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Preliminary communication

Indium monohalide insertion reactions into metal–metal bonds. Crystal structure of $[InCl(THF)\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$

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Abstract

The reaction between InCl and $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ affords $[InCl\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$, **6a** which has been characterised as a THF adduct $[InCl(THF)\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$, **10**, by X-ray crystallography. An additional complex, $[InCl_2\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]^-$, **11**, is also formed in this reaction. Similar products are reported for reactions involving $[M_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (M = Cr, W). The reaction between InCl and $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ affords $[InCl\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$, **17**, and $[InCl_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}]$, whilst that between InI and $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ affords $[InI\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$, **19**.

There are now many compounds that contain transition metal–indium bonds [1,2], and a variety of synthetic methods have been employed in their synthesis. One method involves a formal insertion reaction of an indium monohalide into a metal–metal bond, and one of the earliest examples was reported by Patmore and Graham [3]. These workers described the reaction between InBr and $[Co_2(CO)_8]$ in THF, which afforded a dicobalt–indium bromide complex as a THF adduct $[InBr(THF)\{Co(CO)_4\}_2]$, **1**, although this readily lost THF to give the solvent-free compound which was assumed to have a bromide-bridged, dimeric structure, $[\{(CO)_4Co\}_2In(\mu\text{-}Br)]_2$, **2**. However, the same reaction in benzene gave the cluster complex $[In_3Br_3Co_4(CO)_{15}]$, **3**, [4], the structure of which was confirmed by X-ray crystallography.

Subsequently, Graham reported the reaction between $[Mn_2(CO)_{10}]$ and InBr in a sealed tube at 180 °C, which afforded $[InBr\{Mn(CO)_5\}_2]$, **4b**, [5], which was later synthesised by Mays from the same reactants in refluxing dioxane [6]. Mays also described [6] the synthesis of $[InX\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ (**5a**, X = Cl; **5b**, X = Br) and $[InX\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ (**6a**, X = Cl; **6b**, X = Br) from reactions involving

Table 1

Spectroscopic data for the complexes

Compound	Ir, ν(CO) (cm^{-1}) [a]	NMR [b]	
		^{1}H (δ) [c]	^{13}C (δ) [c,d]
10	1998s, 1976s, 1895s	5.59(C_5H_5) 3.63(THF) 1.78(THF)	91.0(C_5H_5) 68.2(THF) 26.2(THF)
9	1992s, 1970s, 1888s, 1873sh [e]	5.70(C_5H_5)	89.8(C_5H_5)
15	1985s, 1963s, 1888s, 1873sh [f]	5.12(C_5H_5)	87.5(C_5H_5)
14	1979s, 1955s, 1893s, 1873s		
16	1983s, 1961s, 1886s, 1871m	8.92(d,py) 8.15(t,py) 7.75(m,py) 5.08(C_5H_5)	
17	1985s, 1963s, 1929s	4.95(C_5H_5)	82.4(C_5H_5)
19	1987s, 1965s, 1931s	4.95(C_5H_5)	83.0(C_5H_5)

Complex **17** was red, and the others yellow. Satisfactory C and H analyses were obtained for **9**, **10**, **15**, **17** and **19**.

[a] Measured in THF solution unless otherwise stated. [b] Chemical shifts (δ) in ppm, measurements at room temperature. [c] Measured in d^6-acetone unless otherwise stated. [d] ^{1}H decoupled, chemical shifts are positive to high frequency of $SiMe_4$. [e] Values are for the THF adduct (**12**). [f] Values are for the THF adduct (**13**).

$[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ or $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ and InCl or InBr, also in refluxing dioxane. In a later paper [7], Mays provided further details of the synthesis of **5** and **6** and reported the preparation of $[InCl\{Co(CO)_4\}_2]$, **7**, $[InCl\{Re(CO)_5\}_2]$, **8**, and $[InCl\{W(CO)_3(\eta\text{-}C_5H_5)\}_2]$, **9**, by the same method, although many of the reactions were apparently incomplete. The only crystal structure data available on any of

