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Structural Studies of Organomolybdenum Complexes Containing Indium

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The reaction between InCl_3 and 3 equiv of $\text{Na}[\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$ affords the trimolybdenum-indium complex $[\text{In}[\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]_3]$ (**2**), the structure of which was established by X-ray crystallography. Compound **2** crystallizes in the monoclinic space group $P2_1/n$ with $a = 11.463$ (1) Å, $b = 17.854$ (1) Å, $c = 13.572$ (1) Å, $\beta = 101.846$ (8)°, and $Z = 4$. The structure comprises a central trigonal-planar indium atom bonded to three $\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$ fragments via In-Mo bonds. The corresponding reaction between InCl_3 and 2 equiv of $\text{Na}[\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$ affords the anionic dimolybdenum complex $[\text{InCl}_2[\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]_2]^-$, which was also characterized by X-ray crystallography. It crystallizes as the sodium salt, THF solvate $[\text{Na}(\text{THF})_2][\text{InCl}_2[\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]_2]$ (**6**) in the triclinic space group $P\bar{1}$ with $a = 10.750$ (2) Å, $b = 12.457$ (2) Å, $c = 13.609$ (2) Å, $\alpha = 108.569$ (7)°, $\beta = 95.829$ (7)°, and $\gamma = 112.248$ (6)° and contains dimeric units linked by Cl-Na-Cl bridges, each sodium atom being ligated by three chlorines, two THF molecules, and the oxygen of one of the molybdenum-bound carbonyls; $Z = 1$ dimer per unit cell. Reaction between InCl_3 and 1 equiv of $\text{Na}[\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$ also affords an anionic complex, $[\text{InCl}_3[\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]]^-$, characterized by X-ray crystallography. It crystallizes as the sodium salt, THF solvate $[\text{Na}(\text{THF})_2][\text{InCl}_3[\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]]$ (**8**) in the monoclinic space group $P2_1/c$ with $a = 10.160$ (1) Å, $b = 21.116$ (2) Å, $c = 11.862$ (1) Å, and $\beta = 109.304$ (7)° and also comprises dimeric units linked by Cl-Na-Cl bridges; $Z = 2$ dimers per cell. The tungsten analogues of the above three complexes were also prepared and characterized by spectroscopic means. Details of the solution-state properties of all compounds as determined by infrared spectroscopy are discussed.

Introduction

Organotransition-metal complexes containing atoms of the heavier main-group metals are currently the focus of considerable attention, such interest being stimulated by the potential for novel catalytic systems and precursors for "new materials". With particular regard to complexes featuring the heavier elements of group 13, i.e. gallium, indium, and thallium, those of indium have been the most studied.

The earliest report dealing with a metal carbonyl complex of indium was by Hieber et al.,¹ who described the synthesis of $[\text{In}\{\text{Co}(\text{CO})_4\}_3]$ (**1**) together with the gallium and thallium analogues. Further reports concerning **1** have subsequently appeared,² including details of the structure^{2d} and its ability to catalyze the dimerization of norbornadiene,^{2a} and in addition, a number of cobalt-indium halide complexes have also been described.³

The most studied of the transition metals in this respect, however, are manganese and rhenium, for both of which a large number of reports have appeared concerning studies on complexes containing indium. Early studies by Mays et al.⁴ dealt with pentacarbonyl manganese complexes, and later reports by Haupt and co-workers⁵ were concerned with a range of manganese and rhenium carbonyl complexes, many of which were characterized by X-ray diffraction. Examples include $[\text{M}_2(\text{CO})_8\{\mu\text{-InM}(\text{CO})_5\}]$ ($\text{M} = \text{Mn},^{5c} \text{Re}^{5e}$), $[\text{Re}_4(\text{CO})_{12}\{\mu_3\text{-InRe}(\text{CO})_5\}_4]$,^{5d,g} $[\text{M}(\text{CO})_5\text{In}(\mu\text{-X})_2]$ ($\text{M} = \text{Mn}, \text{X} = \text{Cl}, \text{Br}, \text{I};^{5f} \text{M} = \text{Re}, \text{X} = \text{Cl}, \text{Br}, \text{I}^{5i}$), and $[\text{Fe}_2(\text{CO})_8\{\mu\text{-InMn}(\text{CO})_5\}_2]$,^{5h} and a number of related

complexes containing gallium have also been described.⁶

Relatively little attention has been afforded to compounds containing a group 6 transition metal, and structural data on such compounds are scarce. Behrens et al.⁷ have described an interesting complex of indium(I) bromide and $\text{Cr}(\text{CO})_5$, but reports on cyclopentadienyl group 6 metal complexes containing indium are limited to a single account by Mays,⁸ in which no structural details were presented.

As part of a study of organotransition-metal-heavy main-group metal complexes, we have prepared a range of cyclopentadienylmolybdenum and -tungsten compounds containing indium and report herein details of the structures of representative examples and infrared data pertinent to their solution-state properties.

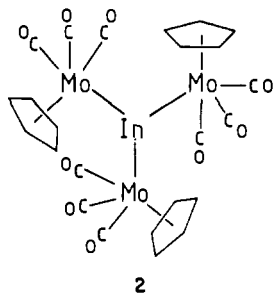
Results and Discussion

The aforementioned report by Mays et al.⁸ described a number of synthetic methods for making transition-metal-indium compounds. Among those compounds reported were examples containing the cyclopentadienyl-molybdenum tricarbonyl fragment, $\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$, which were formulated as $[\text{In}\{\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)\}_3]$, $[\text{InCl}\{\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)\}_2]$, and $[\text{InCl}_2\{\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)\}]$ on the basis of analytical data, with additional characterization being effected by infrared spectroscopy. No structural details were reported on any of these complexes, yet such data are of interest since the molybdenum-indium halide complexes, in particular, are unlikely to be monomeric in the solid state. Moreover, earlier work by Mays,^{4a} on related manganese pentacarbonyl complexes, indicated that interesting solvent-dependent dissociation equilibria might exist in solution.

Addition of a THF solution of InCl_3 to a THF solution containing 3 equiv of $\text{Na}[\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$ afforded, after filtration and crystallization from THF/hexane mixtures, yellow rodlike crystals of the trimolybdenum-indium complex **2**. Characterization was effected by normal spectroscopic methods (Table I) and by an X-ray diffraction study, the results of which are shown in Figure 1. Selected bond distance and angle data are given in Table II, and atomic positional parameters are presented in Table III. The molecule consists of a single indium atom, in a trigonal-planar coordination environment (sum of angles 360.0°),

