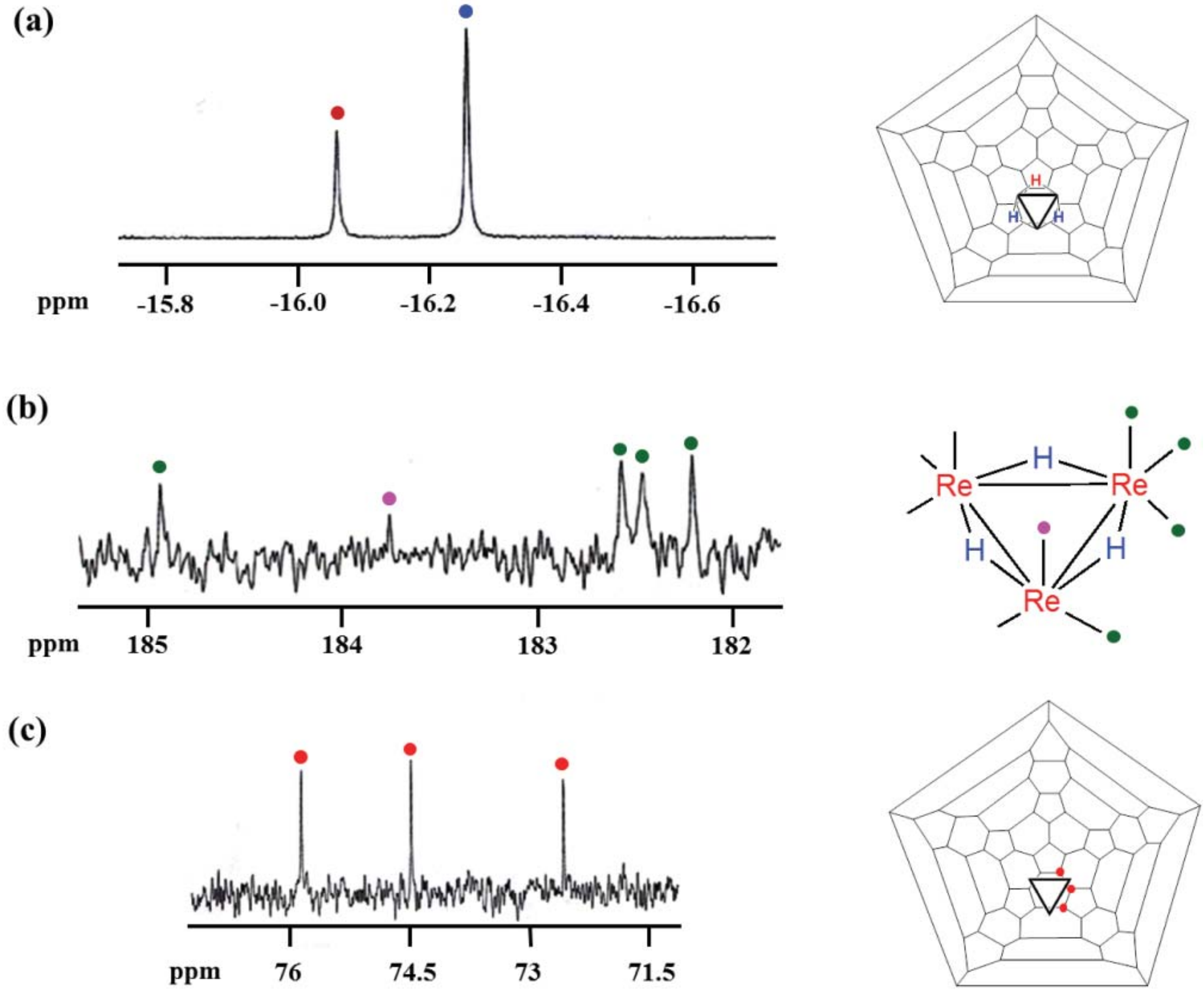


Fig. 2 (a) ^{1}H NMR spectrum (400Hz, CS_2/CD_2Cl_2) of **2** (hydride region). (b) ^{13}C NMR spectrum (100 MHz, CS_2/CD_2Cl_2, 298 K) of **2** (carbonyl region). (c) ^{13}C NMR spectrum (100 MHz, CS_2/CD_2Cl_2, 298 K) of **2** (sp^3 carbon region).

