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SYNTHETIC AND STRUCTURAL STUDIES ON ORGANOTRANSITION METAL–INDIUM THIOCYANATE COMPLEXES

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Abstract—The reaction between $In(NCS)_3$ and two equivalents of $Na[Mo(CO)_3(\eta\text{-}C_5H_5)]$ afforded the indium thiocyanate complex $[In(NCS)\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ (**2**). The complexes $[In(NCS)\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (**3**) and $[In(NCS)\{W(CO)_3(\eta\text{-}C_5H_5)\}_2]$ (**4**) were prepared similarly. The reaction between **2** and $OPPh_3$ afforded the complex $[In(NCS)(OPPh_3)\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ (**5**) and that between **3** and 4-picoline afforded $[In(NCS)(4\text{-picoline})\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (**6**) both of which were characterized by X-ray crystallography. In **5** and **6**, the indium centres are four-coordinate with a distorted tetrahedral coordination geometry and the thiocyanate groups are bonded through the nitrogen atom. The reaction between **2** and [K(18-crown-6)][SCN] affords the ionic complex $[K(18\text{-crown-}6)][In(NCS)_2\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ (**7**) which has also been characterized by X-ray crystallography.

In a series of recent papers,[1–4] we have reported the results of some synthetic and structural studies on a range of organotransition metal–indium halide complexes of the form $[InX\{ML_n\}_2]$ and $[InX(L)\{ML_n\}_2]$, where typically X = Cl, Br, I, $L = X^-$, thf (tetrahydrofuran), pyridine and $ML_n = M(CO)_3(\eta\text{-}C_5H_5)$ (M = Cr, Mo, W) or $M(CO)_2(\eta\text{-}C_5H_5)$ (M = Fe, Ru). In both types of compound, the indium centres are four-coordinate with a distorted tetrahedral geometry, in the former as a result of In—X—In bridges (for related work involving other metal carbonyl fragments, see ref. 1 and refs therein). In this paper, we describe the results of studies on some analogous organotransition metal–indium thiocyanate complexes as part of a more general study on pseudo halide complexes of the heavier *p*-block elements.[5]

RESULTS AND DISCUSSION

A synthesis of indium trithiocyanate, $In(NCS)_3$, was reported in 1966 by Goggin *et al.*[6] from the reaction between $InCl_3$ and three equivalents of NaSCN in dry ethanol, the compound being characterized by elemental analysis and a unit cell determination derived from X-ray powder diffraction data. We carried out a similar preparation, but using KSCN, and obtained a white solid (**1**) in high yield, an infrared spectrum of which (Table 1) showed a $\nu(CN)$ absorption at 2066 cm^{-1}, although there is some doubt as to the true nature

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Table 1. Spectroscopic and analytical data for the complexes

Compound	ν(CO)[b] (cm^{-1})	ν(CN)[b] (cm^{-1})	Analysis[a] (%) N	C	H
1 $In(NCS)_3$		2066s			
2 $[In(NCS)\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$	1999m, 1979s, 1898m	2045m	2.2 (2.1)	31.3 (30.8)	1.4 (1.5)
3 $[In(NCS)\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$	1987s, 1968s, 1931s	2037m	2.6 (2.7)	32.8 (34.2)	1.6 (1.9)
4 $[In(NCS)\{W(CO)_3(\eta\text{-}C_5H_5)\}_2]$	1993s, 1973s, 1890s	2043m	1.9 (1.7)	24.2 (24.3)	1.0 (1.2)
5 $[In(NCS)(OPPh_3)\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$	1994m, 1975s, 1909m, 1896m, 1881m[c]	2049m	1.5 (1.5)	44.6 (44.7)	2.6 (2.7)
6 $[In(NCS)(4\text{-pic})\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$	1985s, 1960s, 1925s				
7 $[K(18\text{-crown-}6)][In(NCS)_2\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$	1988s, 1970s, 1896s	2060s			

[a] Calculated values in parentheses.

[b] Measured in thf solution unless otherwise indicated.