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- (2) (a) Schrauzer, G. N.; Bastian, B. N.; Fosselius, G. A. *J. Am. Chem. Soc.* **1966**, *88*, 4890. (b) Patmore, D. J.; Graham, W. A. G. *Inorg. Chem.* **1966**, *5*, 1586. (c) Robinson, W. R.; Schussler, D. P. *J. Organomet. Chem.* **1971**, *30*, C5. (d) Robinson, W. R.; Schussler, D. P. *Inorg. Chem.* **1973**, *12*, 848.
- (3) (a) Patmore, D. J.; Graham, W. A. G. *Chem. Commun.* **1965**, 591. (b) Ruff, J. K. *Inorg. Chem.* **1968**, *7*, 1499. (c) Cradwick, P. D.; Graham, W. A. G.; Hall, D.; Patmore, D. J. *Chem. Commun.* **1968**, 872. (d) Cradwick, P. D.; Hall, D. J. *Organomet. Chem.* **1970**, *22*, 203. (e) Cradwick, P. D. *J. Organomet. Chem.* **1971**, *27*, 251.
- (4) (a) Hsieh, A. T. T.; Mays, M. J. *Chem. Commun.* **1971**, 1234. (b) Hsieh, A. T. T.; Mays, M. J. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 223. (c) Hsieh, A. T. T.; Mays, M. J. *J. Chem. Soc., Dalton Trans.* **1972**, 516.
- (5) (a) Haupt, H.-J.; Neumann, F. Z. *Anorg. Allg. Chem.* **1972**, *394*, 67. (b) Haupt, H.-J.; Neumann, F. *J. Organomet. Chem.* **1974**, *74*, 185. (c) Preut, H.; Haupt, H.-J. *Chem. Ber.* **1974**, *107*, 2860. (d) Haupt, H.-J.; Neumann, F.; Preut, H. *J. Organomet. Chem.* **1975**, *99*, 439. (e) Preut, H.; Haupt, H.-J. *Chem. Ber.* **1975**, *108*, 1447. (f) Haupt, H.-J.; Wolfes, W.; Preut, H. *Inorg. Chem.* **1976**, *15*, 2920. (g) Preut, H.; Haupt, H.-J. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *B35*, 1205. (h) Preut, H.; Haupt, H.-J. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *B35*, 2191. (i) Haupt, H.-J.; Preut, H.; Wolfes, W. Z. *Anorg. Allg. Chem.* **1979**, *448*, 93.

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- (7) Behrens, H.; Moll, M.; Sixtus, E.; Thiele, G. Z. *Naturforsch., B: Anorg. Chem., Org. Chem.* **1977**, *32B*, 1109.
- (8) Hsieh, A. T. T.; Mays, M. J. *J. Organomet. Chem.* **1972**, *37*, 9.



bonded to three $\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$ fragments via unsupported Mo–In bonds (average Mo–In = 2.878 Å). The bond distance to one molybdenum atom (Mo(3)–In = 2.862 (1) Å) is about 0.02 Å shorter than those distances to the other two (Mo(1)–In = 2.884 (1); Mo(2)–In = 2.887 (1) Å, but this is unlikely to be chemically significant. Simple electron-counting procedures require that the Mo–In bonds have a bond order of unity, with which the derived bond lengths would seem consistent. However, there are no previous reports in the literature of compounds containing unsupported molybdenum–indium bonds. A value derived from the sum of the covalent radii for the two elements is 3.06 Å,⁹ approximately 0.2 Å longer than the observed values in **2**. Such bond shortening should be anticipated, however, since the indium atom is a Lewis acid center with a vacant 5p orbital available to accept electron density from orbitals of the correct symmetry on the molybdenum atoms. Some degree of Mo–In multiple bonding may therefore be present, which might account for any bond shortening observed. Moreover, the orientation of the $\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$ fragments¹¹ suggests that such an interaction is present. Each fragment is oriented such that the Mo_3In plane is coplanar with the symmetry plane of the molybdenum fragment, with overall approximately C_{3h} molecular symmetry. Such an orientation is expected in order that the π -overlap between the molybdenum atom and the vacant indium 5p orbital, as shown in A, is maximized.¹¹ The geometries associated with the carbonyl

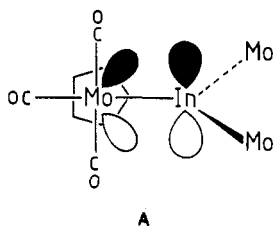


Figure 1. Molecular structure of **2**, showing the atom-numbering scheme adopted. Thermal ellipsoids are drawn at the 50% probability level in this and other figures.

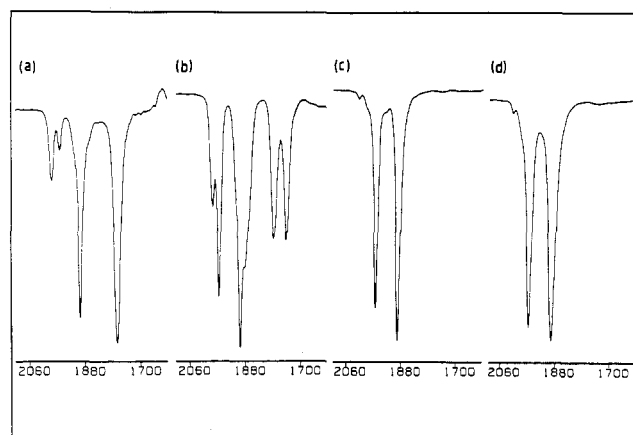


Figure 2. Solution infrared spectra in the carbonyl stretching region for **2**: (a) MeCN; (b) THF; (c) toluene; (d) CH_2Cl_2 .

and cyclopentadienyl ligands are normal and worthy of no special comment, the ligand geometry around each molybdenum atom being of the familiar CpML_4 “piano stool” type.

Of final interest with regard to the structure of **2** are comparisons with the related gallium and thallium complexes, $[\text{Ga}\{\text{W}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)\}_3]$ (**3**)¹² and $[\text{Tl}\{\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)\}_3]$ (**4**).¹³ The former compound is isomorphous and isostructural with **2**,

and so the discussion given above is equally applicable to **3**. It is worth noting, however, that the Ga–W bond lengths in **3** show considerable variation about the mean value, as is also observed for the In–Mo bond lengths in **2**.

The thallium complex, **4**, while similar to **2** and **3** in terms of the gross molecular structure and atom connectivities, has a number of interesting differences. First, the coordination about the thallium atom has a marked distortion toward a trigonal-pyramidal geometry (the thallium atom lies 0.586 (1) Å from the plane of the three molybdenum atoms; the corresponding displacement for the indium atom in **2** is 0.017 (1) Å), and second, the conformations about the Tl–Mo bonds are rather different from those observed for the corresponding In–Mo bonds in **2**. These are represented diagrammatically in B (**2**) and C (**4**). The

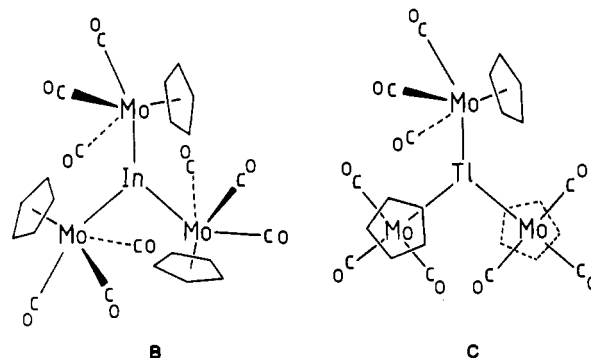
(9) This value is derived from a literature value of 1.44 Å for In(III) (see: Ball, M. C.; Norbury, A. H. *Physical Data for Inorganic Chemists*; Longman: London, 1974) and a value for molybdenum derived from the bond length in $[\text{Mo}_2(\text{CO})_6(\eta\text{-C}_5\text{H}_5)_2]$ (3.235 Å) taken from ref 10.

(10) Adams, R. D.; Collins, D. M.; Cotton, F. A. *Inorg. Chem.* **1974**, *13*, 1086.

(11) Kubacek, P.; Hoffmann, R.; Havlas, Z. *Organometallics* **1982**, *1*, 180. There are two π -donor orbitals on the $\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$ fragment, as discussed in the above reference, and these workers have established that the orbital that lies in a plane perpendicular to the symmetry plane of this fragment (as shown in A in the text) is slightly better disposed toward π -donation than an alternative orthogonal orbital that resides in the plane. This leads to a small orientational preference in $\text{CpM}(\text{CO})_3\text{L}$ complexes that involve a π -interaction between M and L. The observed orientations of all three $\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$ fragments in **2** are, therefore, such as to maximize Mo–In π -bonding in this molecule although, because of the energies involved, the barrier to rotation about the Mo–In bonds is expected to be small.

