

# Synthesis, characterisation and redox behaviour of isocyanide incorporated, chalcogen stabilised mixed-metal clusters <sup>☆</sup>

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## Abstract

Room temperature reaction of a benzene solution of  $[\text{Cp}_2\text{Mo}_2\text{Fe}_2(\text{CO})_7(\mu_3\text{-E})(\mu_3\text{-E}')] (E, E' = \text{Se}_2 \text{ (1), STe (2), SeTe (3)})$  with  $\text{Pr}^i\text{NC}$  or  $\text{Bu}^t\text{NC}$  resulted in the formation of iron bonded isocyanide clusters  $[\text{Cp}_2\text{Mo}_2\text{Fe}_2(\text{RNC})(\text{CO})_6(\mu_3\text{-E})(\mu_3\text{-E}')] (E, E' = \text{Se}, \text{R} = \text{Pr}^i \text{ (5) or Bu}^t \text{ (9); } E = \text{S}, E' = \text{Te}, \text{R} = \text{Pr}^i \text{ (6a, 6b) or R} = \text{Bu}^t \text{ (10a, 10b); } E = \text{Se}, E' = \text{Te}, \text{R} = \text{Pr}^i \text{ (7a, 7b) or R} = \text{Bu}^t \text{ (11a, 11b)})$  and molybdenum bonded isocyanide clusters  $[\text{Cp}_2(\text{RNC})\text{Mo}_2\text{Fe}_2(\text{CO})_6(\mu_3\text{-E})(\mu_3\text{-E}')] (E, E' = \text{Se}, \text{R} = \text{Pr}^i \text{ (13) or Bu}^t \text{ (17); } E = \text{S}, E' = \text{Te}, \text{R} = \text{Pr}^i \text{ (14) or R} = \text{Bu}^t \text{ (18); } E = \text{Se}, E' = \text{Te}, \text{R} = \text{Pr}^i \text{ (15) or R} = \text{Bu}^t \text{ (19)})$ . Two isomers (**a** and **b**) were detected by  $^1\text{H}$  NMR spectroscopy for the mixed-chalcogen clusters **6**, **7**, **10** and **11**, where the isocyanide group is bonded to an iron atom. Thermolytic reaction conditions were necessary for the reaction of  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2\text{Fe}_2(\text{CO})_7(\mu_3\text{-Te})_2] \text{ (4)}$  with  $\text{Pr}^i\text{NC}$  or  $\text{Bu}^t\text{NC}$  to give  $[\text{Cp}_2\text{Mo}_2\text{Fe}_2(\text{RNC})(\text{CO})_6(\mu_3\text{-Te})_2] (R = \text{Pr}^i \text{ (8) or R} = \text{Bu}^t \text{ (12)})$  and  $[\text{Cp}_2(\text{RNC})\text{Mo}_2\text{Fe}_2(\text{CO})_6(\mu_3\text{-Te})_2] (R = \text{Pr}^i \text{ (8)})$ . Compounds **5–19** have been characterised by IR and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. The Se- and Te-bridged compounds have been further characterised by  $^{77}\text{Se}$  and  $^{125}\text{Te}$  NMR spectroscopy. The structures of compounds **12** and **14** were determined by single crystal X-ray diffraction methods. Redox properties of the mixed-metal clusters, **2**, **6**, **8**, **12** and **14** have been studied by cyclic voltammetry in the potential range  $\pm 2.5$  V at 298 K, using a platinum working electrode.

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**Keywords:** Cluster; Mixed metal; Carbonyl; Isonitrile; X-ray diffraction

## 1. Introduction

As part of our ongoing interest in developing facile synthetic methods for the preparation of mixed-metal clusters, we isolated clusters of the type  $[\text{Cp}_2\text{Mo}_2\text{Fe}_2(\text{CO})_7(\mu_3\text{-E})(\mu_3\text{-E}')] (E, E' \text{ are chalcogen atoms})$  from the reaction of  $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-E})(\mu_3\text{-E}')] (E, E' \text{ are chalcogen atoms})$  with  $[\text{Cp}_2\text{Mo}_2(\text{CO})_6]$  [1–4]. Some reactivity studies of this cluster type have already been described. For instance,  $[\text{Cp}_2\text{Mo}_2\text{Fe}_2(\text{CO})_7(\mu_3\text{-E})(\mu_3\text{-E}')] (E, E' \text{ are chalcogen atoms})$  reacts with chalcogen powder ( $E''$ ) to form the clusters,

$[\text{Cp}_2\text{Mo}_2\text{Fe}_2(\text{CO})_6(E)(E')(E'')] (E, E', E'' \text{ are chalcogen atoms})$ , in which two chalcogen atoms are triply bridging and the third quadruply bridging [3]. Under aerobic conditions,  $[\text{Cp}_2\text{Mo}_2\text{Fe}_2(\text{CO})_7(\mu_3\text{-Te})_2]$  reacts with phenylazide to form the imido-bridged dimolybdenum compound,  $[\text{Cp}_2\text{Mo}_2(\text{O})_2(\mu\text{-Te})(\mu\text{-NPh})]$  [5]. Reflux of a benzene solution of  $[\text{Cp}_2\text{Mo}_2\text{Fe}_2(\text{CO})_7(\mu_3\text{-S})(\mu_3\text{-Te})]$ , in the presence of air, forms the oxo-species, *trans*- $[\text{Cp}_2\text{Mo}_2(\text{O})_2(\mu\text{-O})(\mu\text{-Te})]$  and *cis*- $[\text{Cp}_2\text{Mo}_2(\text{O})_2(\mu\text{-O})(\mu\text{-S})]$  [6], while under anaerobic conditions, in presence of PhSH, the hydride-bridged cluster  $[\text{Cp}_2\text{Mo}_2\text{Fe}_2(\text{CO})_5(\mu_3\text{-S})(\mu_3\text{-Te})(\mu\text{-SPh})(\mu_3\text{-H})]$  is formed, which converts to the dimolybdenum compound  $[\text{Cp}_2\text{Mo}_2(\mu\text{-S})(\mu\text{-Te})(\mu\text{-SPh})_2]$  on extended thermolysis [7]. Ligand substitution reactions form an interesting aspect of the overall study of reactivity in mixed-metal clusters. In this regard, we chose to look at

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## 2. Results and discussion

### 2.1. Synthesis and spectroscopic characterisation of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2\text{Fe}_2(\text{CO})_6(\text{CNR})(\mu_3\text{-E})(\mu_3\text{-E}')] \quad (5\text{--}19)$ , ( $E, E' = \text{S, Se or Te}$ )

When a benzene solution of  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2\text{Fe}_2(\text{CO})_7(\mu_3\text{-E})(\mu_3\text{-E}')] \quad (1\text{--}4)$  and isopropyl or *tert*-butyl isocyanide (RNC) was stirred, the isocyanide-substituted derivatives,  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2\text{Fe}_2(\text{CO})_6(\text{CNR})(\mu_3\text{-E})(\mu_3\text{-E}')] \quad (5\text{--}19)$  were isolated, in yields of 28–62% according to Scheme 1. For all except one  $E, E'$  combination, the substitution occurred at room temperature. Thermolytic conditions were necessary for the reaction of  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2\text{Fe}_2(\text{CO})_7(\mu_3\text{-Te})_2] \quad (4)$  with  $\text{Pr}^i\text{NC}$  or  $\text{Bu}^t\text{NC}$ .