[c] KBr disc values for ν(CN) are 2056 and for ν(CO) are 1987, 1966 and 1881 cm^{-1}.

of our material since analytical data for various samples were rather unreproducible and showed the presence of hydrogen possibly resulting from solvent of crystallization. We have assumed that this material is $In(NCS)_3$, at least in part, or some synthetic equivalent thereof, based on the reactions described below. In general, however, rather little is known about indium thiocyanates. There are reports of anionic species such as $[In(NCS)_6]^{3-}$ (see later) and ligand complexes such as $[In(NCS)_3(L)_3]$ (L = pyridine for example)[7] but we will defer comment on most of these compounds to a future publication which will deal with a number of ligand adducts of indium thiocyanato species.[8]

The reaction between "$In(NCS)_3$" and two equivalents of $Na[Mo(CO)_3(\eta\text{-}C_5H_5)]$ in thf solution afforded, after work up, the dimolybdenum–indium complex, $[In(NCS)\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ (**2**) as a yellow/brown powder. Spectroscopic and analytical data (Table 1) were consistent with the anticipated formula, notably the ν(CN) absorption at 2045 cm^{-1}, but we were unable to obtain crystals suitable for X-ray diffraction. Analogous reactions between **1** and two equivalents of either $K[Fe(CO)_2(\eta\text{-}C_5H_5)]$ or $Na[W(CO)_3(\eta\text{-}C_5H_5)]$ afforded the similar compounds $[In(NCS)\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2$ (**3**) and $[In(NCS)\{W(CO)_3(\eta\text{-}C_5H_5)\}_2]$ (**4**) respectively (Table 1); solution infrared spectra for compounds **2**–**4** are shown in Fig. 1(a–c).

Complex **2** was also prepared from the redistribution reaction between the trimolybdenum–indium species, $[In\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_3]$[1,9] and **1** in thf according to Equation (1).

$$2[In\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_3]+In(NCS)_3 \longrightarrow 3[In(NCS)\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2] \quad (1)$$

In the absence of structural data on **2**–**4** we carried out some reactions with Lewis bases in an attempt to prepare adducts of the form $[In(NCS)(L)\{M(CO)_x(\eta\text{-}C_5H_5)\}_2]$. The reaction between complex **2** and one equivalent of $OPPh_3$ in thf afforded, after work up, yellow crystals of the phosphine–oxide adduct $[In(NCS)(OPPh_3)\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ (**5**). Analytical and spectroscopic data (Table 1, Fig. 1(d)) were consistent with the formation of a 1:1 adduct and this was confirmed by X-ray crystallography, the results of which are shown in Fig. 2; selected bond lengths and angles are given in Table 2. The structure is best described as containing a four-coordinate, tetrahedral indium centre attached to two $Mo(CO)_3(\eta\text{-}C_5H_5)$ fragments, a $OPPh_3$ ligand and a thiocyanate group. The In—Mo bond lengths (both 2.816(1) Å) are comparable to those observed in similar