exists as two isomers in solution. ^{1}H NMR of the methylene region for the benzylic protons of the isocyanide ligand reveals a singlet at δ 5.20 for the major isomer, along with a small singlet at δ 5.17 for the minor isomer [see Fig. 3(a)]. Moreover, the ^{1}H NMR spectrum [hydride region see Fig. 3(b)] of **3** shows three singlet resonances at δ –15.6, –15.8, and –16.2, in an intensity ratio of 1:1:1, for the major isomer and two singlet resonances at δ –15.8 and –16.0, in an intensity ratio of 2:1, for the minor isomer. ^{1}H NMR data would appear to correspond to substitution of a benzyl isocyanide ligand on each of the two possible rhenium centers (ratio 2:1) in the C_s symmetric structure of **2** [see Fig. (3c)]. The major isomer may not have the symmetry of the parent complex due to unsymmetrical substitution of carbonyl on the rhenium centre, while the minor isomer retains its symmetry as C_s.

The ^{13}C NMR spectrum of **3** [carbonyl region see Fig. 4(a)] shows 12 resonances for major and minor isomers, implying the absence of any exchange process of carbonyl ligands on each rhenium atom at room temperature. The ^{13}C NMR spectrum of the *sp*^{3} carbon region [see Fig. 4(b)] also shows nine resonances for the isomeric mixture of **3** and two resonances at δ 49.5, and 49.4 in an intensity ratio of 2:1 for the methylene carbons of the isocyanide ligand, which is consistent with existence of an isomeric mixture with a ratio of 2:1.

The electrochemical properties of complexes **1** and **2** have been examined by the cyclic voltammetric method in CB solutions with tetrabutylammonium perchlorate as the supporting electrolyte. Cyclic voltammograms (CVs) of **1** and **2** are shown in Fig. 5. Half-wave potentials ($E_{1/2}$) of **1** and **2**, together with free C_{70}, are summarised in Table 1. All the CVs of **1** and **2** reveal four reversible redox waves that each correspond to a one-electron process. The second reduction of **1** occurs at a potential of –1.23 V, with a significant positive shift (210 mV) relative to that of free C_{70} at –1.44 V. This unusually large positive shift suggests that the one electron accepted through the C_{70} ligand in [**1**]$^-$ is delocalised to the triosmium centre with its strong π-acid carbonyl ligands, as previously proposed for the triosmium-C_{60} analogue.[18] Anionic species [**1**]$^-$ with electron delocalisation to the osmium centre, therefore, undergoes easier reduction *via* the C_{70} ligand than free C_{70}^- to afford [**1**]$^{2-}$. The fourth reduction potential (–1.65 V) of **1** is very close to the third reduction potential (–1.51 V) and even more positive than the third reduction of C_{70} (–1.88 V), which implies that further electron delocalisation from C_{70} to the triosmium cluster occurred in [**1**]$^{3-}$ as well. In the same way, the second (–1.19 V) and third (–1.38 V) reduction potentials of **2** are very close to the first (–1.05 V) and second (–1.19 V) reduction potentials and even more positive than the second (–1.44 V)