The new compounds were characterised by IR, and by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. Furthermore, the Se- and Te-bridged compounds were characterised by  $^{77}\text{Se}$  and  $^{125}\text{Te}$  NMR spectroscopy. The  $^{77}\text{Se}$  NMR spectra display signals in the range  $\delta$  985–1121 ppm, characteristic of  $\mu_3\text{-Se}$  and upfield of signals generally observed for  $\mu_4\text{-Se}$  at  $\sim\delta$  1300 ppm [2,3]. There is a larger variation observed in the  $^{125}\text{Te}$  signals,  $\delta$  257–1160 ppm, but these fall within the range observed previously for  $\mu_3\text{-Te}$ , and well upfield of signals expected for  $\mu_4\text{-Te}$ ,  $\sim\delta$  1600 ppm [3]. The IR spectra of 5–19 show absorptions corresponding to the presence of three types of CO groups: terminal, doubly bridging and semi-triply bridging. The presence of the isocyanide ligand causes a shift to lower frequencies, consistent with substitution of a CO group by a stronger donor but weaker acceptor ligand. The spectra also show the  $\nu_{\text{CN}}$  peak at 2166–2132  $\text{cm}^{-1}$ , appropriate for a terminally bonded isocyanide group. For compounds in which the isocyanide ligand is bonded to an iron atom (5–12) a single signal was observed in the  $^1\text{H}$  NMR spectra of the homo-chalcogen derivatives, 5, 8, 9 and 12, whereas the spectra of the mixed-chalcogen species 6, 7, 10 and 11, indicated the presence of two isomers (Scheme 2). Attempts to separate the isomers proved unsuccessful.

In general, upon substitution, the ligand disposition around the metal core remained unchanged in all cases; i.e. five terminal, one doubly bridging and one semi-

triply bridging ligand; the isocyanide was found terminally bonded to either of the two Fe atoms, (5–12) but only one Mo atom, that was not associated with the semi-triply bridging carbonyl group (13–19), consistent with the preference of *i*-PrNC and *t*-BuNC to adopt terminal rather than bridging bonding modes.

Representative single crystal X-ray analyses were carried out on one Fe-substituted product, compound 12, and one Mo-substituted product, compound 14. Black crystals of 12 were grown from a hexane/dichloromethane solvent mixture at  $-5^\circ\text{C}$ , and its molecular structure is shown in Fig. 1. The metal–metal and metal–tellurium bond distances in 12 are almost identical to those in  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2\text{Fe}_2(\text{CO})_7(\mu_3\text{-Te})_2] \quad (12)$ : Mo–Mo = 2.8886(17) Å; Mo–Fe = 2.908(2) Å, 2.872(2) Å, 2.859(3) Å, 2.855(3) Å; Fe–Fe = 2.417(3) Å; Fe–Te = 2.484(2) Å, 2.478(3) Å; Mo–Te = 2.7163(19) Å, 2.7041(17) Å, 2.6839(19) Å, 2.6727(17) Å;  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2\text{Fe}_2(\text{CO})_7(\mu_3\text{-Te})_2]$ : Mo–Mo = 2.888(1) Å; Mo–Fe = 2.889(2) Å, 2.872(2) Å, 2.863(2) Å, 2.861(2) Å; Fe–Fe = 2.433(2) Å; Fe–Te = 2.472(2) Å, 2.468(2) Å;

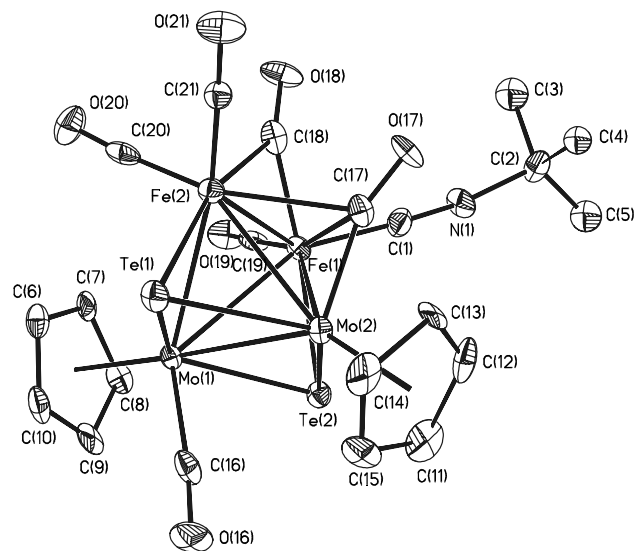
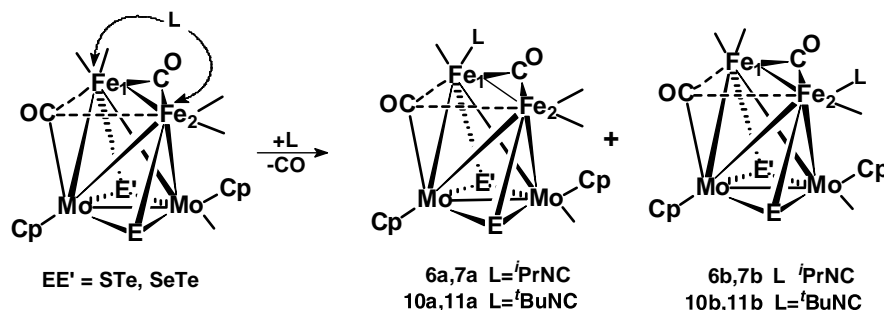


Fig. 1. Molecular structure of  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2\text{Fe}_2\{\text{CNC}(\text{CH}_3)_3\}(\text{CO})_6(\mu_3\text{-Te})_2] \quad (12)$ .



Scheme 2. Formation of two isomers for mixed-chalcogen systems.

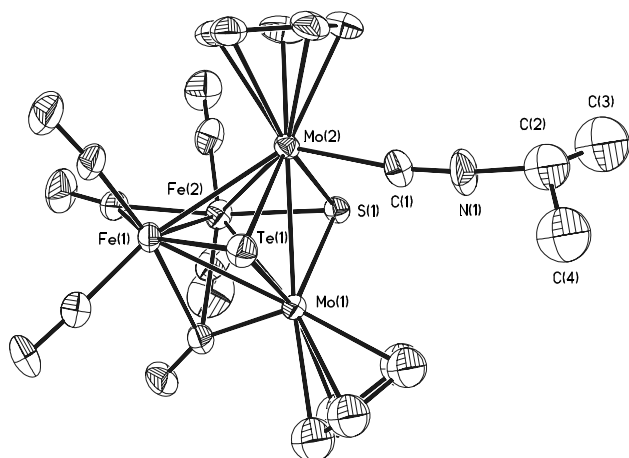


Fig. 2. Molecular structure of  $[(\eta^5\text{-C}_5\text{H}_5)_2\{(\text{CH}_3)_2\text{CHNC}\}\{\text{Mo}_2\text{Fe}_2\}(\text{CO})_6(\mu_3\text{-S})(\mu_3\text{-Te})]$  (**14**).

$\text{Mo}\text{-Te} = 2.684(1) \text{ \AA}$ ,  $2.683(1) \text{ \AA}$ ,  $2.681(1) \text{ \AA}$ ,  $2.673(1) \text{ \AA}$ .<sup>4</sup> The C–N bond distance of  $1.164(16) \text{ \AA}$  in **12** is comparable to the C–N bond distances of the linear  $\text{CNBu}^t$  groups in  $[\text{Fe}(\text{CNBu}^t)_3]$  ( $1.16(1)\text{--}1.19(1) \text{ \AA}$ ) [8].

Green crystals of compound **14** were obtained from a hexane/dichloromethane solvent mixture at  $-5 \text{ }^\circ\text{C}$ . Its molecular structure, shown in Fig. 2 confirms that here too the metal core remains unchanged upon isocyanide substitution. One of the molybdenum atoms has a terminally bonded isopropyl isocyanide group. The C–N distance of  $1.157(11) \text{ \AA}$  in **14** is comparable to that ob-

served for the terminal  $\text{CNPr}^i$  ligand in  $[\text{Mo}(\text{CO})_2(\text{PMe}_3)_3(\text{CNPr}^i)]$  ( $1.14(3) \text{ \AA}$ ) [9].