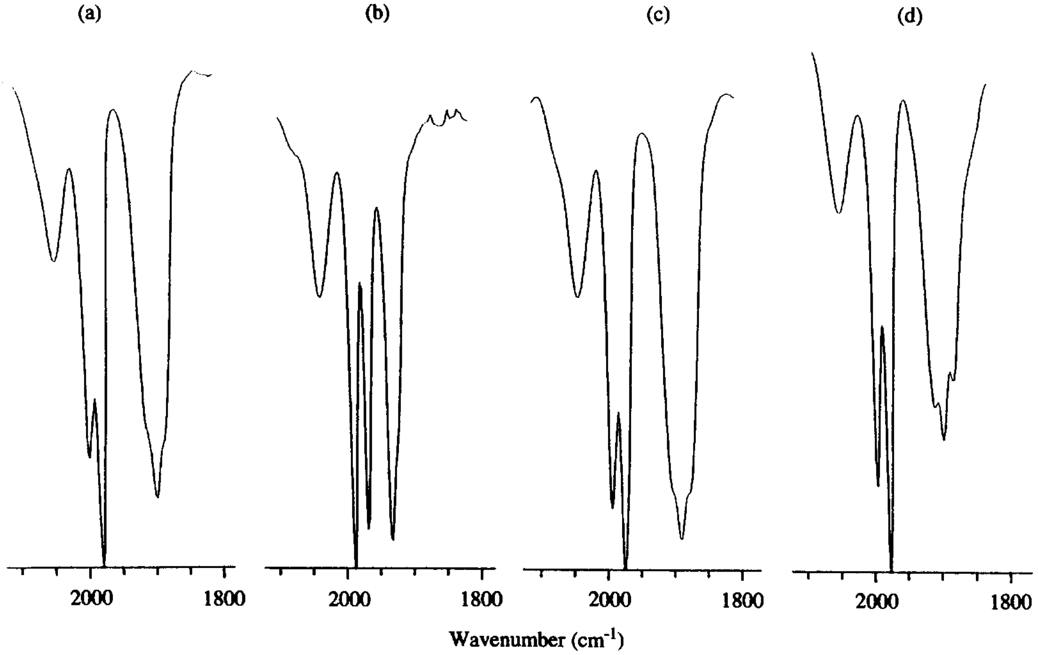

Fig. 1. Infrared spectra recorded in CaF_2 cells in thf solution in the CN and CO region for the complexes. (a) **2**; (b) **3**; (c) **4**; (d) **5**.

complexes[1,3] and the In—O distance (2.208(6) Å) is similar to, although slightly shorter than, the In—O distance in the thf adduct [InCl(thf){Mo(CO)$_3$(η-C_5H_5)}$_2$] (2.301(5) Å).[3] The thiocyanate group is bonded to the indium through the nitrogen (In—N 2.218(8) Å) and is also bent at the nitrogen atom (In—N—C 153.7(8)°), both of which features we will refer to later; accordingly, we have represented this bonding mode by writing the thiocyanate group as NCS in the formulae rather than an alternative SCN to denote bonding through sulphur[5] or a free ion. Other angles of note are the In—O—P angle which is almost linear (175.6(4)°) and the angles around indium, two of which differ substantially from ideal tetrahedral values, namely Mo(1)—In—Mo(2) 135.9(1) and O(1)—In—N 93.6(3)°. With regard to the latter pair of angles, we have previously observed and commented upon similar distortions from idealized tetrahedral values in related halide complexes;[1–4] the near linear In—O—P angle is not uncommon, there being a number of such examples known for phosphine oxide complexes.[10]

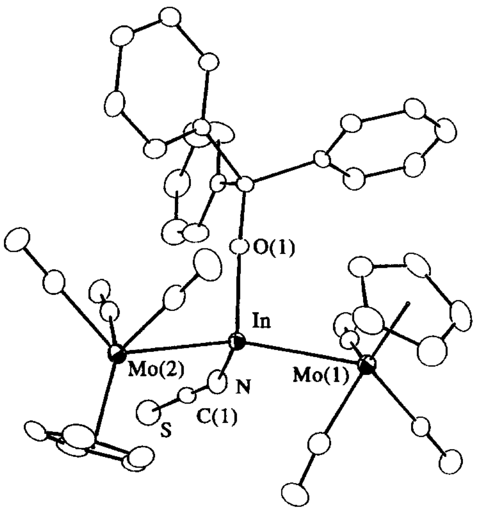

Fig. 2. A view of the molecular structure of **5** showing the atom numbering scheme. Ellipsoids are drawn at the 20% level.