(12) Conway, A. J.; Hitchcock, P. B.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **1975**, 1945.

(13) Rajaram, J.; Ibers, J. A. *Inorg. Chem.* **1973**, *12*, 1313.



extent to which this is significant is uncertain, and any energy differences associated with changes in conformation about these bonds are expected to be small.¹¹

Having established the solid-state structure of **2**, we felt it was of interest to examine its solution-state properties. Accordingly,

Table I. Spectroscopic Data for the Complexes

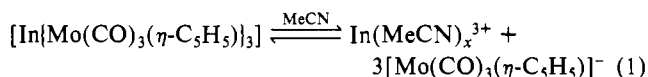
compd	$\nu(\text{CO})/\text{cm}^{-1}$	NMR ^a δ	
		¹ H ^b	¹³ C ^{b,c}
[In{Mo(CO) ₃ (η -C ₅ H ₅) ₃ }] (2)	2024 w, 1967 s, 1892 s ^d 2023 w, 1965 s, 1893 s ^e 1989 m, 1967 s, 1898 s, 1880 m, 1789 m, 1749 m ^f 1990 w, 1963 w, 1897 s, 1777 s ^g	5.45 ^h	93.0 ^h
[In{W(CO) ₃ (η -C ₅ H ₅) ₃ }] (5)	2020 w, 1962 s, 1884 s ^d 2018 w, 1986 m, 1963 s, 1894 s, 1875 m, 1792 m, 1743 m ^f 1983 m, 1959 m, 1890 s, 1772 s ^g	5.54 ^h	91.9 ^h
Na[InCl ₂ {Mo(CO) ₃ (η -C ₅ H ₅) ₂ }] (6)	1990 s, 1968 s, 1899 s, 1882 s ^f 1987 s, 1963 s, 1896 s, 1777 m ^g	5.48 ⁱ	90.8 ⁱ
Na[InCl ₂ {W(CO) ₃ (η -C ₅ H ₅) ₂ }] (7)	1986 m, 1963 s, 1891 m, 1875 m ^f	5.73 ^j	90.3 ^j
Na[InCl ₃ {Mo(CO) ₃ (η -C ₅ H ₅)}] (8)	1994 s, 1903 s ^f 1993 s, 1915 m, 1895 s ^g	5.62 ^j	90.5 ^j
Na[InCl ₃ {W(CO) ₃ (η -C ₅ H ₅)}] (9)	1990 s, 1897 s ^f	5.73 ^j	89.4 ^j

^aChemical shifts (δ) in ppm; measurements at room temperature. ^bValues quoted are for the cyclopentadienyl resonances. ^c¹H decoupled; chemical shifts are positive to high frequency of SiMe₄. ^dRecorded in CH₂Cl₂ solution. ^eRecorded in toluene solution. ^fRecorded in THF solution. ^gRecorded in MeCN solution. ^hRecorded in CD₂Cl₂ solution. ⁱRecorded in THF-d₈ solution. ^jRecorded in acetone-d₆ solution.

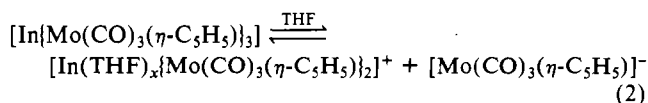
Table II. Selected Bond Lengths (Å) and Bond Angles (deg) for 2

In-Mo(1)	2.884 (1)	In-Mo(2)	2.887 (1)
In-Mo(3)	2.862 (1)	Mo(1)-C(11)	1.961 (4)
Mo(1)-C(12)	1.962 (5)	Mo(1)-C(13)	1.973 (4)
Mo(2)-C(21)	1.975 (4)	Mo(2)-C(22)	1.958 (4)
Mo(2)-C(23)	1.976 (4)	Mo(3)-C(31)	1.971 (5)
Mo(3)-C(32)	1.968 (6)	Mo(3)-C(33)	1.960 (4)
Mo(1)-In-Mo(2)	120.2 (1)	Mo(1)-In-Mo(3)	119.4 (1)
Mo(2)-In-Mo(3)	120.4 (1)	In-Mo(1)-C(11)	121.0 (1)
In-Mo(1)-C(12)	66.8 (2)	C(11)-Mo(1)-C(12)	81.6 (2)
In-Mo(1)-C(13)	66.0 (1)	C(11)-Mo(1)-C(13)	79.8 (2)
C(12)-Mo(1)-C(13)	108.1 (2)	In-Mo(2)-C(21)	121.6 (1)
In-Mo(2)-C(22)	67.0 (1)	C(21)-Mo(2)-C(22)	82.1 (2)
In-Mo(2)-C(23)	66.5 (1)	C(21)-Mo(2)-C(23)	80.4 (2)
C(22)-Mo(2)-C(23)	109.5 (2)	In-Mo(3)-C(31)	121.3 (1)
In-Mo(3)-C(32)	66.9 (1)	C(31)-Mo(3)-C(32)	79.4 (2)
In-Mo(3)-C(33)	67.8 (1)	C(31)-Mo(3)-C(33)	82.2 (2)
C(32)-Mo(3)-C(33)	110.3 (2)		

a number of infrared spectra were obtained in various solvents, details of which are listed in Table I and shown diagrammatically in Figure 2. In CH₂Cl₂ and toluene, both essentially noncoordinating solvents, two sharp absorptions were observed at frequencies characteristic of a Mo(CO)₃(η -C₅H₅) fragment in a MoX(CO)₃(η -C₅H₅) type compound. The spectra in both of these solvents are, therefore, consistent with the solid-state structure being maintained in solution. In contrast, spectra obtained in acetonitrile solution revealed two strong absorptions at much lower frequencies characteristic of the anionic complex, [Mo(CO)₃(η -C₅H₅)]⁻.¹⁴ This suggests that in this solvent, extensive dissociation occurs according to eq 1 although the weaker absorptions at higher



frequency indicate some residual degree of association. In THF solution an intermediate situation appears to exist with absorptions attributable to [Mo(CO)₃(η -C₅H₅)]⁻ (1880 and 1749 cm⁻¹) and a further species different from undissociated 2 (1989, 1967, 1898, and 1789 cm⁻¹). These data suggest a partial degree of dissociation in this latter solvent accordant with eq 2.