## 2.2. Redox properties of compounds **2**, **6**, **8**, **12** and **14**

The redox properties of complexes **2**, **6**, **8**, **12** and **14** (Fig. 3) have been studied in dichloromethane solvent by cyclic voltammetry in the potential range  $\pm 2.5 \text{ V}$  at  $298 \text{ K}$ , using a platinum working electrode. The voltammograms are shown in Fig. 4(a–e).

Complex **2** displays one irreversible oxidative response  $E_{pa}$ , at  $1.0 \text{ V}$  and one irreversible reduction  $E_{pc}$ , at  $-1.07 \text{ V}$  vs. SCE (Fig. 4a). Similarly, complex **14** exhibits both irreversible oxidative ( $E_{pa}$ ) and reductive ( $E_{pc}$ ) responses at  $1.0$  and  $-1.35 \text{ V}$  vs. SCE, respectively (Fig. 4c). However, in the case of **6**, two closely spaced irreversible oxidative responses ( $E^1_{pa}$ ,  $0.77 \text{ V}$  and  $E^2_{pa}$ ,  $0.99 \text{ V}$ ;  $\Delta E_{pa} = 220 \text{ mV}$ ) and two successive quasi-reversible reductions [ $E^{\circ}_{298}$ ,  $V(\Delta E_p, \text{ mV})$ ,  $-0.91$  (90) and  $-1.29$  (120)] (Fig. 4b) have been observed.

Comparison of the redox behaviour of **2** and **14** reveals that, as anticipated from the replacement of a carbonyl ligand on molybdenum by the better donor isonitrile ligand, the more electron-rich cluster is more difficult to reduce. The  $^1\text{H}$  NMR spectrum of **6** in  $\text{CDCl}_3$  indicates the presence of an inseparable mixture of two diastereomers, one with  $\text{Fe1-CN}^i\text{Pr}$  where Fe1 is bonded to  $\mu_3\text{-S}$  in the cluster core and the other with

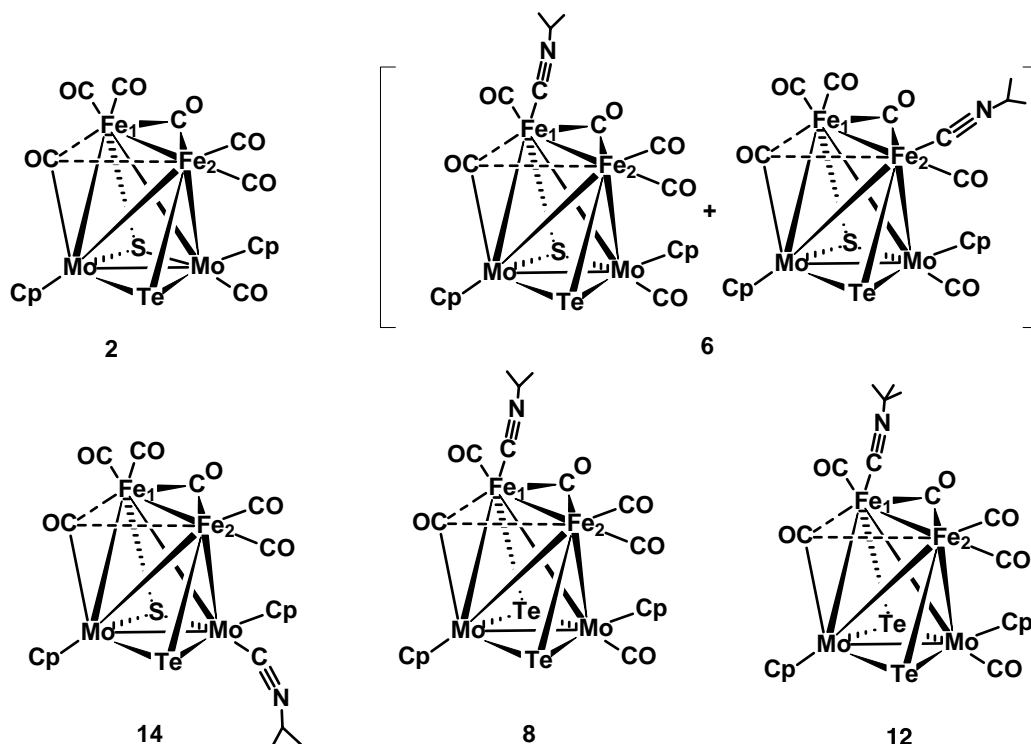


Fig. 3. Structures of compounds **2**, **6**, **8**, **12** and **14**.

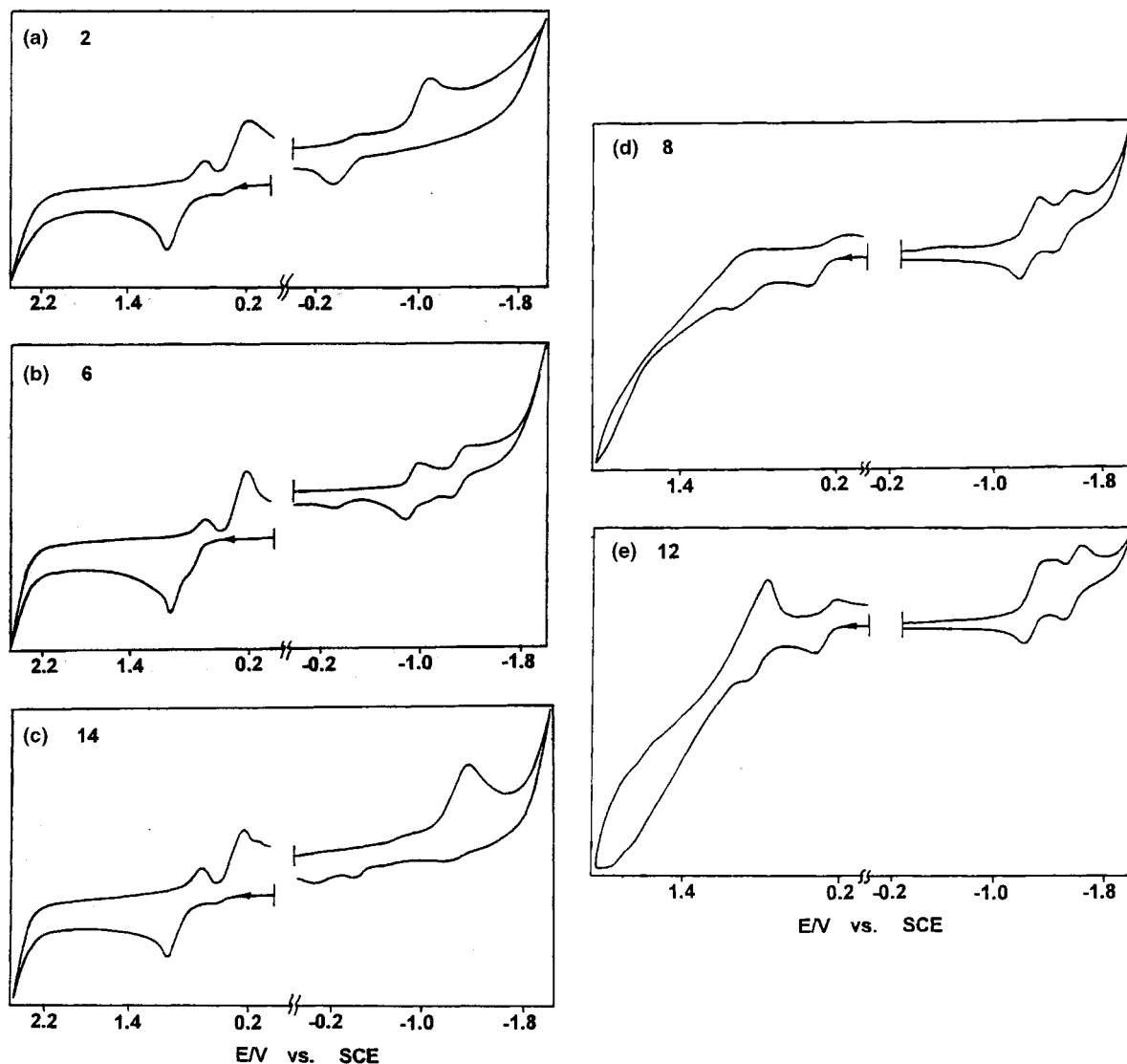


Fig. 4. (a–c) Cyclic voltammograms of **2**, **6** and **14** (d–e) Cyclic voltammograms of **8** and **12**.