The reaction between **3** and 4-picoline (4-pic) afforded, after work up, a small crop of orange crystals of the picoline adduct [In(NCS)(4-pic){Fe(CO)$_2$(η-C_5H_5)}$_2$] (**6**) spectroscopic data for which are given in Table 1. The structure was established by X-ray crystallography which revealed two molecules per asymmetric unit; molecule A is shown in Fig. 3 and molecule B in Fig. 4. Selected bond lengths and angles are given in Table 3. Both molecules are broadly similar, the indium centres being bonded to two Fe(CO)$_2$(η-C_5H_5) fragments, a 4-picoline ligand and the nitrogen of a thiocyanate group. The In—Fe distances are similar to those found in [(InCl{Fe(CO)$_2$(η-C_5H_5)}$_2$)$_2$] and [InCl(PMe$_2$Ph){Fe(CO)$_2$(η-C_5H_5)}$_2$][2] and the In—N (picoline) distances (In(1)—N(110) 2.321(11) and In(2)—N(210) 2.318(12) Å) are similar to that found in the pyridine adduct [InCl(py){Cr(CO)$_3$(η-

Table 2. Selected bond lengths (Å) and angles (°) for complex **5**

In—Mo(1)	2.816(1)	In—Mo(2)	2.816(1)
In—O(1)	2.208(6)	In—N	2.218(8)
P—O(1)	1.495(6)	S—C(1)	1.603(10)
N—C(1)	1.130(12)		
Mo(1)—In—Mo(2)	135.9(1)	Mo(1)—In—O(1)	101.9(2)
Mo(1)—In—N	108.6(3)	Mo(2)—In—O(1)	106.7(2)
Mo(2)—In—N	102.3(3)	O(1)—In—N	93.6(3)
In—O(1)—P	175.6(4)	In—N—C(1)	153.7(8)
S—C(1)—N	177.9(9)		

$C_5H_5)\}_2]$ (2.335(5) Å).[3] For the thiocyanate groups, the relevant distances are In(1)—N(1) 2.214(11) and In(2)—N(2) 2.242(12) Å, similar to **5** and somewhat shorter than the In—N bonds to picoline or pyridine, and the angles at nitrogen are In(1)—N(1)—C(1) 146.9(10) and In(2)—N(2)—C(2) 154.1(11)° also similar to **5**. Significant deviations from idealized tetrahedral bond angles around the indium centre are again evident as noted for **5**. The only significant difference between molecules A and B lies in the conformations about the In—Fe bonds as is evident from a comparison between Figs 3 and 4 which show the molecules in the same view as regards the thiocyanate and 4-picoline groups.

The reaction between **2** and [K(18-crown-6)][SCN] in thf was also carried out with a view to preparing the ionic indium thiocyanate complex [K(18-crown-6)] $[In(NCS)_2\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ (**7**), and this was successful although the compound could only be isolated in low yields. Spectroscopic data (Table 1) were consistent with the expected formula which was confirmed by X-ray crystallography the results of which are shown in Fig. 5 with selected bond lengths and angles listed in Table 4. The anion $[In(NCS)_2\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]^-$, resides on a crystallographic two-fold axis which passes through the indium atom. The geometry around the indium centre is tetrahedral with distortions as commented upon before for **5**, **6** and related structures, with the indium bonded to two $Mo(CO)_3(\eta\text{-}C_5H_5)$ fragments and two thiocyanates through the nitrogen atoms. With regard to the latter, the relevant parameters are In—N 2.199(4) Å and In—N—C 148.9(4)° both similar to the corresponding values in **5** and **6**. The cation consists of a potassium ion at an inversion centre bonded within a 18-crown-6 ligand aspects of which deserve no special comment except that the potassium centre is close to one of the carbonyl oxygens, O(11), which results in infinite chains of anion–cation pairs perpendicular to the monoclinic *b* axis.

The only other structurally characterized indium thiocyanato complexes of which we are aware are $[AsPh_4]_3[In(NCS)_6]$ (**8**)[11] and [K(18-crown-6)]

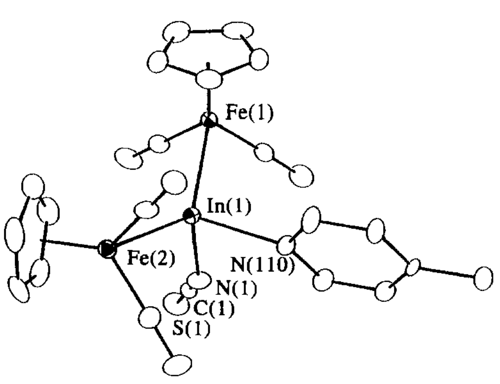

Fig. 3. A view of the structure of molecule A of **6** showing the atom numbering scheme. Ellipsoids are drawn at the 20% level.