In summary, therefore, 2 appears to be predominantly undissociated in the noncoordinating solvents, CH₂Cl₂ and toluene, partially dissociated in THF, and almost fully dissociated in MeCN. Progressive dissociation is thus favored as the donor

Table III. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\text{Å}^2 \times 10^3$) for 2

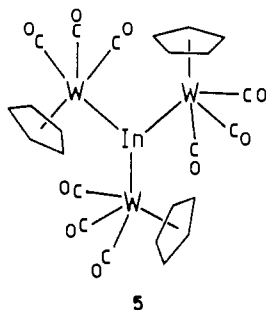
	x	y	z	U_{eq}^a
In	6302.0 (2)	6433.2 (1)	3246.0 (2)	40.9 (1)
Mo(1)	4608.1 (2)	5281.7 (2)	2442.2 (2)	43.3 (1)
Mo(2)	5483.2 (2)	7863.2 (2)	3829.8 (2)	44.6 (1)
Mo(3)	8794.9 (2)	6154.5 (2)	3422.2 (3)	50.4 (1)
C(11)	2891 (4)	5485 (3)	2147 (4)	69 (2)
O(11)	1888 (3)	5602 (3)	1975 (5)	110 (2)
C(12)	4455 (5)	5628 (2)	3781 (4)	69 (2)
O(12)	4277 (6)	5793 (3)	4564 (3)	106 (2)
C(13)	4554 (4)	6167 (2)	1563 (3)	58 (1)
O(13)	4476 (5)	6655 (2)	1009 (3)	96 (2)
C(14)	5371 (6)	4445 (3)	1384 (4)	79 (2)
C(15)	4313 (5)	4175 (3)	1527 (6)	96 (2)
C(16)	4432 (6)	3999 (2)	2510 (7)	104 (3)
C(17)	5596 (6)	4174 (3)	3009 (4)	81 (2)
C(18)	6167 (4)	4465 (2)	2283 (4)	68 (2)
C(21)	6607 (4)	8680 (2)	4338 (3)	60 (1)
O(21)	7223 (4)	9167 (2)	4638 (3)	90 (2)
C(22)	6467 (4)	7321 (3)	4955 (3)	61 (1)
O(22)	7003 (5)	7033 (3)	5675 (3)	100 (2)
C(23)	6338 (3)	7930 (2)	2708 (3)	52 (1)
O(23)	6781 (3)	8029 (2)	2036 (3)	73 (1)
C(24)	3669 (4)	8268 (4)	2846 (5)	85 (2)
C(25)	3944 (4)	8724 (3)	3644 (6)	91 (2)
C(26)	3934 (5)	8328 (5)	4519 (6)	104 (3)
C(27)	3637 (5)	7583 (4)	4235 (7)	109 (3)
C(28)	3485 (4)	7554 (4)	3177 (6)	94 (2)
C(31)	9395 (4)	5147 (3)	3201 (5)	82 (2)
O(31)	9750 (5)	4562 (2)	3092 (6)	123 (3)
C(32)	8085 (4)	5565 (3)	4374 (4)	69 (2)
O(32)	7770 (4)	5211 (3)	4986 (4)	110 (2)
C(33)	7894 (4)	6006 (3)	2044 (4)	63 (1)
O(33)	7459 (4)	5928 (3)	1196 (3)	95 (2)
C(34)	9480 (5)	7339 (3)	3078 (6)	86 (2)
C(35)	10364 (4)	6853 (3)	3071 (6)	91 (2)
C(36)	10721 (4)	6555 (3)	4000 (8)	121 (4)
C(37)	9971 (7)	6913 (4)	4648 (6)	105 (3)
C(38)	9232 (4)	7387 (3)	4000 (5)	79 (2)

^a $U_{\text{eq}} = 1/3(\text{trace of the orthogonalized } U_{ij} \text{ matrix})$.

ability of the solvent increases. We note also that similar observations have been described by Mays et al.^{4a} for the analogous trimanganese complex [InMn(CO)₅]₃, which is reported to be fully dissociated in DMF and partially dissociated in MeCN, the cationic species being of the form [In(MeCN)₂]₃[Mn(CO)₅]₂⁺.

The related tungsten complex, 5, was also synthesized by a route identical with that used for the synthesis of 2. Solution-state infrared data for 5 (see Table I) in CH₂Cl₂, THF, and MeCN are essentially identical with those obtained for 2 in the same solvents and indicate that solvent-dependent dissociation occurs to a similar extent, as represented in eq 1 and 2, for both complexes. The only point of difference between 2 and 5 is one of general stability in solution, which is noticeably less for 5 than

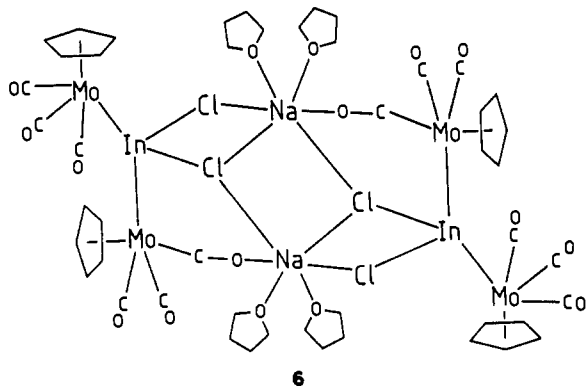
(14) Crotty, D. E.; Corey, E. R.; Anderson, T. J.; Glick, M. D.; Oliver, J. P. *Inorg. Chem.* 1977, 16, 920.



5

for **2**, making high recrystallized yields of the tungsten complex difficult to obtain.

After investigation of the reaction of InCl_3 with 3 equiv of $[\text{M}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]^-$ ($\text{M} = \text{Mo}, \text{W}$), it was of interest to examine the corresponding 2:1 and 1:1 reactions. The former reaction has been described by Mays⁸ for both molybdenum and tungsten and is reported to yield the complexes $[\text{InCl}_2\{\text{M}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)_2\}]$ ($\text{M} = \text{Mo}, \text{W}$), which were characterized by elemental analysis. Treatment of a solution of InCl_3 with 2 equiv of $\text{Na}[\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$ afforded a yellow solution from which block yellow crystals of **6** were obtained after filtration and crystallization from



6

THF/hexane. Infrared and NMR data (Table I) indicated a single compound, but it was evident from the ^1H NMR spectrum and from microanalytical data that the crystals contained THF. In order to determine the solid-state structure of this material, a single-crystal X-ray diffraction study was undertaken, the results of which are shown in Figure 3. Selected bond distance and angle data are listed in Table IV, and atomic positional parameters are presented in Table V. The basic molecular unit of **6** comprises an indium atom bonded to two chlorine atoms and two $\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$ fragments, with the geometry around the indium being tetrahedral, although this is somewhat distorted as evidenced by the angles $\text{Cl}(1)\text{-In-Cl}(2) = 90.4(1)^\circ$ and $\text{Mo}(1)\text{-In-Mo}(2) = 129.4(1)^\circ$. The reaction described has thus proceeded with the elimination of only 1 equiv of NaCl , resulting in a compound containing the anion $[\text{InCl}_2\{\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)_2\}]^-$ and a sodium counteranion. As shown in Figure 3 and the diagram, an interesting dimeric association exists in the crystals of **6**, the halves of the dimer being related by a crystallographic center of inversion. The sodium ions reside in an approximately octahedral coordination environment, ligated by two THF molecules, two chlorine atoms from one $\text{Mo}_2\text{InCl}_2^-$ ion, one chlorine atom from the other $\text{Mo}_2\text{InCl}_2^-$ ion, and a carbonyl oxygen from one of the $\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$ fragments. It is this latter interaction that is the most noteworthy, although "isocarbonyl" interactions involving electropositive metals are not uncommon. Nevertheless, the interaction is weak as evidenced by the long sodium-oxygen bond length ($\text{Na-O}(23') = 2.768(5) \text{ \AA}$; cf. the bonds to the THF oxygens: $\text{Na-O}(31) = 2.361(5) \text{ \AA}$ and $\text{Na-O}(41) = 2.324(6) \text{ \AA}$) and the deviations from normality in the carbonyl group, which are only minor ($\text{C}(23)\text{-O}(23) = 1.150(7) \text{ \AA}$, $\text{Mo}(2)\text{-C}(23)\text{-O}(23) = 173.7(4)^\circ$).