Fe<sub>2</sub>-CN<sup>i</sup>Pr where Fe<sub>2</sub> is bonded to μ<sub>3</sub>-Te in the cluster core, and this may account for the observation of two oxidative and two reductive responses in **6** (Fig. 4b). In contrast, we note that only a single isomer of **14**, is produced, and this gives rise to only one oxidation and one reduction process.

The splitting of the anodic waves in Fig. 4b is observed to be enhanced appreciably in case of **8** with two oxidative responses at  $E^1_{pa}$ , 0.384 V and  $E^2_{pa}$ , 0.933 V ( $\Delta E_p = 549$  mV) and two reductive responses  $E^{\circ}_{298}$ , V ( $\Delta E_p$ , mV) at -1.28 (150) and -1.52 (130) (Fig. 4d). Similarly, **12** exhibits oxidative responses at  $E^1_{pa}$ , 0.37 V and  $E^2_{pa}$ , 0.89 V ( $\Delta E_{pa} = 520$  mV) and reductive responses  $E^{\circ}_{298}$ , V ( $\Delta E_p$ , mV) at -1.30 (180) and -1.57 (130) (Fig. 4e). The larger splitting in **8** ( $\Delta E_{pa} = 540$  mV) and **12** ( $\Delta E_{pa} = 520$  mV) compared to **6** ( $\Delta E_{pa} = 220$  mV) is possibly attributable to the presence of different chalcogen combinations in the cluster cores. The presence of a (μ<sub>3</sub>-Te)<sub>2</sub> unit in the cluster core of **8** and **12**

increases the electron density at the iron centres relative to that of **6**, where (μ<sub>3</sub>-S)(μ<sub>3</sub>-Te) is present which in turn decreases the potentials as expected. Moreover, the decrease in anodic potentials and increase in cathodic potentials in **12** as compared to **8** is rationalisable in terms of the replacement of an isopropyl isocyanide group by the more electron-donating *t*-butyl isocyanide group.

### 3. Experimental section

#### 3.1. General procedures

All reactions and other manipulations were carried out using standard Schlenk techniques under an inert atmosphere of argon. All solvents were deoxygenated immediately prior to use. Infrared spectra were recorded on a Nicolet Impact 400 FTIR spectrophotometer, as *n*-

Table 1  
Experimental conditions for the preparation of **5–19**

Reactants/mg (mmol)	Reaction conditions (Time, temperature)	Compound	Yield mg (%)	Analysis (%) Calculated (Found)	mp/°C <sup>a</sup>
[Cp <sub>2</sub> Mo <sub>2</sub> Fe <sub>2</sub> Se <sub>2</sub> (CO) <sub>7</sub> ]+[(CH <sub>3</sub> ) <sub>2</sub> CHCN] 100 (0.13) 15 μlt (0.17)	10 h, 25 °C	<b>5</b>	30 (28)	C, 28.96 (28.44); H, 2.05 (2.57); N 1.69 (1.78)	130–132
		<b>13</b>	63 (59)	C, 28.96 (28.35); H, 2.05 (2.17); N 1.69 (1.72)	134–135
[Cp <sub>2</sub> Mo <sub>2</sub> Fe <sub>2</sub> STe(CO) <sub>7</sub> ]+[(CH <sub>3</sub> ) <sub>2</sub> CHCN] 100 (0.13) 15 μlt (0.17)	12 h, 25 °C	<b>6a + 6b</b>	52 (48)	C, 28.8 (28.22); H, 2.04 (2.19); N 1.68 (1.71)	131–134
		<b>14</b>	31 (29)	C, 28.8 (28.46); H, 2.04 (2.12); N 1.68 (1.72)	140–142
[Cp <sub>2</sub> Mo <sub>2</sub> Fe <sub>2</sub> SeTe(CO) <sub>7</sub> ]+[(CH <sub>3</sub> ) <sub>2</sub> CHCN] 100 (0.12) 15 μlt (0.17)	20 h, 25 °C	<b>7a + 7b</b>	40 (38)	C, 27.35 (27.00); H, 1.94 (2.18); N 1.59 (1.65)	141–143
		<b>15</b>	37 (35)	C, 27.35 (26.95); H, 1.94 (2.30); N 1.59 (1.64)	148–150
[Cp <sub>2</sub> Mo <sub>2</sub> Fe <sub>2</sub> Te <sub>2</sub> (CO) <sub>7</sub> ]+[(CH <sub>3</sub> ) <sub>2</sub> CHCN] 100 (0.11) 15 μlt (0.17)	20 h, 60 °C	<b>8</b>	35 (34)	C, 25.92 (25.85); H, 1.84 (2.21); N, 1.47 (1.50)	145–147
		<b>16</b>	26 (25.5)	C, 25.92 (25.56); H, 1.84 (2.16); N, 1.47 (1.53)	153–154
[Cp <sub>2</sub> Mo <sub>2</sub> Fe <sub>2</sub> Se <sub>2</sub> (CO) <sub>7</sub> ]+[(CH <sub>3</sub> ) <sub>3</sub> CCN] 100 (0.13) 20 μlt (0.18)	10 h, 25 °C	<b>9</b>	34 (31)	C, 29.98 (29.6); H, 2.26 (2.51); N, 1.66 (1.68)	136–137
		<b>17</b>	60 (55)	C, 29.98 (29.3); H, 2.26 (2.47); N, 1.66 (1.73)	140–142
[Cp <sub>2</sub> Mo <sub>2</sub> Fe <sub>2</sub> STe(CO) <sub>7</sub> ]+[(CH <sub>3</sub> ) <sub>3</sub> CCN] 100 (0.13) 20 μlt (0.18)	12 h, 25 °C	<b>10a + 10b</b>	49 (45)	C, 29.91 (29.64); H, 2.26 (2.31); N, 1.66 (1.69)	141–142
		<b>18</b>	33 (30)	C, 29.91 (29.53); H, 2.26 (2.45); N, 1.66 (1.72)	146–148
[Cp <sub>2</sub> Mo <sub>2</sub> Fe <sub>2</sub> SeTe(CO) <sub>7</sub> ]+[(CH <sub>3</sub> ) <sub>3</sub> CCN] 100 (0.12) 20 μlt (0.18)	20 h, 25 °C	<b>11a + 11b</b>	45 (42)	C, 28.3 (27.85); H, 2.15 (2.24); N 1.57 (1.68)	155–157
		<b>19</b>	36 (34)	C, 28.3 (27.75); H, 2.15 (2.34); N 1.57 (1.61)	147–149
[Cp <sub>2</sub> Mo <sub>2</sub> Fe <sub>2</sub> Te <sub>2</sub> (CO) <sub>7</sub> ]+[(CH <sub>3</sub> ) <sub>3</sub> CCN] 100 (0.11) 20 μlt (0.18)	20 h, 60 °C	<b>12</b>	65 (62)	C, 26.9 (26.26); H, 2.04 (2.29); N 1.5 (1.64)	140–141

<sup>a</sup> With decomposition.