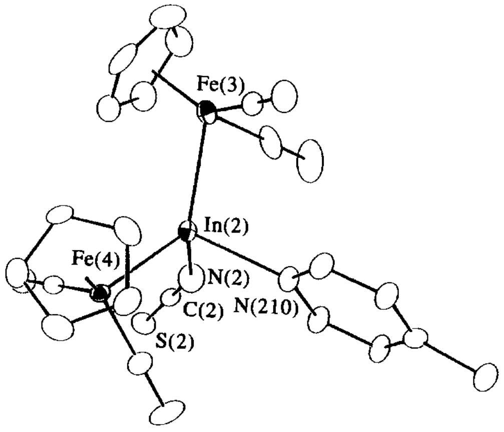

Fig. 4. A view of the structure of molecule B of **6** showing the atom numbering scheme. Ellipsoids are drawn at the 20% level.

Table 3. Selected bond lengths (Å) and angles (°) for complex **6**

Molecule A		Molecule B	
In(1)—Fe(1)	2.540(2)	In(2)—Fe(3)	2.549(2)
In(1)—Fe(2)	2.553(2)	In(2)—Fe(4)	2.544(2)
In(1)—N(1)	2.214(11)	In(2)—N(2)	2.242(12)
In(1)—N(110)	2.321(11)	In(2)—N(210)	2.318(12)
S(1)—C(1)	1.602(13)	S(2)—C(2)	1.580(12)
N(1)—C(1)	1.151(16)	N(2)—C(2)	1.152(16)
Fe(1)—In(1)—Fe(2)	129.9(1)	Fe(3)—In(2)—Fe(4)	132.5(1)
Fe(1)—In(1)—N(1)	106.9(3)	Fe(3)—In(2)—N(2)	107.3(3)
Fe(1)—In(1)—N(110)	105.1(4)	Fe(3)—In(2)—N(210)	107.7(4)
Fe(2)—In(1)—N(110)	109.2(4)	Fe(4)—In(2)—N(210)	105.9(4)
Fe(2)—In(1)—N(1)	108.5(3)	Fe(4)—In(2)—N(2)	106.6(3)
N(1)—In(1)—N(110)	89.9(4)	N(2)—In(2)—N(210)	87.9(4)
In(1)—N(1)—C(1)	146.9(10)	In(2)—N(2)—C(2)	154.1(11)
S(1)—C(1)—N(1)	178.8(11)	S(2)—C(2)—N(2)	179.0(11)

$[K(18\text{-crown-}6)(H_2O)]_2[In(NCS)_6]\cdot 2H_2O$ (**9**)[12] both of which contain the $[In(NCS)_6]^{3-}$ anion. In the former case, **8**, two crystallographically independent anions are present in the crystal both of which have a geometry around the indium centres which is close to regular octahedral with all thiocyanates *N*-bonded and with In—N bond lengths ranging from 2.06(2) to 2.16(1) Å (av. 2.13 Å) and In—N—C angles from 153(2) to 171(2)° (av. 165°). The distances are similar to those found in **5–7** although the angles at nitrogen are larger probably as a consequence of the larger coordination number at indium in **8**. In **9**, an octahedral anion is also present with the thiocyanates bonded through nitrogen and In—N distances ranging from 2.177(4) to 2.197(3) Å (av. 2.186 Å).