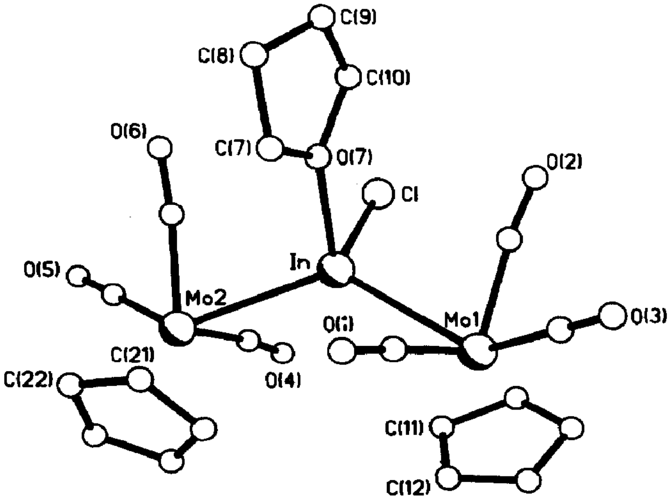
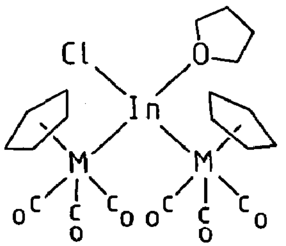


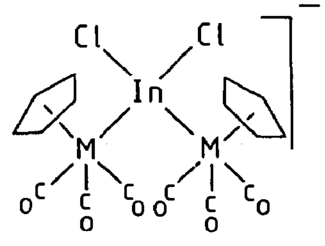
Fig. 1. The molecular structure of **10** with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (degrees): In–Mo(1) 2.814(1), In–Mo(2) 2.835(1), In–Cl 2.437(2), In–O(7) 2.301(5); Mo(1)–In–Mo(2) 128.2(1), Mo(1)–In–Cl 109.3(1), Mo(2)–In–Cl 110.5(1), Mo(1)–In–O(7) 104.0(2), Mo(2)–In–O(7) 106.1(2), Cl–In–O(7) 92.5(2).

these compounds, except **3**, were provided by Haupt [8] for the dimanganese complexes $[\{(CO)_5Mn\}_2In(\mu\text{-}X)]_2$ (**4a**, X = Cl; **4b**, X = Br; **4a**, X = I), which are dimeric and were synthesised from the appropriate indium monohalide and $[Mn_2(CO)_{10}]$ in xylene at 125 °C. We report here some of our preliminary observations in this area.

Refluxing a suspension of InCl in toluene containing a slight excess of dissolved $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ gave a yellow precipitate during $3\frac{1}{2}$ hours. Removal of the solvent, followed by washing of the solid with toluene to remove the excess of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ and recrystallisation from THF/hexane mixtures gave yellow crystals of $[InCl(THF)\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$, **10**, which was characterised by spectroscopic and analytical methods (Table 1) and by X-ray crystallography. The structure revealed is shown in Fig. 1 *, and contains a four-coordinate indium centre in a tetrahedral coordination environment bonded to two $Mo(CO)_3(\eta\text{-}C_5H_5)$ fragments, a chlorine atom, and the oxygen of a THF molecule. The THF molecule is not readily lost from crystals of **10** even under vacuum, as evident from the integrals obtained in the ^1H NMR spectrum and the microanalytical data. In the absence of THF (i.e. before THF addition to the yellow solid obtained from toluene) the above compound is identical to **6a** reported by Mays [6], and probably exists as a chlorine-bridged dimer analogous to **4a** [8] **.



10, M = Mo; 12, M = W; 13, M = Cr



11, M = Mo

However, the reaction between InCl and $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ in toluene is not quite so straightforward. Sometimes, although without any apparent differences in

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* The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

Crystal data for 10: $C_{20}H_{18}ClInO_7Mo_2$, $M = 712.51$, monoclinic, space group $P2_1/a$, a 16.217(6), b 9.048(3), c 17.246(5)Å, β 111.11(3)°, U 2360(1) Å^3, $Z = 4$, D_c 2.00 g cm^{-3}. Intensities of 4594 reflections (quadrant of data with $2\theta_{max}$ 50°) were measured on an Enraf Nonius CAD4F diffractometer with graphite monochromated Mo-K_α radiation ($\lambda = 0.71069$ Å) and corrected for absorption ($\mu = 21.27$ cm^{-1}). 4136 independent reflections with $I > 3\sigma(I)$ were used in the structure analysis by direct methods and full matrix least-squares refinement on F. H atoms were included in calculated positions and anisotropic thermal parameters were assigned to other atoms. The final R is 0.034 ($R_w = 0.039$).