Retention of one chloride ion in the structure of **6** is unsurprising in view of the known Lewis acidity of indium(III), and a similar

Table IV. Selected Bond Lengths (\AA) and Bond Angles (deg) for **6**

In-Mo(1)	2.859 (1)	In-Mo(2)	2.842 (1)
In-Cl(1)	2.511 (1)	In-Cl(2)	2.542 (1)
Mo(1)-C(11)	1.959 (6)	Mo(1)-C(12)	1.965 (6)
Mo(1)-C(13)	1.961 (4)	Mo(2)-C(21)	1.971 (7)
Mo(2)-C(22)	1.969 (5)	Mo(2)-C(23)	1.957 (5)
Cl(1)-Na	2.888 (2)	Cl(2)-Na	2.772 (2)
Na-O(41)	2.324 (6)	Na-O(31)	2.361 (5)
Na-O(23')	2.768 (5)	Na-Cl(2')	2.990 (3)
Mo(1)-In-Mo(2)	129.4 (1)	Mo(1)-In-Cl(1)	109.8 (1)
Mo(2)-In-Cl(1)	103.3 (1)	Mo(1)-In-Cl(2)	103.3 (1)
Mo(2)-In-Cl(2)	113.7 (1)	Cl(1)-In-Cl(2)	90.4 (1)
In-Mo(1)-C(11)	127.3 (2)	In-Mo(1)-C(12)	69.1 (1)
C(11)-Mo(1)-C(12)	78.0 (3)	In-Mo(1)-C(13)	72.5 (2)
C(11)-Mo(1)-C(13)	79.3 (2)	C(12)-Mo(1)-C(13)	106.7 (2)
In-Mo(2)-C(21)	128.8 (1)	In-Mo(2)-C(22)	70.8 (1)
C(21)-Mo(2)-C(22)	79.9 (3)	In-Mo(2)-C(23)	70.4 (2)
C(21)-Mo(2)-C(23)	79.9 (2)	C(22)-Mo(2)-C(23)	107.2 (2)
In-Cl(1)-Na	94.4 (1)	In-Cl(2)-Na	96.5 (1)
In-Cl(2)-Na'	122.4 (1)	Na-Cl(2)-Na'	88.9 (1)
Cl(1)-Na-Cl(2)	78.6 (1)	Cl(1)-Na-O(31)	93.0 (1)
Cl(2)-Na-O(31)	102.9 (1)	Cl(1)-Na-O(41)	94.6 (1)
Cl(2)-Na-O(41)	168.0 (1)	O(31)-Na-O(41)	87.1 (2)
Cl(1)-Na-Cl(2')	125.4 (1)	Cl(2)-Na-Cl(2')	91.1 (1)
O(31)-Na-Cl(2')	141.2 (1)	O(41)-Na-Cl(2')	84.8 (2)
Cl(1)-Na-O(23')	150.4 (1)	Cl(2)-Na-O(23')	75.2 (1)
O(31)-Na-O(23')	79.9 (2)	O(41)-Na-O(23')	113.5 (2)
Cl(2')-Na-O(23')	68.9 (1)		

Table V. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$) for **6**

	x	y	z	U_{eq}^a
In	4378.4 (3)	2960.1 (2)	6505.1 (2)	46.2 (1)
Mo(1)	1826.3 (4)	3191.6 (3)	6374.1 (3)	55.8 (2)
Mo(2)	6773.8 (4)	4187.8 (3)	8251.3 (3)	50.9 (1)
Cl(1)	5355 (1)	3285 (1)	4968 (1)	71 (1)
Cl(2)	3592 (1)	603 (1)	5597 (1)	59 (1)
Na	4729 (2)	669 (2)	3866 (1)	71 (1)
C(11)	951 (5)	3607 (5)	7545 (4)	74 (2)
O(11)	458 (5)	3850 (5)	8256 (3)	106 (2)
C(12)	1794 (4)	1969 (5)	7006 (4)	63 (2)
O(12)	1661 (4)	1211 (4)	7356 (3)	88 (2)
C(13)	3307 (5)	4827 (5)	7355 (4)	75 (3)
O(13)	4090 (5)	5826 (4)	7924 (5)	119 (2)
C(14)	-148 (9)	2626 (18)	5114 (7)	139 (7)
C(15)	834 (19)	3734 (12)	5139 (7)	146 (7)
C(16)	1895 (9)	3510 (11)	4805 (6)	122 (5)
C(17)	1541 (10)	2275 (11)	4546 (4)	116 (6)
C(18)	280 (12)	1757 (8)	4734 (6)	124 (4)
C(21)	7377 (6)	3522 (5)	9246 (4)	84 (3)
O(21)	7727 (6)	3143 (5)	9828 (4)	128 (3)
C(22)	5100 (5)	3630 (4)	8782 (3)	65 (2)
O(22)	4188 (5)	3357 (4)	9171 (3)	103 (2)
C(23)	6788 (5)	2680 (4)	7227 (4)	71 (2)
O(23)	6926 (4)	1856 (4)	6647 (3)	110 (2)
C(24)	7092 (5)	5829 (4)	7664 (4)	69 (2)
C(25)	8221 (6)	5560 (5)	7581 (5)	88 (3)
C(26)	8933 (5)	5828 (5)	8612 (6)	101 (3)
C(27)	8194 (6)	6277 (4)	9342 (4)	86 (3)
C(28)	7093 (5)	6276 (4)	8741 (4)	68 (2)
O(31)	2858 (4)	323 (3)	2547 (3)	90 (2)
C(32)	2979 (7)	1167 (6)	2034 (6)	111 (4)
C(33)	1595 (9)	778 (7)	1398 (8)	140 (5)
C(34)	802 (8)	-520 (7)	1235 (7)	124 (4)
C(35)	1525 (7)	-674 (6)	2132 (7)	109 (4)
O(41)	6105 (5)	1034 (4)	2689 (4)	106 (3)
C(42)	7170 (10)	2138 (11)	2760 (10)	163 (7)
C(43)	7907 (18)	1829 (22)	2015 (15)	305 (15)
C(44)	7059 (19)	478 (19)	1292 (12)	239 (14)
C(45)	6037 (15)	-5 (10)	1837 (9)	168 (8)

^a $U_{\text{eq}} = 1/3(\text{trace of the orthogonalized } U_{ij} \text{ matrix})$.

complex incorporating $\text{Co}(\text{CO})_4$ fragments has been previously reported, viz. $[\text{InBr}_2\{\text{Co}(\text{CO})_4\}_2]^-$.^{3c}

As previously mentioned, Mays et al.⁸ report a neutral complex, $[\text{InCl}\{\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)_2\}]$, from the reaction between InCl_3 and

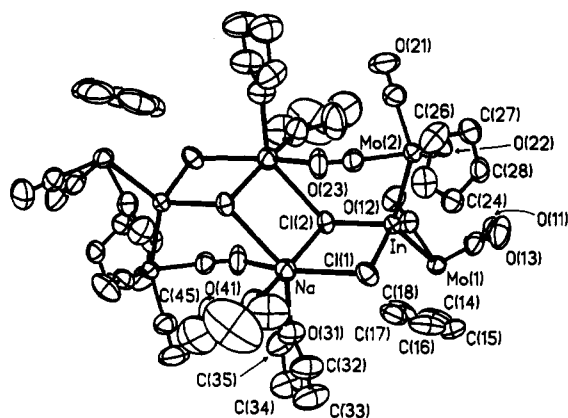


Figure 3. Molecular structure of 6, showing the atom-numbering scheme adopted.