hexane solutions in 0.1 mm path length cells. Elemental analyses were performed using a Carlo-Erba automatic analyser. <sup>1</sup>H, <sup>13</sup>C, <sup>77</sup>Se, <sup>125</sup>Te NMR spectra were recorded on a Varian VXR-300S spectrometer in CDCl<sub>3</sub>. The operating frequency for <sup>125</sup>Te was 94.70 MHz with a pulse width of 9.5 μs and a delay of 1.0 s. <sup>125</sup>Te NMR spectra were referenced to Me<sub>2</sub>Te (δ = 0 ppm). The <sup>77</sup>Se NMR measurements were made at an operating frequency of 57.23 MHz using 90° pulses with a 1.0 s delay and 1.0 s acquisition time and referenced to Me<sub>2</sub>Se (δ = 0). Electrochemical measurements were carried out using a PAR model 273 A potentiostat/galvanostat. A platinum working electrode, a platinum auxiliary electrode and a saturated calomel reference electrode (SCE) were used in a three-electrode configuration. Tetraethyl

ammonium perchlorate (TEAP) was the supporting electrolyte, and the solute concentration was ~10<sup>-3</sup> M. The half-wave potential *E*<sub>298</sub><sup>o</sup> was set equal to 0.5 (*E*<sub>pa</sub> + *E*<sub>pc</sub>), where *E*<sub>pa</sub> and *E*<sub>pc</sub> are the anodic and cathodic cyclic voltammetric peak potentials, respectively. For irreversible processes *E*<sub>pa</sub> and *E*<sub>pc</sub> are considered. It should be noted that while doing the cyclic voltammetric experiments we encountered electrode poisoning. Therefore, the electrodes were treated with acid-water and dried prior to each scan. Electronic spectra were recorded using a Shimadzu UV-2100 spectrophotometer.

The starting materials [Cp<sub>2</sub>Mo<sub>2</sub>Fe<sub>2</sub>(CO)<sub>7</sub>(μ<sub>3</sub>-E)(μ<sub>3</sub>-E')] (where EE' = Se<sub>2</sub>, STe, Te<sub>2</sub>, SeTe) were prepared as reported in literature [1–4]. Details of the quantities of

Table 2  
Spectral data for compound 5–19

Compound	I.R. ( $\nu$ ) ( $\text{cm}^{-1}$ )	$^1\text{H}$ NMR ( $\delta$ )	$^{13}\text{C}$ NMR ( $\delta$ )	$^{77}\text{Se}$ NMR	$^{125}\text{Te}$ NMR
<b>5</b>	<sup>a</sup> 2145.2(m), 2133.1(m), 2001.3(s), 1955.4(s), 1944.8(vs), 1847.3(m, br), 1740(w) <sup>b</sup> 1991.9(s), 1958.9(vs, br), 1828.2(m, br), 1735(w)	5.4, 5.09( $\text{C}_5\text{H}_5$ ), 4.31(m, CH), 1.31(dd, $\text{CH}_3$ )	93.56, 91.05( $\text{C}_5\text{H}_5$ ), 23.29( $\text{CH}_3$ ), 44.5(CH), 137.1(CN), 210, 214(CO)	1050.6, 985.5	–
<b>6a</b>	<sup>a</sup> 2145.2(w), 2132.7(w), 2000.8(vs), 1953.1(s), 1940.4(vs), 1843.7(m, br), 1742.0(w)	5.39, 5.08( $\text{C}_5\text{H}_5$ ), 3.87(m, CH), 1.32(t, $\text{CH}_3$ )	93.83, 91.22( $\text{C}_5\text{H}_5$ ), 23.67( $\text{CH}_3$ ), 53.5(CH), 135.35(CN), 215, 213(CO)	–	1160.4, 1129
<b>6b</b>	<sup>b</sup> 1991.8(s), 1953.4(vs, br), 1818(m, br), 1737(w)	5.40, 5.09( $\text{C}_5\text{H}_5$ ), 4.07(m, CH), 1.44(dd, $\text{CH}_3$ )	–	–	–
<b>7a</b>	<sup>a</sup> 2142(w), 2135.3(w), 2000.8(vs), 1951.2(vs), 1933.1(vs), 1839.2(m, br), 1736.6(w)	5.34, 5.05( $\text{C}_5\text{H}_5$ ), 3.87(m, CH), 1.32(t, $\text{CH}_3$ )	93.14, 90.79( $\text{C}_5\text{H}_5$ ), 19.3( $\text{CH}_3$ ), 41.93(CH), 163.2(CN), 200, 204(CO)	1086.3	365.8, 500.4
<b>7b</b>	<sup>b</sup> 2127(m, br), 1988.3(s), 1939(vs, br), 1813(m, br), 1735.2(w)	5.35, 5.053( $\text{C}_5\text{H}_5$ ), 4.06(m, CH), 1.42(t, $\text{CH}_3$ )	–	–	–
<b>8</b>	<sup>a</sup> 2144(w), 2132(w), 1997.4(vs), 1947.6(vs), 1923(vs), 1830(m, br), 1737(w) <sup>b</sup> 2125.4(m), 1986.4(vs), 1936.0(vs), 1927.6(vs), 1812.5(m, br), 1734(w)	5.3, 5.01( $\text{C}_5\text{H}_5$ ), 3.88(m, CH), 1.307(t, $\text{CH}_3$ )	91.93, 89.94( $\text{C}_5\text{H}_5$ ), 23.89( $\text{CH}_3$ ), 41.2(CH), 164.1(CN), 213, 216(CO)	–	328, 462.3
<b>9</b>	<sup>a</sup> 2001.2(s), 1956.7(s), 1945(vs), 1847(m), 1741(w) <sup>b</sup> 2055(m), 1992.3(s), 1958(vs, br), 1818.6(m), 1737(w)	5.39, 5.09( $\text{C}_5\text{H}_5$ ), 1.38(s, $\text{CH}_3$ )	93.65, 90.23( $\text{C}_5\text{H}_5$ ), 30.02( $\text{CH}_3$ ), 53.8(C), 166.5(CN), 212, 216(CO)	1065.6, 1108.4	–
<b>10a</b>	<sup>a</sup> 2133(w, br), 1999.4(s), 1951.4(s), 1941.9(vs), 1842.1(w, br), 1741.7(w)	5.48, 5.17( $\text{C}_5\text{H}_5$ ), 1.38(s, $\text{CH}_3$ )	93.5, 90.8( $\text{C}_5\text{H}_5$ ), 29.7( $\text{CH}_3$ ), 55.4(C), 161(CN), 210, 208(CO)	–	1056, 1084.7
<b>10b</b>	<sup>b</sup> 1989.1(s), 1949(br, vs), 1819.9(m, br),	5.30, 5.09( $\text{C}_5\text{H}_5$ ), 1.38(s, $\text{CH}_3$ )	–	–	–
<b>11a</b>	<sup>a</sup> 2136(m, br), 1999.3(vs), 1950(vs), 1935(vs), 1837(w, br), 1743(w)	5.34, 5.05( $\text{C}_5\text{H}_5$ ), 1.38(s, $\text{CH}_3$ )	92.9, 90.0( $\text{C}_5\text{H}_5$ ), 29.4( $\text{CH}_3$ ), 55.2(C), 162(CN), 214, 210(CO)	1025.2, 1121.6	257.3, 405.3
<b>11b</b>	<sup>b</sup> 1987.7(s), 1942.1(vs, br), 1819.1(m, br), 1751.7(w)	5.338, 5.046( $\text{C}_5\text{H}_5$ ), 1.38(s, $\text{CH}_3$ )	–	–	–