** The complex $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (Mo≡Mo) is not an intermediate in the reaction between InCl and $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ in refluxing toluene since we found that it does not react with InCl to afford **6a**/**10** under similar conditions. We did, however, obtain low yields of a yellow compound with the following infrared spectrum; ν(CO) (THF) 1993s, 1968m, 1903s, br. This compound is also formed, in low yield, from $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and $InCl_3$ under similar conditions, and as one of the products in the reaction between $InCl_3$ and $[In\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_3]$. We do not know its structure, but its IR spectrum suggests the presence of an $In\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2$ unit. This latter reaction also affords **6a**/**10** and **11**.

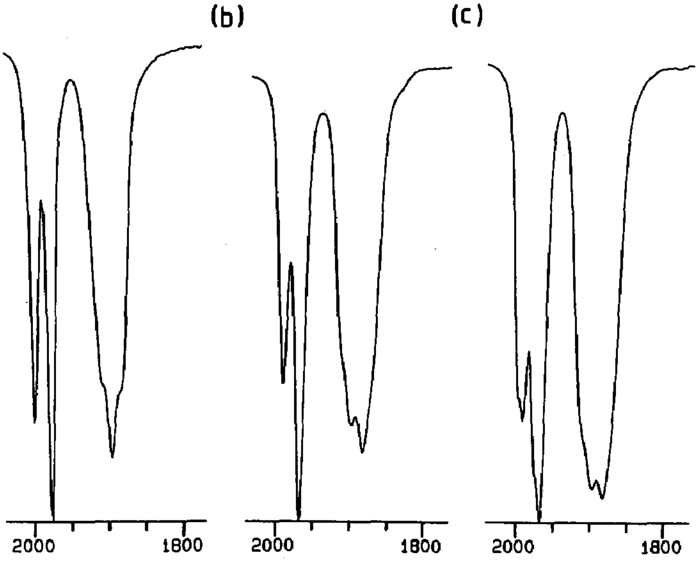

Fig. 2. Infrared spectra in THF solution for **10** (a); **11** (b) (see also ref. 2) and a mixture of **10** and **11** obtained from one reaction (c). The values for **10** are in Table 1, those for **11** are 1991, 1967, 1897, 1882 cm^{-1}.

the reaction conditions, appreciable quantities of a second complex were formed, which we assume to be $[InCl_2\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]^-$, **11**, on the basis of the similarity of the IR spectrum to that of the compound previously obtained from the reaction between $InCl_3$ and two equivalents of $Na[Mo(CO)_3(\eta\text{-}C_5H_5)]$, and characterised as the sodium salt, $[Na(THF)_2][InCl_2\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ by X-ray crystallography [2]. Although the IR spectra of **11** are similar to those of **10**, they are consistently and reproducibly different, as can be seen from Fig. 2. The chlorophilicity of **6a**/**10** resulting in **11** is not surprising in view of the Lewis acidity of indium [2], and Cradwick [9] has reported a similar type of complex, viz. $[Et_4N][InBr_2\{Co(CO)_4\}_2]$, resulting from the formation of **1** (as outlined above) in the presence of $[Et_4N]Br$. Nevertheless, the nature of the cation associated with **11** is not clear.

The reaction between InCl and $[W_2(CO)_6(\eta\text{-}C_5H_5)_2]$ in toluene was much slower than that involving the molybdenum complex, but yellow crystalline $[InCl(THF)\{W(CO)_3(\eta\text{-}C_5H_5)\}_2]$, **12**, was isolated in low yield after work-up and recrystallisation from THF/hexane. The THF is readily lost, however, to give **9**, data for which are given in Table 1. (The IR spectra recorded in THF solution are of **12** rather than **9**, *vide supra*.)