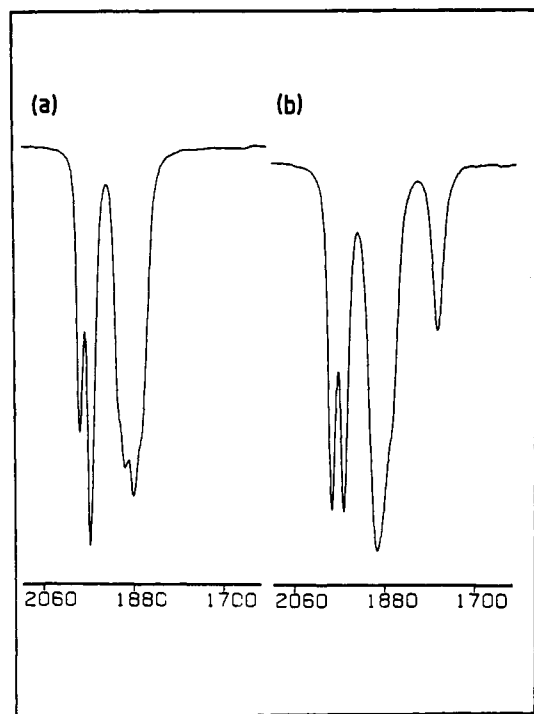


Figure 4. Solution infrared spectra in the carbonyl stretching region for 6: (a) THF; (b) MeCN.

2 equiv of $\text{Na}[\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$ rather than an ionic sodium chloride adduct, i.e. 6, described herein. The only difference in experimental procedures occurs during recrystallization, with Mays reporting crystallization from THF/water whereas crystals of 6 were obtained from THF/hexane. It is possible that crystallization employing the former solvent system allows ready dissolution of NaCl into the aqueous phase, thereby enabling a molybdenum-indium complex free of sodium chloride to be isolated.

Solution infrared data for 6 are presented in Table I and displayed in Figure 4. Spectra obtained in THF are consistent with the presence of the undissociated Mo_2InCl_2 anion being present in solution although the discrete dimeric structure observed in the solid state is unlikely to be preserved intact. Spectra obtained in acetonitrile, however, revealed a medium-strength absorption at 1777 cm^{-1} , which is assigned to the anion, $[\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]^-$. This is indicative of partial molybdenum-indium bond heterolysis, although complete dissociation in this solvent does not occur, in contrast to analogous results observed for the trimolybdenum compound, 2.

The tungsten analogue, $\text{Na}[\text{InCl}_2[\text{W}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]_2]$ (7), was also prepared, spectroscopic details of which are listed in Table I. The appearance of the infrared spectra indicate that the solution-state properties of 7 are analogous to those of 6.

Table VI. Selected Bond Lengths (Å) and Bond Angles (deg) for 8

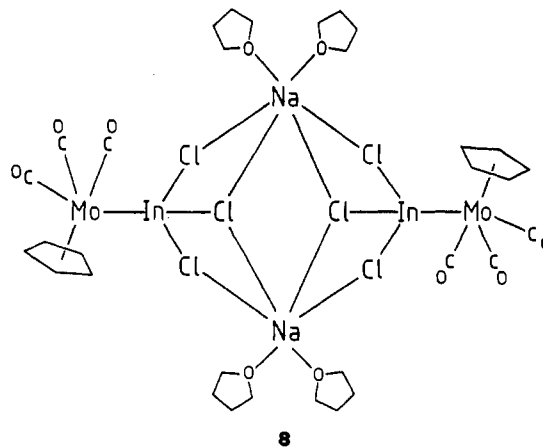
In-Mo	2.739 (1)	In-Cl(1)	2.450 (2)
In-Cl(2)	2.405 (2)	In-Cl(3)	2.422 (2)
Mo-C(1)	1.980 (6)	Mo-C(2)	1.964 (8)
Mo-C(3)	1.981 (6)	Cl(1)-Na	2.930 (3)
Cl(1)-Na'	2.934 (3)	Cl(2)-Na	2.886 (3)
Cl(3)-Na'	2.878 (3)	Na-O(11)	2.341 (5)
Na-O(21)	2.358 (7)		
Mo-In-Cl(1)	116.8 (1)	Mo-In-Cl(2)	123.3 (1)
Cl(1)-In-Cl(2)	96.2 (1)	Mo-In-Cl(3)	115.6 (1)
Cl(1)-In-Cl(3)	97.3 (1)	Cl(2)-In-Cl(3)	103.0 (1)
In-Mo-C(1)	71.4 (2)	In-Mo-C(2)	131.8 (2)
C(1)-Mo-C(2)	81.0 (3)	In-Mo-C(3)	70.7 (2)
C(1)-Mo-C(3)	105.1 (2)	C(2)-Mo-C(3)	79.8 (3)
In-Cl(1)-Na	91.3 (1)	In-Cl(1)-Na'	91.1 (1)
Na-Cl(1)-Na'	97.2 (1)	In-Cl(2)-Na	93.3 (1)
In-Cl(3)-Na'	93.0 (1)		

Table VII. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\text{Å}^2 \times 10^3$) for 8

	x	y	z	U_{eq}^a
In	6390.9 (4)	5417.9 (2)	3085.2 (3)	53.5 (1)
Mo	8395.6 (4)	5322.8 (2)	2016.7 (3)	54.8 (1)
Cl(1)	6931 (1)	4944 (1)	5072 (1)	62 (1)
Cl(2)	5564 (2)	6413 (1)	3579 (1)	86 (1)
Cl(3)	4256 (2)	4839 (1)	2123 (1)	85 (1)
C(1)	6877 (7)	5873 (3)	1020 (5)	68 (2)
O(1)	6022 (6)	6188 (2)	400 (4)	95 (2)
C(2)	9528 (7)	5966 (3)	1568 (6)	84 (3)
O(2)	10201 (7)	6343 (3)	1313 (6)	122 (3)
C(3)	9173 (6)	5778 (3)	3555 (5)	71 (2)
O(3)	9691 (5)	6030 (3)	4443 (4)	101 (2)
C(4)	7524 (8)	4345 (3)	1247 (10)	125 (4)
C(5)	8524 (13)	4527 (4)	735 (7)	112 (4)
C(6)	9762 (10)	4546 (4)	1600 (10)	117 (5)
C(7)	9643 (9)	4392 (3)	2654 (7)	105 (3)
C(8)	8301 (10)	4263 (3)	2498 (8)	105 (4)
Na	5401 (2)	5947 (1)	5816 (2)	68 (1)
O(11)	7216 (5)	6584 (2)	7003 (4)	98 (2)
C(12)	7893 (11)	7041 (4)	6522 (8)	125 (4)
C(13)	8693 (17)	7428 (6)	7505 (10)	195 (8)
C(14)	8504 (15)	7205 (5)	8575 (9)	161 (6)
C(15)	7541 (9)	6694 (4)	8246 (7)	105 (3)
O(21)	3724 (7)	6720 (2)	5808 (5)	116 (3)
C(22)	2720 (11)	6899 (5)	4702 (12)	149 (6)
C(23)	2703 (22)	7580 (6)	4762 (16)	256 (11)
C(24)	2979 (19)	7716 (8)	5944 (16)	275 (11)
C(25)	3744 (16)	7190 (5)	6612 (12)	176 (7)

^a $U_{\text{eq}} = 1/3(\text{trace of the orthogonalized } U_{ij} \text{ matrix})$.