<b>12</b>	<sup>a</sup> 2135(m, br), 2000(vs), 1948.5(vs), 1919(vs), 1833.8(w), 1736(w) <sup>b</sup> 1985.9(vs), 1934(vs, br), 1815.6(w, br).	5.29, 5.01(C <sub>5</sub> H <sub>5</sub> ), 1.36(s, CH <sub>3</sub> ) 1.43(d, CH <sub>3</sub> )	91.3, 89.5(C <sub>5</sub> H <sub>5</sub> ), 30.1(CH <sub>3</sub> ), 54.2(C), 167.3(CN), 211, 214(CO)	–	330, 396.5
<b>13</b>	<sup>a</sup> 2157(m, br), 2014(s), 1997.3(s), 1820(w, br), 1744(w) <sup>b</sup> 2003.6(vs), 1976.5(vs), 1941.8(s), 1813(w), 1733(w)	5.41, 5.07(C <sub>5</sub> H <sub>5</sub> ), 4.07(m, CH), 1.43(d, CH <sub>3</sub> )	92.6, 90.58(C <sub>5</sub> H <sub>5</sub> ), 23.05(CH <sub>3</sub> ), 44.82(CH), 136.3(CN), 215, 213(CO)	1110.0	–
<b>14</b>	<sup>a</sup> 2166.4(w), 2137(w), 2012.4(s), 1991.6(s), 1950(s), 1839(w, br), 1736(w) <sup>b</sup> 2002(vs), 1975.3(vs), 1940.6(s), 1813(w, br), 1750(w)	5.40, 5.06(C <sub>5</sub> H <sub>5</sub> ), 4.04(m, CH), 1.405(ddd, CH <sub>3</sub> )	92.2, 90.6(C <sub>5</sub> H <sub>5</sub> ), 23.2(CH <sub>3</sub> ), 43.5(CH), 133.2(CN), 211, 214(CO)	–	814.6
<b>15</b>	<sup>a</sup> 2157.8(w), 2137(w), 2013.4(s), 1989.4(s), 1953(vs), 1835(w, br), 1742(w) <sup>b</sup> 2002.6(vs), 1975.2(vs), 1941(s), 1820.7(m, br), 1754.8(w).	5.35, 5.01(C <sub>5</sub> H <sub>5</sub> ), 4.06(m, CH), 1.38(ddd, CH <sub>3</sub> )	91.92, 90.35(C <sub>5</sub> H <sub>5</sub> ), 23.62(CH <sub>3</sub> ), 42.8(CH), 133.67(CN)	1098.6	560.8
<b>16</b>	<sup>a</sup> 2155.6(w), 2134(w), 2015(s), 1989.0(s), 1955(vs), 1840(w, br), 1743(w) <sup>b</sup> 2004.0(vs), 1974.5(vs), 1940.7(s), 1819.3(m), 1752.4(w)	5.3, 4.96(C <sub>5</sub> H <sub>5</sub> ), 3.99(m, CH), 1.33(ddd, CH <sub>3</sub> )	91.05, 89.81(C <sub>5</sub> H <sub>5</sub> ), 23.39(CH <sub>3</sub> ), 48.3(CH), 129.6(CN), 213, 211	–	478.3
<b>17</b>	<sup>a</sup> 2153.2(w), 2137(w), 2013.1(s), 1990.5(s), 1953.2(s), 1838(w, br), 1739.6(w) <sup>b</sup> 2002.5(vs), 1974.2(vs), 1942.8(m), 1813.2(w), 1743(w)	5.41, 5.07(C <sub>5</sub> H <sub>5</sub> ), 1.5(s, CH <sub>3</sub> )	92.38, 90.55(C <sub>5</sub> H <sub>5</sub> ), 28.6(CH <sub>3</sub> ), 55.3(C), 164.5(CN), 214, 209	1104.8	–
<b>18</b>	<sup>a</sup> 2154(w), 2139(w), 2013(s), 1988.9(vs), 1953(vs), 1836.7(m, br), 1743(w) <sup>b</sup> 2001.6(vs), 1973.3(vs), 1943(m, br), 1814.2(w), 1741(w)	5.40, 5.05(C <sub>5</sub> H <sub>5</sub> ), 1.46(s, CH <sub>3</sub> )	92.7, 90.4(C <sub>5</sub> H <sub>5</sub> ), 29.5(CH <sub>3</sub> ), 55.6(C), 166(CN), 211, 215(CO)	–	839.0
<b>19</b>	<sup>a</sup> 2157(w), 2138.2(w), 2012(vs), 1989(s), 1950(vs), 1834(w), 1742(w) <sup>b</sup> 2002.3(vs), 1974(vs), 1942(s), 1819(m, br), 1753(w).	5.35, 5.01(C <sub>5</sub> H <sub>5</sub> ), 1.44(s, CH <sub>3</sub> )	91.83, 90.16(C <sub>5</sub> H <sub>5</sub> ), 30.48(CH <sub>3</sub> ), 53.4(C), 162.8(CN), 210, 216	1116.2	680.2

<sup>a</sup> *n*-hexane.<sup>b</sup> CH<sub>2</sub>Cl<sub>2</sub>.



Table 3  
Crystal data and structure refinement for **12** and **14**

Identification code	<b>12</b>	<b>14</b>
Empirical formula	C <sub>21</sub> H <sub>19</sub> Fe <sub>2</sub> Mo <sub>2</sub> N O <sub>6</sub> Te <sub>2</sub>	C <sub>20</sub> H <sub>17</sub> Fe <sub>2</sub> Mo <sub>2</sub> N O <sub>6</sub> S Te
Formula weight	940.15	830.59
Temperature	299(2) K	299(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	P2(1)/c
<i>a</i> , Å	16.615(6)	14.325(7)
<i>b</i> , Å	10.507(4)	12.315(6)
<i>c</i> , Å	29.659(11)	15.775(9)
$\beta$ , degree	98.987(7)	116.364(9)
Volume	5114 (3) Å <sup>3</sup>	2493(2) Å <sup>3</sup>
<i>Z</i>	8	4
Density (calculated)	2.442 Mg/m <sup>3</sup>	2.213 Mg/m <sup>3</sup>
Absorption coefficient	4.344 mm <sup>-1</sup>	3.389 mm <sup>-1</sup>
<i>F</i> (000)	3520	1584
Crystal size	0.05 × 0.08 × 0.12 mm <sup>3</sup>	0.5 × 0.3 × 0.1 mm <sup>3</sup>
$\theta$ range for data collection	1.39° to 22.50°	1.59° to 25.00°
Index ranges	-17 ≤ <i>h</i> ≤ 17, -11 ≤ <i>k</i> ≤ 11, -31 ≤ <i>l</i> ≤ 31	-17 ≤ <i>h</i> ≤ 17, -14 ≤ <i>k</i> ≤ 14, -18 ≤ <i>l</i> ≤ 18
Reflections collected	15,314	18,485
Independent reflections	3346 [ <i>R</i> ( <i>int</i> ) = 0.1383]	4375 [ <i>R</i> ( <i>int</i> ) = 0.0386]
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	3346/0/288	4375/0/259
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.978	1.037
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> 1 = 0.0522, <i>wR</i> 2 = 0.0890	<i>R</i> 1 = 0.0473, <i>wR</i> 2 = 0.1246
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1173, <i>wR</i> 2 = 0.1070	<i>R</i> 1 = 0.0646, <i>wR</i> 2 = 0.1357
Largest different peak and hole	1.250 and -1.015 e.Å <sup>-3</sup>	2.492 and -0.918 e.Å <sup>-3</sup>
Ratio of min to max apparent transmission	0.740012	0.551528

starting materials used and the yields of products obtained are given in Table 1. See Table 2 for spectral data.