As with all thiocyanate complexes, the question of the bonding mode arises since, as indicated above, this group can bond either through nitrogen (NCS) or sulphur (SCN), or both in a bridging environment. The data presented herein for complexes **5–7** and that previously reported for **8** and **9** reveal that the *N*-bonded mode is clearly favoured where indium is concerned. In general, it is observed that thiocyanates are bonded through nitrogen to hard acid centres whereas softer acids tend to bond through sulphur,[7] and our results are therefore in keeping with the known hardness of indium(III) which is as expected for this fairly electropositive metal. In contrast to the results presented here, we have observed that in related bismuth complexes, the thiocyanate group is generally *S*-bonded which is in keeping with the softer character of bismuth(III).[5]

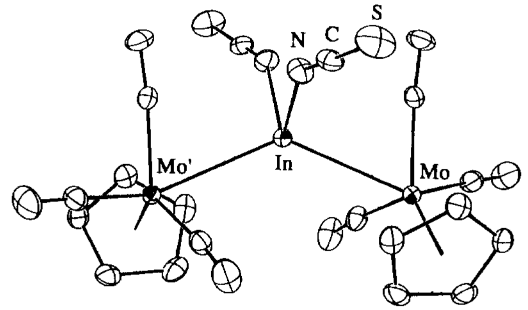

Fig. 5. A view of the structure of the $[In(NCS)_2\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]^-$ anion in **7** showing the atom numbering scheme. Ellipsoids are drawn at the 20% level. Primed atoms are related to unprimed atoms by the symmetry operation $-x$, y, $1/2-z$, a two-fold axis.

As a final word, we should comment on the nature of the infrared spectra for the complexes listed in Table 1 and shown (for **2–5**) in Fig. 1. These data are all for thf solutions of the complexes and, as we commented in ref. 5, such data must be treated with caution in view of the possibility of heterolytic dissociation in solution. The type of dissociation we have in mind is to give complexes of the form $[In(thf)_x(ML_n)_2]^+$ and free thiocyanate anion which we considered unlikely for the bismuth complexes, but is a very real possibility here since we have obtained good evidence for a similar type of dissociation in related indium halide complexes.[3,9] Thus, in the complexes **2–5**, the fact that the υ(CN) peak always occurs at 2043 ± 6 cm^{-1}, which is very close to that reported for free SCN (2053 cm^{-1}, see ref. 7), is indicative of such dissociation occurring, although in **1** and **7**, the υ(CN) peak is at a higher frequency around 2066 cm^{-1} which is well within the range for *N*-bound NCS groups.[7] Nevertheless,

Table 4. Selected bond lengths (Å) and angles (°) for complex **7**

In—Mo	2.8271(3)	In—N	2.199(4)
S—C	1.605(5)	N—C	1.152(5)
Mo—In—Mo′	132.7(1)	Mo—In—N	100.5(1)
Mo—In—N	110.0(1)	N—In—N′	98.2(2)
In—N—C	148.9(4)	S—C—N	178.4(4)

despite any ambiguity associated with these thf solution spectra, they are useful as a fingerprint for the compounds concerned and are presented here with that aid in mind.

EXPERIMENTAL

General considerations

All experiments were performed under dry, oxygen-free dinitrogen using standard Schlenk techniques. All solvents were dried and distilled over appropriate drying agents immediately prior to use. Infrared spectra were recorded in thf solution in CaF_2 cells on a Nicolet 20 SXB FTIR spectrophotometer and microanalytical data were obtained at the University of Newcastle. $InCl_3$ and KSCN were procured commercially and used without further purification. $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$[13] and $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$[14] were prepared by literature methods. [K(18-crown-6)]SCN was prepared according to ref. 5.

Preparations

$In(NCS)_3$ (**1**) was prepared according to ref. 6 but using KSCN instead of NaSCN. The product was recrystallized from thf/hexane.

$[In(NCS)\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ (**2**). $In(NCS)_3$ (0.212 g, 0.735 mmol) was dissolved in thf (10 cm^3) and added to a stirred solution of $Na[Mo(CO)_3(\eta\text{-}C_5H_5)]$, derived from a Na/Hg reduction of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (0.360 g, 0.735 mmol) in thf (10 cm^3). The reaction mixture was stirred for 1 h which afforded a green solution. The solvent was removed by vacuum and the resulting brown solid was dissolved in CH_2Cl_2 (20 cm^3). After filtration through Celite the solvent volume of the filtrate was reduced by half and an overlayer of hexane (30 cm^3) was added. Solvent diffusion at -22°C over a period of days produced **2** as a yellow/brown solid (42%).