The reaction between InCl_3 and 1 equiv of $\text{Na}[\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$ afforded, after filtration and crystallization from THF/hexane, colorless crystals of the monomolybdenum complex, 8. Spectroscopic details are given in Table I, and the structure



was established by X-ray crystallography, the results of which

Table VIII. Crystallographic Data

compd	2	6	8
chem formula	C ₂₄ H ₁₅ InMo ₃ O ₉	C ₄₈ H ₅₂ Cl ₄ In ₂ Mo ₄ Na ₂ O ₁₆	C ₃₂ H ₄₂ Cl ₆ In ₂ Mo ₂ Na ₂ O ₁₀
fw	850.0	1686.1	1266.9
cryst color	yellow	pale yellow	colorless
cryst size, mm	0.5 × 0.5 × 0.5	0.4 × 0.4 × 0.5	0.2 × 0.4 × 0.5
cryst system	monoclinic	triclinic	monoclinic
space group	P2 ₁ /n	P $\bar{1}$	P2 ₁ /c
a, Å	11.463 (1)	10.750 (2)	10.160 (1)
b, Å	17.854 (1)	12.457 (2)	21.116 (2)
c, Å	13.572 (1)	13.609 (2)	11.862 (1)
α, deg		108.569 (7)	
β, deg	101.846 (8)	95.829 (7)	109.304 (7)
γ, deg		112.248 (6)	
V, Å ³	2718.5	1546.9	2401.8
Z	4	1	2
d _{calc} , g cm ⁻³	2.077	1.810	1.752
μ, mm ⁻¹	2.19	1.74	1.83
F(000)	1624	824	1240
2θ range, deg	3–50	3–45	3–50
index ranges:			
h	-13 to 13; 9 to 13	-11 to 11	-12 to 12; -12 to -3
k	0 to 21; -21 to 0	-13 to 13	0 to 25; -25 to 0
l	0 to 16; -16 to 0	0 to 14	0 to 14; -14 to 0
no. of reflns measd	5280	4043	5798
no. of unique reflns	4803	4043	4240
no. of reflns with F > 4σ _c (F)	4289	3707	2798
transmission factors	0.208–0.325	0.633–0.738	0.489–0.598
R _{int}	0.024		0.017
weighting: A ₁ , A ₂ , A ₃ , A ₄ , A ₅ , A ₆	11, 56, 90, -29, 23, -106	12, -16, 29, -28, 17, 8	15, -20, 31, -35, 21, -11
R	0.0265	0.0258	0.0288
R _w	0.0257	0.0246	0.0271
S	1.16	1.08	1.02
no. of params	335	344	245
shift/esd: max, mean	0.009, 0.002	0.080, 0.015	0.030, 0.008
extinction param x	8.2 (6) × 10 ⁻⁷	1.44 (8) × 10 ⁻⁶	2.0 (2) × 10 ⁻⁷
max, min in diff map, e Å ⁻³	0.53, -0.56	0.37, -0.29	0.40, -0.27

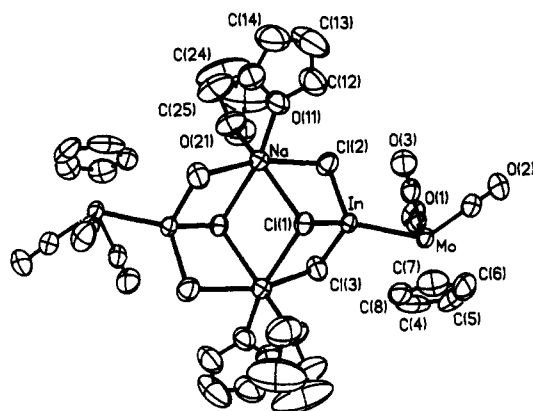


Figure 5. Molecular structure of 8, showing the atom-numbering scheme adopted.

are shown in Figure 5. Selected bond distance and angle data are given in Table VI, and atomic positional parameters are presented in Table VII.

A similar situation is revealed for 8 as was observed for 6 in that NaCl elimination has not occurred. The molecule is dimeric and resides on a crystallographic center of inversion. Each molybdenum is bonded to a cyclopentadienyl ligand, three carbonyls, and an indium trichloride group, which constitute the formally anionic part of the molecule, viz [InCl₃Mo(CO)₃(η-C₅H₅)]⁻. The counteranion is sodium, each of these being coordinated to four chlorine atoms (two from each of the MoIn anions) and two THF molecules in an approximately octahedral environment as shown in Figure 5 and the diagram. The geometries around the molybdenum and indium atoms are "four-legged piano stool" and tetrahedral, respectively.

The anionic part of 8 may be viewed as a Lewis acid-base adduct comprising [Mo(CO)₃(η-C₅H₅)]⁻ and InCl₃, and in this regard, comparison with a report by Burlitch et al.¹⁵ is appropriate,

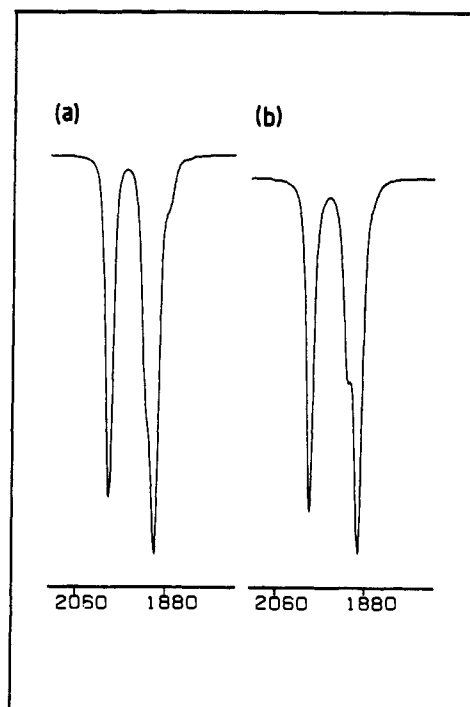


Figure 6. Solution infrared spectra in the carbonyl stretching region for 8: (a) THF; (b) MeCN.

in which a similar interaction involving [W(CO)₃(η-C₅H₅)]⁻ and InPh₃ is described.

Infrared spectra of 8 obtained in THF (Figure 6 and Table I) showed two strong absorptions at 1994 and 1903 cm⁻¹ consistent with the Mo–In bond remaining intact in this solvent. Moreover,

(15) Burlitch, J. M.; Petersen, R. B. *J. Organomet. Chem.* 1970, 24, C65.

spectra obtained in MeCN were essentially identical (Figure 6 and Table I) and showed no sign of any absorption at about 1777 cm^{-1} (attributable to the anion, $[\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]^-$) and, hence, any detectable degree of dissociation.

Thus, infrared data in MeCN for **2**, **6**, and **8** reveal that for **2** nearly complete dissociation (i.e. molybdenum-indium bond heterolysis) occurs, whereas for **6** dissociation is only partial and for **8** it is negligible. In THF, dissociation is only observed for **2**. The most obvious explanation for these observations is that the Lewis acidity of the indium center increases as the number of attached chlorines increases, i.e. $\mathbf{8} > \mathbf{6} > \mathbf{2}$, and therefore the molybdenum-indium bonds become stronger and less labile. Consistent with this view are the observed Mo-In bond lengths in the three complexes, viz. average Mo-In = 2.739 \AA in **8**, average Mo-In = 2.850 \AA in **6**, and Mo-In = 2.878 \AA in **2**, which become progressively longer as the number of chlorine atoms decreases.