### 3.2. Reaction of [Cp<sub>2</sub>Mo<sub>2</sub>Fe<sub>2</sub>(CO)<sub>7</sub>(μ<sub>3</sub>-E)(μ<sub>3</sub>-E')] (*E*, *E'* = S, S; S, Te; Se, Te; Te, Te) with RNC [*R* = *i*Pr or *t*Bu]

A benzene solution of [Cp<sub>2</sub>Mo<sub>2</sub>Fe<sub>2</sub>(CO)<sub>7</sub>(μ<sub>3</sub>-E)(μ<sub>3</sub>-E')] was stirred with RNC (*R* = (CH<sub>3</sub>)<sub>2</sub>CH or (CH<sub>3</sub>)<sub>3</sub>C) at room temperature for the chalcogen combination EE' = Se<sub>2</sub>, STe and SeTe and at 60 °C for EE' = Te<sub>2</sub>. The reaction was monitored using thin layer chromatography. After completion of the reaction, the solution was filtered to remove any insoluble material and the solvent was removed from the filtrate. The residue was dissolved in dichloromethane and chromatographic work-up was performed. Using (30/70 v/v) *n*-hexane-dichloromethane solvent mixtures as eluent, two fractions were isolated. The first fraction was a black compound which was shown to bear an isocyanide ligand at an iron centre, [Cp<sub>2</sub>Mo<sub>2</sub>Fe<sub>2</sub>(RNC)(CO)<sub>6</sub>(μ<sub>3</sub>-E)(μ<sub>3</sub>-E')], [*E* = *E'* = Se, *R* = (CH<sub>2</sub>)<sub>2</sub>CH (**5**) or (CH<sub>3</sub>)<sub>3</sub>C (**9**); *E* = *E'* = Te, *R* = (CH<sub>3</sub>)<sub>2</sub>CH (**8**) or (CH<sub>3</sub>)<sub>3</sub>C (**12**); *E* = S, *E'* = Te, *R* = (CH<sub>3</sub>)<sub>2</sub>CH (**6a**, **6b**) or *R* = (CH<sub>3</sub>)<sub>3</sub>C (**10a**, **10b**); *E* = Se, *E'* = Te, *R* = (CH<sub>3</sub>)<sub>2</sub>CH (**7a**, **7b**) or *R* = (CH<sub>3</sub>)<sub>3</sub>C (**11a**, **11b**)] For mixed-chalcogen combinations two isomers of the iron-monosubstituted isocyanide complexes

were identified by NMR spectroscopy, but could not be separated by TLC. The second fraction was characterised as a green compound in which substitution had occurred at a molybdenum centre, [Cp<sub>2</sub>(RNC)Mo<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>(μ<sub>3</sub>-E)(μ<sub>3</sub>-E')], [*E* = *E'* = Se, *R* = (CH<sub>3</sub>)<sub>2</sub>CH (**13**) or (CH<sub>3</sub>)<sub>3</sub>C (**17**); *E* = *E'* = Te, *R* = (CH<sub>3</sub>)<sub>2</sub>CH (**16**); *E* = S, *E'* = Te, *R* = (CH<sub>3</sub>)<sub>2</sub>CH (**14**) or *R* = (CH<sub>3</sub>)<sub>3</sub>C, (**18**); *E* = Se, *E'* = Te, *R* = (CH<sub>3</sub>)<sub>2</sub>CH (**15**) or *R* = (CH<sub>3</sub>)<sub>3</sub>C (**19**)]. UV data: **2**, (dichloromethane; λ<sub>max</sub>, nm (ε, M<sup>-1</sup> cm<sup>-1</sup>): 596 (1710), 506 (3220), 382 (7920), 295 (28,190), 233 (64,220); **6**, (dichloromethane; λ<sub>max</sub>, nm (ε, M<sup>-1</sup> cm<sup>-1</sup>): 594 (1930), 484 (3334), 381 (8190), 294 (28,045), 232 (65,682); **8**, (dichloromethane; λ<sub>max</sub>, nm (ε, M<sup>-1</sup> cm<sup>-1</sup>): 600 (1915), 475 (3542), 374 (7589), 303 (27,865), 234 (66,721); **12**, (dichloromethane; λ<sub>max</sub>, nm (ε, M<sup>-1</sup> cm<sup>-1</sup>): 590 (1920), 482 (3289), 378 (9682), 288 (26,531), 235 (65,890); **14**, (dichloromethane; λ<sub>max</sub>, nm (ε, M<sup>-1</sup> cm<sup>-1</sup>): 606 (1246), 472 (2013), 371 (5530), 286 (21,883), 231 (47,344).

### 3.3. Crystal structure determination of **12** and **14**

Crystals of compounds **12** and **14** suitable for X-ray diffraction analysis were grown from hexane-dichloromethane solvent mixtures by slow evaporation of the solvents at -5 °C. Relevant crystallographic data and details of measurements are given in Table 3. Selected

Table 4  
Selected bond lengths [Å] and angles [°] for **12**

Mo(1)–Te(2)	2.6727(17)	Fe(1)–C(1)	1.852(17)
Mo(1)–Te(1)	2.6839(19)	Fe(1)–C(18)	1.891(18)
Mo(1)–Fe(2)	2.859(3)	Fe(1)–Fe(2)	2.417(3)
Mo(1)–Mo(2)	2.8886(17)	Fe(1)–Te(2)	2.478(3)
Mo(1)–Fe(1)	2.908(2)	Fe(2)–C(18)	2.010(16)
Mo(2)–C(17)	1.981(17)	Fe(2)–Te(1)	2.484(2)
Mo(2)–Te(1)	2.7041(17)	C(1)–N(1)	1.164(16)
Mo(2)–Te(2)	2.7163(19)	N(1)–C(2)	1.478(19)
Mo(2)–Fe(1)	2.855(3)	O(17)–C(17)	1.174(16)
Mo(2)–Fe(2)	2.872(2)	O(18)–C(18)	1.171(17)
Te(2)–Mo(1)–Te(1)	116.15(6)	Te(2)–Fe(1)–Mo(2)	60.76(6)
Te(2)–Mo(1)–Fe(2)	96.41(6)	Fe(2)–Fe(1)–Mo(1)	65.40(8)
Te(1)–Mo(1)–Fe(2)	53.13(5)	Te(2)–Fe(1)–Mo(1)	58.86(6)
Te(2)–Mo(1)–Mo(2)	58.32(5)	Mo(2)–Fe(1)–Mo(1)	60.16(6)
Te(1)–Mo(1)–Mo(2)	57.92(4)	Fe(1)–Fe(2)–Te(1)	115.86(10)
Fe(2)–Mo(1)–Mo(2)	59.94(5)	Fe(1)–Fe(2)–Mo(1)	66.28(7)
Te(2)–Mo(1)–Fe(1)	52.50(5)	Te(1)–Fe(2)–Mo(1)	59.81(6)
Te(1)–Mo(1)–Fe(1)	95.83(6)	Fe(1)–Fe(2)–Mo(2)	64.68(7)
Fe(2)–Mo(1)–Fe(1)	49.53(7)	Te(1)–Fe(2)–Mo(2)	60.14(6)
Mo(2)–Mo(1)–Fe(1)	59.01(5)	Mo(1)–Fe(2)–Mo(2)	60.54(6)
Te(1)–Mo(2)–Te(2)	114.02(5)	Fe(2)–Te(1)–Mo(1)	67.07(7)
Te(1)–Mo(2)–Fe(1)	96.64(6)	Fe(2)–Te(1)–Mo(2)	67.06(6)
Te(2)–Mo(2)–Fe(1)	52.75(6)	Mo(1)–Te(1)–Mo(2)	64.84(5)
Te(1)–Mo(2)–Fe(2)	52.80(5)	Fe(1)–Te(2)–Mo(1)	68.62(6)
Te(2)–Mo(2)–Fe(2)	95.16(6)	Fe(1)–Te(2)–Mo(2)	66.49(6)
Fe(1)–Mo(2)–Fe(2)	49.92(6)	Mo(1)–Te(2)–Mo(2)	64.82(5)
Te(1)–Mo(2)–Mo(1)	57.24(4)	N(1)–C(1)–Fe(1)	176.0(15)
Te(2)–Mo(2)–Mo(1)	56.84(6)	C(1)–N(1)–C(2)	167.0(16)
Fe(1)–Mo(2)–Mo(1)	60.83(5)	O(17)–C(17)–Mo(2)	155.3(12)
Fe(2)–Mo(2)–Mo(1)	59.53(5)	O(17)–C(17)–Fe(2)	120.7(11)
C(1)–Fe(1)–Fe(2)	130.6(5)	O(17)–C(17)–Fe(1)	120.5(11)
Fe(2)–Fe(1)–Te(2)	114.92(10)	O(18)–C(18)–Fe(1)	146.2(14)
C(1)–Fe(1)–Mo(2)	104.6(5)	O(18)–C(18)–Fe(2)	137.3(14)
Fe(2)–Fe(1)–Mo(2)	65.40(8)		

