THE SYNTHESIS OF COMPLEXES CONTAINING TRANSITION METAL–INDIUM BONDS

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SUMMARY

Some new complexes containing indium bonded to molybdenum, tungsten, rhenium, iron and cobalt have been synthesised in a comparative study of the relative utility of the various methods available for the preparation of such complexes. Some spectroscopic properties of a selection of the new complexes are recorded.

INTRODUCTION

Although a number of complexes containing Group IIIB metal–transition metal bonds are known, such complexes have received less attention than those containing Group IIB or IVB elements as the main group metal. We have previously reported studies on the preparation and reactions of tris(pentacarbonylmanganese)-thallium[1] and of a series of cationic, neutral, and anionic complexes containing indium–manganese bonds[2,3]. As an extension of this latter study we have synthesised by several different routes, a number of complexes in which indium is bonded to other transition metals, and in this paper we report the preparation and characterisation of these new complexes as an illustration of the use and scope of these different synthetic methods.

EXPERIMENTAL

General

All manipulations were performed under nitrogen or in a conventional Pyrex vacuum line. Reactions involving volatile materials were carried out in Rotaflo greaseless tap-ampoules. Commercial hydrated indium trichloride was dehydrated *in vacuo* at 150° followed by sublimation at ca. 600°.

Infrared spectra in the carbonyl region (2100–1800 cm^{-1}) were recorded on a Perkin–Elmer 257 grating instrument and were calibrated against carbon monoxide. Mass spectra were recorded on an A.E.I. MS 9 mass spectrometer with an ionising energy of 70 eV.

Preparations

Method 1. *Metathesis between transition metal carbonyl anions and InX$_3$ in THF solution*

(a). $[C_5H_5(CO)_3Mo]_3In$. A solution of $C_5H_5(CO)_3Mo^-Na^+$, prepared by

sodium amalgam (15 ml, 1–2%) reduction of $[C_5H_5(CO)_3Mo]_2Hg$ or $[C_5H_5Mo-(CO)_3]_2$ (1.56 mmole) in 25 ml of dry THF, was added to solid anhydrous $InCl_3$ (231 mg, 1.04 mmole) and the mixture was vigorously stirred for $\frac{1}{2}$ h. Removal of the solvent *in vacuo* left a yellow residue which was extracted with acetone to give the crude product (94% yield) on subsequent evaporation. Crystallisation from a large volume of hot toluene or from a mixture of acetone and water gave pure micro-crystalline $[C_5H_5(CO)_3Mo]_3In$.

(*b*). $[C_5H_5(CO)_3Mo]_2InBr$. A mixture of anhydrous $InBr_3$ (450.7 mg, 1.27 mmole) and $C_5H_5(CO)_3Mo^-Na^+$, prepared from $[C_5H_5(CO)_3Mo]_2Hg$ or $[C_5H_5-Mo(CO)_3]_2$ (1.27 mmole) by sodium amalgam (12 ml, 1–2%) reduction in 25 ml of THF, was stirred for 1 h. The solvent was removed under reduced pressure and the remaining yellow residue was thoroughly washed with water and recrystallised from a THF/water mixture to give the pure complex. Yield 86%.

(*c*). $C_5H_5(CO)_3MoInCl_2$. A 1/1 molar (1.32 mmole) mixture of anhydrous $InCl_3$ and $C_5H_5(CO)_3Mo^-Na^+$, prepared as described above, was stirred for $\frac{1}{2}$ h in 25 ml of THF. The solvent was then evaporated *in vacuo* and the yellow residue washed with water and recrystallised from a THF/water mixture to give the pure complex. Yield 87%.

Method 2. Metathesis between transition metal carbonylanions and $InX_3 \cdot 3H_2O$ in water

$[(CO)_5Re]_3In$. An aqueous solution of $InCl_3 \cdot 3H_2O$ (0.251 g, 0.91 mmole) was added to solid $Re(CO)_5^-$ Na^+, prepared by sodium amalgam (10 ml, 1–2%) reduction of $Re_2(CO)_{10}$ (0.890 g, 1.365 mmole) in THF, under an atmosphere of car-bon monoxide and the mixture was vigorously agitated for 5 min. The precipitated product was filtered, washed well with water and dried *in vacuo* over phosphoric oxide. The product was obtained as intensely yellow microcrystals by recrystallisation from hot toluene. Yield 86%.