In the case of $[Cr_2(CO)_6(\eta\text{-}C_5H_5)_2]$, the reaction with InCl occurred readily in toluene at room temperature, and crystallisation of the product from THF/hexane gave $[InCl(THF)\{Cr(CO)_3(\eta\text{-}C_5H_5)\}_2]$, **13**, along with variable amounts of a second compound which we assume to be $[InCl_2\{Cr(CO)_3(\eta\text{-}C_5H_5)\}_2]^-$, **14**. Like **12**, **13** readily loses THF, to give $[InCl\{Cr(CO)_3(\eta\text{-}C_5H_5)\}_2]$, **15**. Solution IR spectra for **12**, **13** and **14** are shown in Fig. 3. We have also characterised the pyridine adduct of **15**, $[InCl(py)\{Cr(CO)_3(\eta\text{-}C_5H_5)\}_2]$, **16**, from the reaction between **13** and an excess of pyridine, and relevant data are given in Table 1.

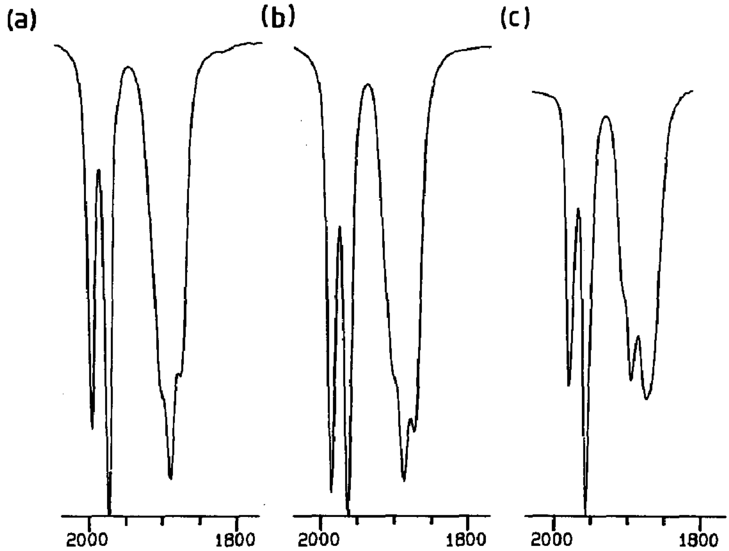

Fig. 3. Infrared spectra in THF solution for **12** (a); **13** (b); and **14** (c).

The reaction between InCl and $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ in refluxing toluene (3–4 hours) took a rather different course. Crystallisation of the product from THF/hexane afforded a small yield of red crystals characterised as $[InCl\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$, **17** (**5a**), but the major product isolated was a yellow powder which was shown by IR (ν(CO) (THF), 1996s, 1946s cm^{-1}) and microanalytical data to be $[InCl_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}]$ (cf. Mays' report of the reaction in dioxane [6]). We are not sure of the extent to which **17** exists as a THF adduct (the crystals contain very little as judged by ^1H NMR and microanalysis and show no obvious signs of solvent loss, but in THF solution the situation may be different) but the infrared spectrum is quite different from that of $[InCl_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]^-$, **18**, ($\nu$(CO), 1984m, 1959s, 1916s cm^{-1}), which was previously isolated as a minor product from the reaction between $InCl_3$ and $Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$[10].

It is clear that the reactions between InCl and metal–metal bonded dimers are complex and give mixtures of products. Thus the reactions are not always ideal as routes to useful amounts of pure materials suitable for reactivity studies. We thus decided to examine the effect of changing the halide, and examined some analogous reactions involving indium mono-iodide, InI, the most stable of the indium(I) halides. The reaction between InI and $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ in refluxing toluene (1 h) proceeded more readily than the corresponding reaction with InCl, and afforded a yellow powder. Crystallisation from CH_2Cl_2/hexane mixtures gave, in good yield, yellow-brown crystals of $[InI\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$, **19**, which was characterized by spectroscopic and analytical methods (Table 1). The only other observed product (along with unchanged $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$) was a small amount of $[FeI(CO)_2(\eta\text{-}C_5H_5)]$, there being no evidence of an InI_2 complex, $[InI_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}]$, analogous to the chloro-derivative formed in the reaction with InCl. The use of InI is, therefore, synthetically advantageous in this instance, and we are currently exploring a variety of other reactions with InI.

Further, more detailed, studies on all of these reactions are in progress.

Note added in proof. The structures of **14**, as its sodium salt, and **16** have been confirmed by X-ray crystallography.

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