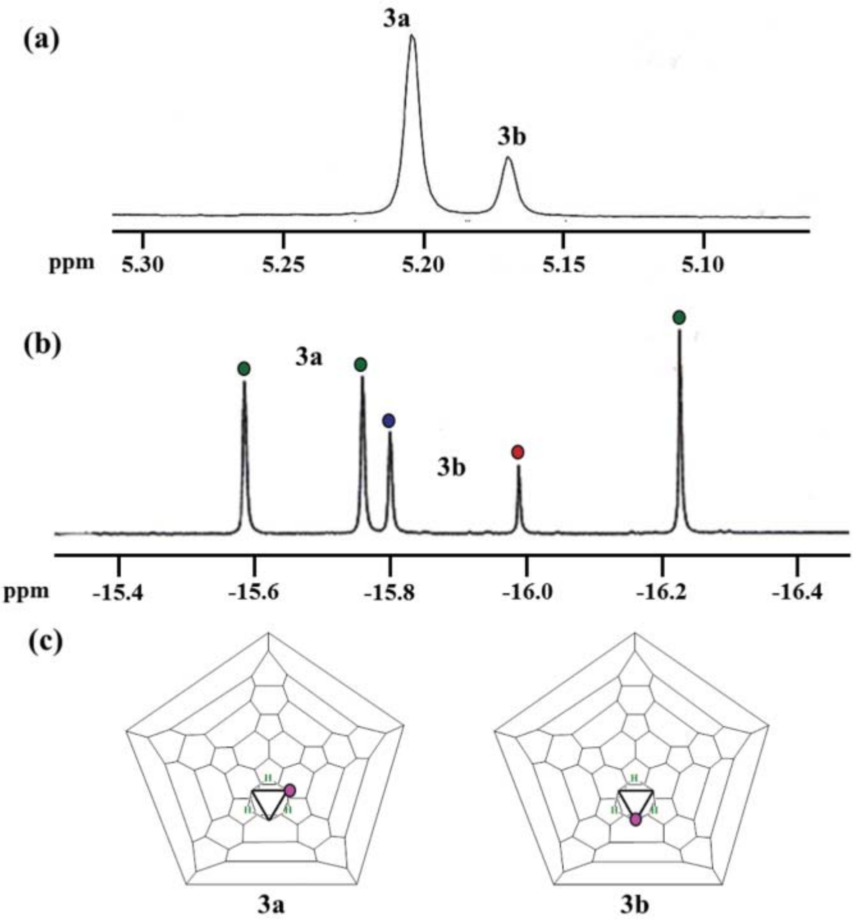


Fig. 3 ^1H NMR spectrum (400Hz, $CDCl_3$) of **3**. (a) methylene region. (b) hydride region. (c) projection diagrams of two possible rhenium centres regarding substitution reaction in complex **2**.

and third (–1.88 V) reduction potential of C_{70}, respectively. This observation also implies that electron delocalisation from C_{70} to the trirhenium centre occurred in [**2**]$^-$ and [**2**]$^{2-}$ as well.

In conclusion, C_{70}-triosmium and trirhenium complexes, $[Os_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_{70})]$ (**1**), $[Re_3(\mu\text{-H})_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_{70})]$ (**2**), have been synthesised and characterised in this work. From the spectroscopic data (IR, MS, ^1H and ^{13}C NMR), we found that the metal cluster is coordinated to the near polar C_6 ring in C_{70}, so that the symmetry of **1** and **2** were reduced to C_s. Furthermore, a regioisomeric mixture was found in the benzylisocyanide derivatives of **2**, due to the two possible rhenium centres (ratio 2:1) in the C_s symmetric structure of **2**. Electrochemical studies of compound **1** and **2** reveal that C_{70}-mediated electron transfer to metal cluster takes place in C_{70}-metal cluster complexes, which have the μ_3-η^2:η^2:η^2 bonding mode.

Experimental

All the reactions were carried out under a dinitrogen atmosphere with use of standard Schlenk techniques. Solvents were dried over the appropriate drying agents and distilled immediately before use. C_{70} (98%, SES research) was used without further purification. $PhCH_2N$=PPh_3[26] and $Re_3(\mu\text{-H})_3(CO)_{11}(NCMe)$[27] were prepared according to the literature methods. Preparative TLC plates were prepared with silica gel GF_{254} (type 60, E. Merck). IR spectra were obtained on a Bruker EQUINOX-55 FT-IR spectrophotometer. ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker Avance-400 spectrometer. Positive ion FAB mass spectra (FAB^+) were obtained by the staff of the Korea Basic Science Center, and all *m/z* values were referenced to ^{192}Os.

$Os_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_{70})$ (**1**): An acetonitrile solution (3 mL) of anhydrous Me_3NO (12.0 mg, 0.156 mmol) to a dichloromethane/acetonitrile (50/4 mL) solution of $[Os_3(CO)_{12}]$ (65 mg, 0.071 mmol) was added dropwise at room temperature, and the reaction mixture was stirred for 1 h. After evaporation of the solvent *in vacuo*, the residue was dissolved in chlorobenzene (5 mL). The resulting yellow solution was added dropwise to a chlorobenzene (50 mL) solution of C_{70} (50 mg, 0.060 mmol), and the reaction mixture was stirred at 80 °C for 30 min to give a blue-green solution. The solution was concentrated to *ca* 10 mL under vacuum, and the resulting solution was heated to reflux for 90 min. After solvent removal *in vacuo*, the residue was purified by column chromatography (silica gel, CS_2) to afford the desired $[Os_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_{70})]$ (**1**) as a reddish-brown solid (11 mg, 0.006 mmol, 11%). IR (CS_2) ν (CO) 2082 (s), 2046 (vs), 2016 (m), 2002 (m), 1984 (sh) cm^{-1}; ^{13}C NMR (*o*-dichlorobenzene-d_2, 298 K) δ 176.1 (s, 6CO), 175.6 (s, 3CO). The ^{13}C NMR signal from the unbounded sp^2 carbon in the C_{70} ligand cannot be assigned because it overlapped with solvent signal, 58.2 (2C, C_{70} sp^3 carbon), 54.8 (2C, C_{70} sp^3 carbon), 51.0 (2C, C_{70} sp^3 carbon); MS (FAB^+) *m/z* 1763 (M^+).