$[In(NCS)\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (**3**). $In(NCS)_3$ (0.256 g, 0.884 mmol) was dissolved in thf (10 cm^3) and added to a stirred solution of $Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$, derived from a NaK reduction of $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.313 g, 0.884 mmol) in thf (10 cm^3). The reaction mixture was stirred for 1 h which afforded a brown solution. The solvent was removed by vacuum and the resulting solid was dissolved in CH_2Cl_2 (20 cm^3). After filtration through Celite the solvent volume of the filtrate was reduced by half and an overlayer of hexane (30 cm^3) was added. Solvent diffusion at -22°C over a period of days produced **3** as a yellow/brown crystalline solid (52%).

$[In(NCS)\{W(CO)_3(\eta\text{-}C_5H_5)\}_2]$ (**4**). $In(NCS)_3$ (0.155 g, 0.538 mmol) was dissolved in thf (10 cm^3) and added to a stirred solution of $Na[W(CO)_3(\eta\text{-}C_5H_5)]$, derived from a Na/Hg reduction of $[W_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (0.358 g, 0.538 mmol) in thf (10 cm^3). The reaction mixture was stirred for 1 h which afforded a yellow/brown solution. The solvent was removed by vacuum and the resulting solid was dissolved in CH_2Cl_2 (20 cm^3). After filtration through Celite the solvent volume of the filtrate was reduced by half and an overlayer of hexane (30 cm^3) was added. Solvent diffusion at -22°C over a period of days produced **4** as a yellow/brown solid (45%).

$[In(NCS)(OPPh_3)\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ (**5**). Complex (**2**) (0.068 g, 0.102 mmol) was stirred with $OPPh_3$ (0.028 g, 0.102 mmol) in thf (10 cm^3) for 1 h. After this time, the thf was removed in *vacuo* and the resulting yellow solid dissolved in CH_2Cl_2 (5 cm^3). Hexane (8 cm^3) was then added as an overlayer and crystallization by solvent diffusion at -22°C over a period of days afforded **5** as yellow crystals suitable for X-ray diffraction (60%). $^{31}P\text{-}\{^1H\}$ NMR. (H_3PO_4) $\delta + 32.3$ (s, Ph_3PO).

$[In(NCS)(4\text{-pic})\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (**6**). Complex **3** (0.015 g, 0.285 mmol) was stirred with an excess of 4-picoline (0.4 cm^3, 4.11 mmol) in thf (10 cm^3) for 20 min. After this time, hexane (15 cm^3) was added as an overlayer and crystallization by solvent diffusion at -22°C over a period of days afforded a small amount of orange crystals of **6**, one of which was suitable for X-ray diffraction.

Due to the low yield of crystalline material from this reaction, we were unable to obtain satisfactory analytical data.

$[K(18\text{-crown-6})][In(NCS)_2\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ (**7**). Complex **2** (0.043 g, 0.065 mmol) was stirred with [K(18-crown-6)][SCN] (0.025 g, 0.069 mmol) in thf (10 cm^3) for 1 h. After this time, hexane (20 cm^3) was added as an overlayer and crystallization by solvent diffusion at −22°C over a period of days afforded some crystals of **7** embedded within a yellow powder. One of the crystals was suitable for X-ray diffraction but satisfactory analytical data was not obtained on bulk samples of the yellow material.

X-Ray crystallography

Crystallographic data and details of the data collection procedures and structure refinement for all structures are presented in Table 5. The following section deals with the structure of **5**; data for **6**, where different, are given in square brackets [ ] and data for **7** in curly brackets { }. Data were collected on a Enraf–Nonius Turbo-CAD4 diffractometer, running under CAD4-Express software, and with graphite monochromated X-radiation ($\lambda = 0.71069$ Å). Accurate unit cell parameters were determined by refinement of setting angles of 25 reflections. Standard reflections were

Table 5. Crystallographic and structure solution data for compounds **5**, **6** and **7**