Method 3. Metal exchange

$[C_5H_5(CO)_3W]_3In$. $[C_5H_5(CO)_3W]_2Hg$ (0.1 mmole) in THF (10 ml) was shaken with an excess of powdered indium. After stirring for 24 h at room temperature the yellow solution was decanted from the metals and the solvent removed *in vacuo* to give a bright yellow solid. Crystallisation from a large volume of hot toluene gave the pure complex. Yield 90%.

Method 4. Insertion of InX into metal–metal bonds

$[C_5H_5(CO)_2Fe]_2InCl$. An equimolar (1.5 mmole) mixture of $[C_5H_5Fe(CO)_2]_2$ and InCl in 25 ml of dioxane was refluxed for 6 h. TLC analysis showed the presence of a yellow band as well as some unreacted starting materials, but no further conversion took place even on prolonged heating. The solvent was removed *in vacuo* and the solid residue, dissolved in a small volume of acetone, was chromatographed on a silica gel column. Unreacted $[C_5H_5Fe(CO)_2]_2$ was first removed by eluting with a 1/3 benzene/light petroleum (b.p. 30–40°) mixture and further elution with THF gave an orange-brown solution. This was concentrated to a small volume and addition of light petro-leum followed by cooling to $-30°$ afforded the crystalline product. Yield 55%.

Method 5. Insertion of InX into metal–halogen bonds

$C_5H_5(CO)_2FeInBr_2$. An equimolar (1.5 mmole) mixture of $C_5H_5(CO)_2FeBr$ and InBr was stirred for $\frac{1}{2}$ h at room temperature in 25 ml of THF. The yellowish-brown solution was filtered, concentrated to a small volume and treated with an excess of light petroleum (b.p. 30–40°). The precipitated solid was recrystallised from THF/light petroleum to give the yellow microcrystalline complex, $C_5H_5(CO)_2FeInBr_2 \cdot$ THF.

This product was subjected to evacuation at ca. 1×10^{-3} mm for 4 h at ambient temperatures. The product remaining then analysed correctly for the solvent-free product.

Method 6. Reaction of InX with transition metal–mercury complexes

$[Co(CO)_4]_2InCl$. An equimolar (2.1 mmole) mixture of $[Co(CO)_4]_2Hg$ and InCl in 25 ml of dry THF was stirred at room temperature for 1 h, after which the solvent was evaporated. The residue was extracted with light petroleum (b.p. 30–40°) and the pale yellow solution concentrated under a stream of nitrogen to give the product as needle-like crystals. Yield 89%.

Method 7. Reaction of In(CH₃)₃ with transition metal hydride complexes

This method can be used to prepare all those trisubstituted complexes for which the transition metal hydrides are reasonably stable at room temperature (Mn, Re, Mo, W). No evidence was obtained in any of the reactions carried out, e.g. between $C_5H_5(CO)_3MH$ (M = Mo or W) and $In(CH_3)_3$, for intermediates of the type $[C_5H_5(CO)_3M]_{3-n}In(CH_3)_n$ ($n = 1$ or 2) even when a deficiency of the hydride was used. The procedure used was to condense a stoicheiometric amount of $In(CH_3)_3$ into a 100 ml flask containing ca. 0.5 mmole of the hydride complex at $-196°$. The flask was allowed to warm up to room temperature and was left until gas evolution had subsided. All volatile materials were then pumped away leaving the product in near quantitative yield. If necessary it could then be recrystallised as already described.

DISCUSSION

The methods of preparation described in the experimental section have all been used previously in the synthesis of metal–metal bonded complexes, and only a brief discussion of their relative merits as applied to indium is required. The most generally applicable method of synthesis is (1) and it may be used in the synthesis of all the new complexes described in this paper. It can, however, fail if the desired neutral product interacts strongly with halide ion, since anionic species are then formed by combination with the sodium halide present in solution[3]. For example, attempts to synthesise $C_5H_5(CO)_3MoInBr_2$ by this method were unsuccessful, although $[Et_4N]^+[C_5H_5(CO)_3MoInBr_3]^-$ could be readily isolated on addition of Et_4NBr to the reaction mixture[4].