$Re_3(\mu\text{-H})_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_{70})$ (**2**): A chlorobenzene solution (60 mL) of $[Re_3(\mu\text{-H})_3(CO)_{11}(NCMe)]$ (151.7 mg, 0.167 mmol) and C_{70} (60.0 mg, 0.0833 mmol) was heated under reflux for 3 h. Evaporation of the solvent and purification by preparative TLC (silicagel, CS_2) produced compound **2** (63.3 mg, 0.0413 mmol, 48%, R_f = 0.9) as a red brown solid: IR (CS_2) *ν* (CO) 2074 (s), 2048 (s), 2008 (m), 1987 (m), 1927 (m) cm^{-1}; ^1H NMR (400 MHz, CS_2/ext.CD_2Cl_2, 298 K) –16.1 (s), –16.3; $^{13}C(^1H)$ NMR (100 MHz, CS_2/ext.CD_2Cl_2, 298 K) 184.9 (s, 2CO), 183.8 (1CO), 182.6 (2CO), 182.5 (2CO), 182.2 (2CO), 159.5 (1C), 154.6 (2C), 152.8 (1C), 152.1 (2C), 152.0 (2C), 150.8 (2C),

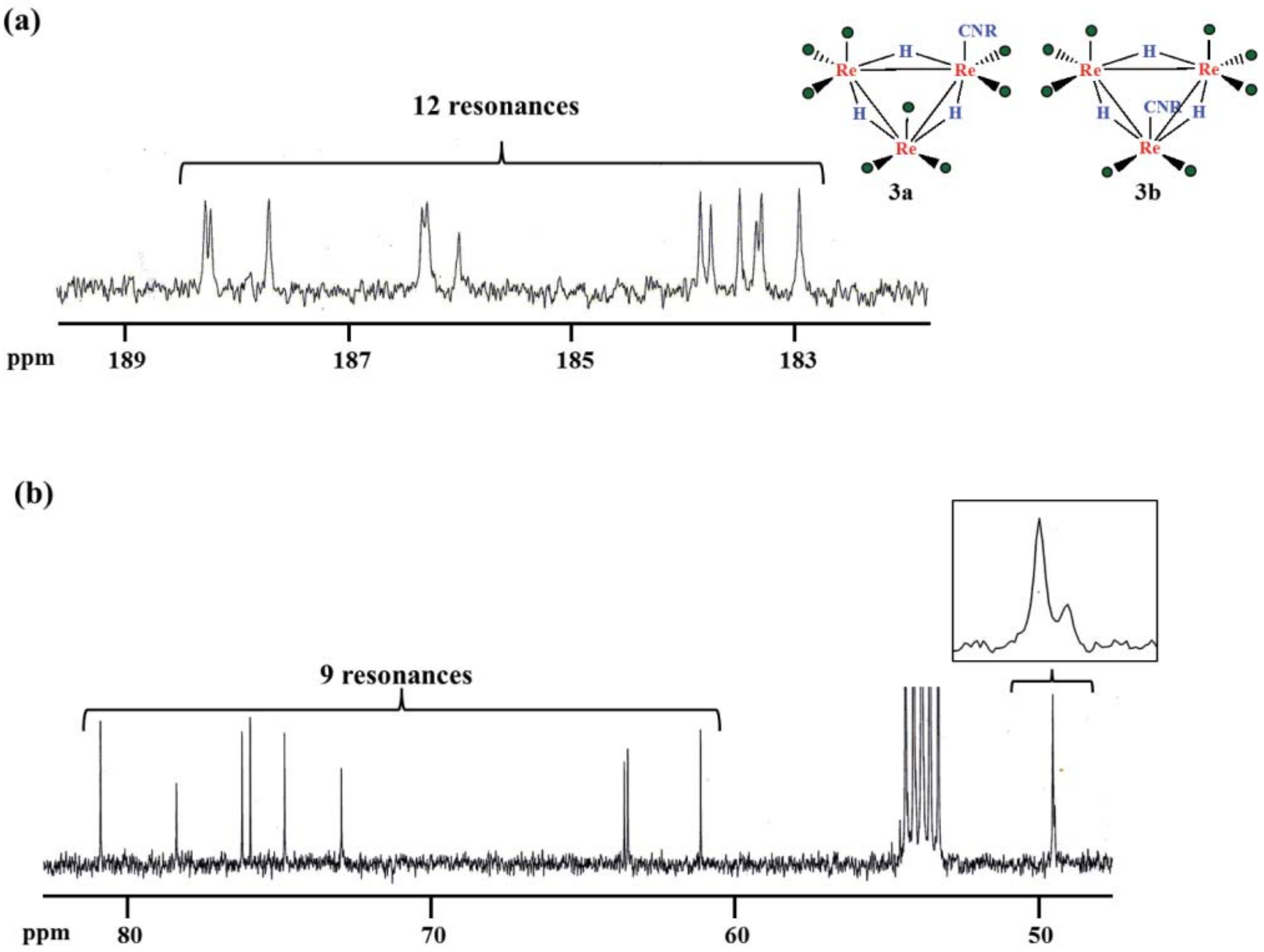


Fig. 4 ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **3**. (a) carbonyl region (b) sp^3 carbon region.

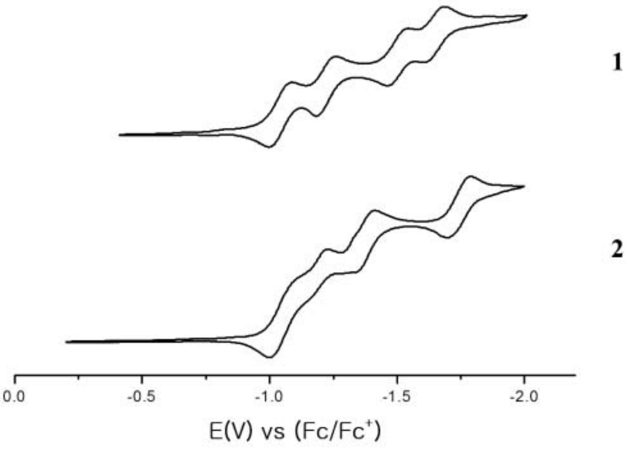


Fig. 5 Cyclic voltammograms of **1** and **2** in dry deoxygenated chlorobenzene (0.1 M $[(n\text{-}Bu)_4N][ClO_4]$). Scan rate = 5mV s^{-1}.