bond lengths and bond angles for **12** and **14** are given in Tables 4 and 5, respectively. X-ray crystallographic data were collected from single crystal samples of **12** ( $0.12 \times 0.08 \times 0.05 \text{ mm}^3$ ), and **14** ( $0.50 \times 0.30 \times 0.10 \text{ mm}^3$ ), mounted on glass fibres. Data were collected using a P4 Bruker diffractometer, equipped with a Bruker SMART 1 K charge coupled device (CCD) area detector, using the program SMART [10], and a rotating anode, using graphite-monochromated Mo  $K_{\alpha}$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The crystal-to-detector distance was 4.987 cm, and the data collection was carried out in  $512 \times 512$  pixel mode, utilising  $2 \times 2$  pixel binning. The initial unit cell parameters were determined by a least-squares fit of the angular settings of the strong reflections, collected by a  $12^\circ$  scan in 40 frames over three different sections of reciprocal space (120 frames in total). A complete sphere of data was collected, to better than  $0.8 \text{ \AA}$  resolution at 298 K. Upon completion of the data collection, the first 50 frames were recollected in order to improve the decay correction analyses. Processing was carried out using the program SAINT [11], which applied Lorentz and polarisation corrections to the three-di-

mensionally integrated diffraction spots. The program SADABS [12], was utilised for the scaling of diffraction data, the application of a decay correction, and an empirical absorption correction based on redundant reflections for all data sets. The structures were solved by using the direct-methods procedure in the Bruker SHELXTL program library [13], and refined by full-matrix least squares methods on  $F^2$  with anisotropic thermal parameters for all non-hydrogen atoms with the exception of the isopropyl moiety and one Cp ring in **14**, and three methyl carbons within the *t*-butyl group of **12**. The *tert*-butyl amine moiety in **12** contained a slight rotational disorder, which could not be modelled effectively and therefore required anisotropic refinement of these carbons. The disorder of the Cp ring in **14** was not resolvable. The molecular packing illustrated that this disorder contributed directly to a positional disorder of the isopropyl group, which was also refined isotropically. Hydrogen atoms were added as fixed contributors at calculated positions, with isotropic thermal parameters based on the carbon atom to which they were bonded.

Table 5  
Selected bond lengths [Å] and bond angles [°] for 14

Mo(1)–C(15)	1.964(9)	Fe(1)–C(15)	2.375(10)
Mo(1)–S(1)	2.373(2)	Fe(1)–Fe(2)	2.488(2)
Mo(1)–Te(1)	2.6700(13)	Fe(1)–Te(1)	2.4923(16)
Mo(1)–Fe(2)	2.7658(16)	Fe(2)–C(16)	1.963(9)
Mo(1)–Fe(1)	2.8166(16)	Fe(2)–S(1)	2.214(2)
Mo(1)–Mo(2)	2.8394(18)	Fe(2)–C(15)	2.444(10)
Mo(2)–C(1)	2.088(9)	N(1)–C(1)	1.157(11)
Mo(2)–S(1)	2.368(2)	N(1)–C(2)	1.457(16)
Mo(2)–Te(1)	2.6552(14)	C(2)–C(3)	1.44(2)
Mo(2)–Fe(2)	2.8050(16)	C(2)–C(4)	1.47(2)
Mo(2)–Fe(1)	2.8432(16)	O(15)–C(15)	1.180(11)
Fe(1)–C(16)	1.941(9)	O(16)–C(16)	1.151(10)
C(15)–Mo(1)–S(1)	105.2(3)	Te(1)–Mo(2)–Fe(1)	53.78(4)
C(15)–Mo(1)–Te(1)	101.9(3)	Fe(2)–Mo(2)–Fe(1)	52.28(5)
S(1)–Mo(1)–Te(1)	110.39(7)	Mo(1)–Mo(2)–Fe(1)	59.43(3)
C(15)–Mo(1)–Fe(2)	59.4(3)	Fe(2)–Fe(1)–Te(1)	112.32(5)
S(1)–Mo(1)–Fe(2)	50.33(6)	Fe(2)–Fe(1)–Mo(1)	62.48(4)
Te(1)–Mo(1)–Fe(2)	99.10(5)	Te(1)–Fe(1)–Mo(1)	60.02(4)
C(15)–Mo(1)–Fe(1)	56.2(3)	Fe(2)–Fe(1)–Mo(2)	63.07(4)
S(1)–Mo(1)–Fe(1)	94.44(7)	Te(1)–Fe(1)–Mo(2)	59.26(4)
Te(1)–Mo(1)–Fe(1)	53.95(4)	Mo(1)–Fe(1)–Mo(2)	60.22(4)
Fe(2)–Mo(1)–Fe(1)	52.94(5)	S(1)–Fe(2)–Fe(1)	108.54(7)
C(15)–Mo(1)–Mo(2)	109.7(3)	S(1)–Fe(2)–Mo(1)	55.59(6)
S(1)–Mo(1)–Mo(2)	53.13(6)	Fe(1)–Fe(2)–Mo(1)	64.58(5)
Te(1)–Mo(1)–Mo(2)	57.53(4)	S(1)–Fe(2)–Mo(2)	54.78(7)
Fe(2)–Mo(1)–Mo(2)	60.04(4)	Fe(1)–Fe(2)–Mo(2)	64.65(4)
Fe(1)–Mo(1)–Mo(2)	60.35(4)	Mo(1)–Fe(2)–Mo(2)	61.28(4)
C(1)–Mo(2)–S(1)	83.4(3)	Fe(1)–Te(1)–Mo(2)	66.97(4)
C(1)–Mo(2)–Te(1)	80.7(3)	Fe(1)–Te(1)–Mo(1)	66.03(4)
S(1)–Mo(2)–Te(1)	111.05(7)	Mo(2)–Te(1)–Mo(1)	64.44(5)
C(1)–Mo(2)–Fe(2)	129.9(3)	Fe(2)–S(1)–Mo(2)	75.41(7)
S(1)–Mo(2)–Fe(2)	49.80(5)	Fe(2)–S(1)–Mo(1)	74.08(7)
Te(1)–Mo(2)–Fe(2)	98.48(4)	Mo(2)–S(1)–Mo(1)	73.59(8)
C(1)–Mo(2)–Mo(1)	80.6(3)	C(1)–N(1)–C(2)	171.9(13)
S(1)–Mo(2)–Mo(1)	53.28(6)	N(1)–C(1)–Mo(2)	172.5(9)
Te(1)–Mo(2)–Mo(1)	58.03(3)	O(16)–C(16)–Fe(1)	140.1(9)
Fe(2)–Mo(2)–Mo(1)	58.68(3)	O(16)–C(16)–Fe(2)	140.7(9)
C(1)–Mo(2)–Fe(1)	130.0(3)	S(1)–Mo(2)–Fe(1)	93.86(6)

#### 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 181258 and 181259. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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