	5	**6**	**7**
Compound formula	$C_{35}H_{25}InMo_2NO_7PS$	$C_{21}H_{17}Fe_2InN_2O_4S$	$C_{30}H_{34}InKMo_2N_2O_{12}S_2$
M_r	941.32	619.95	1024.52
Space group	$P2_1/c$	$P2_1/c$	$C2/c$
Crystal system	monoclinic	monoclinic	monoclinic
a (Å)	12.4674(9)	16.748(2)	20.5823(7)
b (Å)	13.7117(9)	15.947(2)	7.6460(4)
c (Å)	21.4426(11)	17.281(2)	25.591(2)
β (°)	104.186(5)	91.03(1)	101.556(4)
V (Å^3)	3553.8(4)	4614(1)	3945.7(4)
θ range for cell (°)	$17.5 < \theta < 21.3$	$17.5 < \theta < 20.8$	$17.7 < \theta < 20.9$
Z	4	8	4
D_{calc} (g cm^{-3})	1.76	1.78	1.72
$F(000)$	1848	2448	2032
μ(Mo-K_α) (cm^{-1})	14.59	23.34	14.44
T (K)	298	298	298
Scan mode	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$
θ range (°)	$2 < \theta < 25$	$2 < 2\theta < 25$	$2 < 2\theta < 25$
Cryst size (mm)	$0.43 \times 0.23 \times 0.03$	$0.3 \times 0.3 \times 0.2$	$0.35 \times 0.3 \times 0.2$
Range of transmission coefficients	0.78–1.13	0.85–1.16	0.86–1.11
No. of data collected	6794	8704	3831
No. of unique data	6234	8092	3461
hkl range	$-14 \rightarrow 14, 0 \rightarrow 16, -25 \rightarrow 0$	$-19 \rightarrow 19, -19 \rightarrow 0, -20 \rightarrow 0$	$-24 \rightarrow 24, -9 \rightarrow 0, -30 \rightarrow 0$
R_{merge}	0.029	0.046	0.027
Observability criterion	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 3\sigma(I)$
No. of data in refinement	3470	4351	2869
No. of refined parameters	379	492	246
Final R	0.042	0.056	0.025
Final R_w	0.039	0.055	0.035
Goodness of fit, S	1.15	1.75	1.55
Largest remaining feature in electron density map (e Å^{-3})	+0.56 (max), −0.51 (min)	+1.21 (max), −0.64 (min)	+0.42 (max), −0.49 (min)
Shift/esd in last cycle	0.0079 (max), 0.0009 (av)	0.12 (max), 0.02 (av)	0.0034 (max), 0.0006 (av)

measured every 2 h during data collection, and no significant variation in intensities was noted [a 2 % decay over 68 h was observed and a linear correction applied]. Corrections were applied for Lorentz-polarization and absorption (DIFABS[15]) effects. The structure was solved for the In and Mo atoms [In and Fe atoms] by heavy atom methods (SHELXS86[16]). Subsequent difference syntheses gave all other atomic positions. All non-hydrogen atoms were allowed anisotropic thermal motion. Hydrogen atoms were included at calculated positions (C—H 0.96 Å), and were assigned fixed isotropic thermal parameters 1.2 times that of the attached C atom. The C_5H_5 and C_6H_5 groups were refined as rigid groups with idealized geometries [the C_5H_5 and 4-picoline groups were refined as rigid groups with idealized geometries] {H atoms were allowed freely refined isotropic thermal parameters}. Refinement was by full-matrix least-squares, with the function $\Sigma w(|F_o|-|F_c|)^2$ minimized, and with the weighting scheme $w = [\sigma^2(F_o)]^{-1}$ used and judged satisfactory. $\sigma(F_o)$ was estimated from counting statistics. Neutral atom scattering factors were taken from ref. 17 with corrections for anomalous dispersion. All calculations were carried out on a MicroVAX 3600 computer using the Glasgow GX suite of programs[18] or SHELXS86[16] for structure solution.

Supplementary material available from the Cambridge Crystallographic Data Centre comprises complete tables of bond lengths and angles, atomic positional parameters, thermal parameters and hydrogen atom coordinates.

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