For the trisubstituted complex (i.e. those with three indium–transition metal bonds) methods (1), (2), (3) and (7) all, in general, give satisfactory results and the choice will be determined primarily by the availability of starting materials. However, (2) cannot be used if the transition metal carbonyl anion, e.g. $C_5H_5(CO)_2Fe^-$, is readily hydrolysed by water and (3) may be slow if the mercury-containing species is not very soluble in THF. This metal exchange reaction can also be used to prepare

indium complexes from the corresponding thallium complexes[4]. Method (7) proceeds in near-quantitative yield, but there may be some contamination with the decomposition products of the transition metal hydride if this is at all unstable at room temperature.

For the complexes containing both indium–transition metal and indium–halogen bonds (1) is the most widely applicable method. Method (4), the insertion of indium halides into metal–metal bonds, has the disadvantage that reaction only occurs readily at room temperature for $Co_2(CO)_8$[5]. For other transition metals such as manganese[6,7], iron, molybdenum and tungsten, higher temperatures are required and, even so, reaction may not go to completion. In contrast, insertion into metal–halogen bonds, (5), takes place readily at room temperature for all these transition metals, and the method suffers only from the fact that many of the required transition metal halides are not readily accessible. Method (6) proceeds at room temperature for $Hg[Co(CO)_4]_2$ but the reaction of InX with other transition metal–mercury complexes again requires higher temperatures.

TABLE 1

ANALYTICAL DATA AND METHODS OF PREPARATION OF NEW COMPLEXES

Complex	Method of preparation used[a]	Colour	Analysis found (calcd.) (%)		
			C	H	X
$[C_5H_5(CO)_3Mo]_3In$	1,2,3,7	Bright yellow	34.1 (33.9)	1.8 (1.8)	
$[C_5H_5(CO)_3W]_3In$	1,2,3,7	Bright yellow	25.5 (25.9)	1.4 (1.4)	
$[C_5H_5(CO)_3Mo]_2InCl$	1,4[b],6	Yellow	29.9 (30.0)	1.8 · (1.6)	5.2 (5.5)
$[C_5H_5(CO)_3Mo]_2InBr$	1,4,6	Yellow	28.2 (28.0)	1.8 (1.5)	11.2 (11.7)
$[C_5H_5(CO)_3W]_2InCl$	1,4[b],6	Yellow	23.8 (23.5)	1.6 (1.2)	4.0 (4.3)
$C_5H_5(CO)_3MoInCl_2$	1,5	Light yellow	22.5 (22.3)	1.3 (1.2)	16.1 (16.5)
$In[Re(CO)_5]_3$	1,2,3,7	Intense yellow	16.6 (16.5)		
$ClIn[Re(CO)_5]_2$	1,4[b]	Yellow	15.2 (15.0)		4.8 (4.4)
$Cl_2InRe(CO)_5$	1,5	Pale yellow	11.6 (11.7)		13.5 (13.9)
$[C_5H_5(CO)_2Fe]_2InCl$	1,4[b],6	Yellow-brown	33.6 (33.3)	2.2 (2.0)	7.1 (7.0)
$C_5H_5(CO)_2FeInCl_2$	1,5	Yellow	22.9 (23.2)	1.6 (1.4)	18.7 (19.6)
$C_5H_5(CO)_2FeInBr_2$	1,5	Yellow	18.7 (18.6)	1.2 (1.1)	35.0 (35.4)
$C_5H_5(CO)_2FeInBr_2$, THF	1,5	Yellow	25.6 (25.2)	3.1 (2.5)	
$ClIn[Co(CO)_4]_2$	1,4,6	Yellow	19.3 (19.5)		6.6 (7.2)

[a] For numbering of methods see experimental section. [b] Reaction incomplete.