150.6 (2C), 150.4 (2C), 150.2 (2C), 150.0 (1C), 149.5(2C), 149.3 (2C), 149.1 (1C), 148.9 (2C), 148.4 (2C), 148.0 (2C), 147.9 (2C), 147.5 (2C), 147.4 (2C), 147.2 (2C), 147.1 (2C), 146.6 (2C), 146.0 (2C), 145.6 (2C), 145.0 (2C) 144.4 (2C), 144.1 (2C), 143.4 (2C), 143.3 (2C), 133.3 (2C), 132.3 (2C), 132.1 (2C), 130.9 (2C), 129.8 (2C), 75.9 (2C, C_{70} sp^3 carbon), 74.5 (2C, C_{70} sp^3 carbon), 72.6 (2C, C_{70} sp^3 carbon); MS (FAB⁺) *m/z* 1656 (M⁺).

$Re_3(\mu\text{-}H)_3(CO)_8(CNCH_2Ph)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{70})$ (**3**): A chlorobenzene solution (20 mL) of **2** (30.0 mg, 0.0196 mmol) and $Ph_3P{=}NCH_2Ph$ (14.4 mg, 0.0392 mmol) was stirred at room temperature for 3.5 h. Evaporation of the solvent and separation by TLC (CS_2) afforded compound **3** (16.7 mg, 0.0103 mmol, 53%, R_f = 0.5) as a red-brown solid: IR (CS_2) ν (NC) 2178 (m); ν (CO) 2060 (vs), 2043 (s), 2011 (s), 1986 (m), 1971 (s), 1954 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 298 K) Major isomer: 7.6–7.3 (m, 5H), 5.20 (s, 2H), –15.6 (s, 1H), –15.8 (s, 1H) –16.2 (s, 1H), Minor isomer: 7.6 – 7.3 (m, 5H), 5.17 (s, 2H), –15.8 (s, 2H), –16.0 (s, 1H); MS (FAB⁺) *m/z* 1744 (M⁺).

Table 1 Half-wave potentials ($E_{1/2}$ *versus* E^o_{Fc/Fc^+}) of free C_{70}, **1** and **2**

Compound	$E_{1/2}^{0/-1}$	$E_{1/2}^{-1/-2}$	$E_{1/2}^{-2/-3}$	$E_{1/2}^{-3/-4}$	Solvent
C_{70}	–1.06	–1.44	–1.88	–2.34	CB
$[Os_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{70})]$ (**1**)	–1.05	–1.23	–1.51	–1.65	CB
$[Re_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{70})]$ (**2**)	–1.05	–1.19	–1.38	–1.75	CB

CB, Chlorobenzene.

Received 23 January 2013; accepted 14 February 2013
Paper 1301743 doi: 10.3184/174751913X13639616845172

References

1 W. Kratschmer, L.D. Lamb, K. Fostiropoulos and D.R. Huffman, *Nature*, 1990, **347**, 354.
2 F. Diederich and C. Thilgen, *Science*, 1996, **271**, 317.
3 C. Thilgen, A. Herrmann and F. Diederich, *Angew. Chem. Int. Ed.*, 1997, **36**, 2268.
4 N. Martín, L. Sánchez, B. Illescas and I. Pérez, *Chem. Rev.*, 1998, **98**, 2527.

5 A.H.H. Stephens and M.L.H. Green, *Adv. Inorg. Chem.*, 1996, **44**, 1.
6 P. Mathur, I. Mavunkal and S. Umbarkar, *J. Cluster Sci.*, 1998, **9**, 393.
7 A.L. Balch and M.M. Olmstead, *Chem. Rev.*, 1998, **98**, 2123.
8 P.J. Fagan, J.C. Calabrese and B. Malone, *Science*, 1991, **252**, 1160.
9 W.Y. Yeh, *Angew. Chem. Int. Ed.*, 2011, **50**, 12046.
10 R.S. Koefod, M.F. Hudgens and J.R. Shapley, *J. Am. Chem. Soc.*, 1991, **113**, 8957.
11 P.J. Fagan, J.C. Calabrese and B. Malone, *J. Am. Chem. Soc.*, 1991, **113**, 9408.
12 Y.-Y. Wu and W.-Y. Yeh, *Organometallics*, 2011, **30**, 4792.
13 Y. Matsuo and E. Nakamura, *Chem. Rev.*, 2008, **108**, 3016.
14 D.V. Konarev, S.S. Khasanov, E.I. Yudanova and R.N. Lyubovskaya, *Eur. J. Inorg. Chem.*, 2011, 816.
15 K. Lee, H. Song and J.T. Park, *Acc. Chem. Res.*, 2002, **36**, 78.
16 H.-F. Hsu and J.R. Shapley, *J. Am. Chem. Soc.*, 1996, **118**, 9192.
17 J.T. Park, H. Song, J.-J. Cho, M.-K. Chung, J.-H. Lee and I.-H. Suh, *Organometallics*, 1998, **17**, 227.
18 H. Song, K. Lee, J.T. Park and M.-G. Choi, *Organometallics*, 1998, **17**, 4477.
19 K. Lee, Z.-H. Choi, Y.-J. Cho, H. Song and J.T. Park, *Organometallics*, 2001, **20**, 5564.
20 H. Song, Y. Lee, Z.-H. Choi, K. Lee, J.T. Park, J. Kwak and M.-G. Choi, *Organometallics*, 2001, **20**, 3139.
21 B.K. Park, M.A. Miah, H. Kang, K. Lee, Y.-J. Cho, D.G. Churchill, S. Park, M.-G. Choi and J.T. Park, *Organometallics*, 2005, **24**, 675.
22 K. Lee, Y.J. Choi, Y.-J. Cho, C.Y. Lee, H. Song, C.H. Lee, Y.S. Lee and J.T. Park, *J. Am. Chem. Soc.*, 2004, **126**, 9837.
23 G. Lee, Y.-J. Cho, B.K. Park, K. Lee and J.T. Park, *J. Am. Chem. Soc.*, 2003, **125**, 13920.
24 H.-F. Hsu, S.R. Wilson and J.R. Shapley, *Chem. Commun.*, 1997, 1125.
25 H.-F. Hsu and J.R. Shapley, *J. Organomet. Chem.*, 2000, **599**, 97.
26 K.-W. Lee and L.A. Singer, *J. Org. Chem.*, 1974, **39**, 3780.
27 M.I. Bruce and P.J. Low, *J. Organomet. Chem.*, 1996, **519**, 221.