Analytical data for all the new complexes prepared in this study are given in Table 1 and infrared data for all the trisubstituted complexes listed, and for those mixed complexes containing chlorine and either molybdenum, rhenium or iron as ligands are given in Table 2. The trisubstituted complexes most probably have planar metal atom skeletons in the solid state, with the indium atom being three-coordinated but mass spectroscopic studies[4] on the mixed complex $(CO)_5MnInCl_2$ suggest that this molecule is dimeric, at least in the gas phase, and dimeric structures have also been previously postulated for related cobalt complexes[5] such as $[Co(CO)_4]_2InBr$. In these it is suggested that the indium atoms are four-coordinate with two bridging halogen atoms, and the new complexes of this type described here are almost certainly analogous. Mass spectroscopic studies on the complexes listed in Table 2 show that, of those containing halogen, only $(CO)_5ReInCl_2$ gives rise to dimeric species such as $(CO)_nRe_2In_2Cl_4^+$ ($n=2$ and 5) and $(CO)_nRe_2In_2Cl_2^+$ ($n=2$, 5 and 9). Of the trisubstituted complexes only $[Re(CO)_5]_3In$ shows the molecular ion, which is of low intensity, but all the complexes show series of fragment ions in which the metal atom framework is intact and only carbonyl groups have been lost.

TABLE 2

INFRARED SPECTRA OF NEW COMPLEXES IN THE CARBONYL STRETCHING REGION

Complex	Phase	$\nu(C-O)$ (cm^{-1})
$[C_5H_5(CO)_3Mo]_3In$	Nujol	1997 m(sh), 1968 vs, 1924 m, 1886 s, 1866 s
	CHCl$_3$	1998 ms, 1976 vs, 1911 m(sh), 1890 vs, 1867 m(sh)
$[C_5H_5(CO)_3Mo]_2InCl$	Nujol	1995 s(sh), 1981 s, 1973 s(sh), 1937 ms 1927 ms, 1927 m(sh), 1918 ms, 1883 vs, 1869 s(sh)
	CHCl$_3$	2001 s, 1979 vs, 1911 s(sh), 1893 vs(br)
$C_5H_5(CO)_3MoInCl_2$	Nujol	1998 vs, 1970 w(sh), 1937 ms, 1929 ms, 1885 s, 1876 s(sh)
	CHCl$_3$	2001 vs, 1979 s, 1909 s, 1898 s
$[C_5H_5(CO)_3W]_3In$	Nujol	1996 m(sh), 1962 vs, 1899 s(sh), 1874 s, 1855 vs
	CHCl$_3$	a
$In[Re(CO)_5]_3$	Nujol	2087 ms(sh), 2080 s, 2039 m, 2014 ms, 1973 vs(br), 1943 ms(br)
	CHCl$_3$	2102 mw, 2088 ms, 2047 vs, 2005 s, 1982 s, 1964 m(sh)
$ClIn[Re(CO)_5]_2$	Nujol	2117 mw, 2097 ms, 2013 vs(br), 1964 s(sh), 1951 ms(sh)
	CHCl$_3$	2113 w, 2102 mw, 2089 vs, 2049 vs, 2007 s, 1983 s, 1965 m(sh)
$Cl_2InRe(CO)_5$	Nujol	2115 mw, 2092 s, 2029 s(sh, br), 1971 vs, 1951 ms(sh)
	CHCl$_3$	2117 w(sh), 2090 s, 2047 vs, 2022 s(sh), 2010 vs, 1986 ms(sh)
$[C_5H_5(CO)_2Fe]_2InCl$	Nujol	1988 vs, 1963 vs, 1924 s, 1912 vs
$C_5H_5(CO)_2FeInCl_2$	Nujol	1987 m(sh), 1972 s, 1956 s, 1925 vs

a Insufficiently soluble.

A notable omission from the list of complexes in Table 2 is the trisubstituted complex $[C_5H_5(CO)_2Fe]_3In$. Although this may be prepared by any of the methods used for the other trisubstituted complexes, except (7), it is extremely air- and moisture-sensitive and we were unable to obtain an analytically pure sample. The other complexes we have prepared are all essentially unaffected by exposure to air and moisture for short periods.

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