Details of the analogous tungsten complex, **9**, are presented in Table I, and these data indicate that **8** and **9** are similar in all respects.

Mays⁸ has also reported the reaction that produces **8**, though not **9**, but as with **6**, the formula is given as the NaCl-free, neutral compound $[\text{InCl}_2\{\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)\}]$. As discussed for **6**, the reasons for this difference are probably a result of the crystallization procedures used.

Experimental Section

General Procedures. All experiments were performed by using standard Schlenk techniques under an atmosphere of dry oxygen-free dinitrogen. All solvents were freshly distilled over appropriate drying agents immediately prior to use. ^1H and ^{13}C NMR spectra were recorded on a Bruker WP200 spectrometer operating at 200.13 and 50.324 MHz, respectively. Infrared spectra were recorded on a Nicolet 20 SXB FTIR spectrophotometer, and mass spectra were obtained on Kratos MS9 and MS80 instruments. Microanalytical data were obtained at the University of Newcastle.

Indium trichloride was procured commercially and used without purification. The cyclopentadienyl-metal carbonyl dimers, $[\text{M}_2(\text{CO})_6(\eta\text{-C}_5\text{H}_5)_2]$ (M = Mo, W) were prepared by the method of Manning et al.¹⁶ Infrared and ^1H and ^{13}C NMR data for all the complexes described are presented in Table I.

Preparation of $[\text{In}\{\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)\}_3]$ (2**).** The method used was similar to one described by Mays et al.⁸ A stirred solution of $\text{Na}[\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$, derived from a sodium amalgam reduction of $[\text{Mo}_2(\text{CO})_6(\eta\text{-C}_5\text{H}_5)_2]$ (0.567 g, 1.16 mmol), in THF (10 mL) was cooled to $-78\text{ }^\circ\text{C}$ and maintained at this temperature. To this was added a solution of InCl_3 (0.171 g, 0.77 mmol) in THF (10 mL) over a period of a few minutes with continuous stirring. During addition, a marked deepening of the yellow color was observed together with the formation of a gray precipitate. After complete addition, the reaction mixture was allowed to warm to room temperature and was stirred for a further 30 min. Filtration through Celite, followed by removal of all volatiles, afforded a yellow oil, which was redissolved in the minimum of THF (5 mL). Yellow rodlike crystals were obtained by solvent diffusion from THF/hexane mixtures at $-20\text{ }^\circ\text{C}$. These crystals proved unsuitable for X-ray diffraction since, on removal of the mother liquor, they rapidly became opaque and lost crystallinity. However, suitable platelike single crystals of **2** were obtained from CH_2Cl_2 /hexane mixtures.

The tungsten complex, **5**, was synthesized in an analogous manner from $\text{Na}[\text{W}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$. However, recrystallized yields from either THF/hexane or CH_2Cl_2 /hexane mixtures were substantially less than those obtained with the molybdenum system. Satisfactory microanalytical data on both complexes were obtained for crystals isolated from CH_2Cl_2 /hexane.

Anal. Calcd for $\text{C}_{24}\text{H}_{15}\text{O}_9\text{Mo}_3\text{In}$ (**2**): C, 33.9; H, 1.8. Found: C, 33.9; H, 1.6. Calcd for $\text{C}_{24}\text{H}_{15}\text{O}_9\text{W}_3\text{In}$ (**5**): C, 25.9; H, 1.4. Found: C, 25.7; H, 1.2.

Electron impact mass spectra for **2** did not reveal a molecular ion but showed a signal centered at m/e 768 corresponding to the fragment $\text{InMo}_2(\text{CO})_6(\text{C}_5\text{H}_5)_3$, i.e. $\text{P} - 3\text{CO}$. Additional signals were observed as follows: m/e 712, $\text{P} - 5\text{CO}$; m/e 656, $\text{P} - 7\text{CO}$; m/e 628, $\text{P} - 8\text{CO}$; m/e 600, $\text{P} - 9\text{CO}$; m/e 605, $\text{P} - \text{Mo}(\text{CO})_3(\text{C}_5\text{H}_5)$; m/e 549, $\text{P} - \text{Mo}(\text{C}-\text{O})_3(\text{C}_5\text{H}_5) - 2\text{CO}$. The highest mass signal observed in spectra obtained by FAB was centered at m/e 605, $\text{P} - \text{Mo}(\text{CO})_3(\text{C}_5\text{H}_5)$, corresponding

to the fragment $\text{InMo}_2(\text{CO})_6(\text{C}_5\text{H}_5)_2$. This latter result obtained by FAB is not surprising since the sample was prepared from a THF solution of **2** in which solvent partial dissociation is known to occur (see text).

Similar EI spectra were obtained for **5**, the highest mass signal being centered at m/e 1031, corresponding to $\text{P} - 3\text{CO}$, i.e. $\text{InW}_3(\text{CO})_6(\text{C}_5\text{H}_5)_3$. Additional signals were observed as follows: m/e 919, $\text{P} - 7\text{CO}$; m/e 891, $\text{P} - 8\text{CO}$; m/e 863, $\text{P} - 9\text{CO}$; m/e 781, $\text{P} - \text{W}(\text{CO})_3(\text{C}_5\text{H}_5)$.

Preparation of $[\text{Na}(\text{THF})_2][\text{InCl}_2\{\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)\}_2]$ (6**).** The method used was similar to one described by Mays et al.⁸ A solution of 2 equiv of $\text{Na}[\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$ (0.403 g of $[\text{Mo}_2(\text{CO})_6(\eta\text{-C}_5\text{H}_5)_2]$, 0.82 mmol, Na/Hg reduction) in THF (20 mL) was added to a stirred solution of InCl_3 (0.182 g, 0.82 mmol) in THF (10 mL) at room temperature and the reaction mixture allowed to stir for 30 min. Filtration through Celite followed by removal of all volatiles afforded a yellow-brown oil. This was redissolved in the minimum of THF (5 mL), and block yellow crystals of **6** were obtained by solvent diffusion from THF/hexane mixtures at $-20\text{ }^\circ\text{C}$.

Yellow crystals of the tungsten complex, **7**, were produced in an analogous manner. Satisfactory microanalytical data for **6** and **7** were not obtained since crystals of both compounds lose THF slowly when they are removed from the mother liquor.

Both EI and FAB mass spectra obtained for **6** showed signals centered at m/e 605, corresponding to the fragment $\text{InMo}_2(\text{CO})_6(\text{C}_5\text{H}_5)_2$, as the highest mass peaks. More informative EI spectra were obtained for **7** that revealed a signal centered at m/e 815 corresponding to $\text{InClW}_2(\text{C}-\text{O})_6(\text{C}_5\text{H}_5)_2$, i.e. $\text{7} - \text{Cl}$. Additional signals were observed as follows: m/e 780, $\text{7} - 2\text{Cl}$; m/e 724, $\text{7} - 2\text{Cl} + 2\text{CO}$; m/e 787, $\text{7} - \text{Cl} + \text{CO}$; m/e 759, $\text{7} - \text{Cl} + 2\text{CO}$; m/e 703, $\text{7} - \text{Cl} + 4\text{CO}$.

Preparation of $[\text{Na}(\text{THF})_2][\text{InCl}_3\{\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)\}]$ (8**).** Compound **8** and the analogous tungsten complex, **9**, were synthesized in a manner identical with that described for **6** except that only 1 equiv of the metal carbonylate anion was used. Colorless crystals of both compounds were obtained from THF/hexane at $-20\text{ }^\circ\text{C}$ but, as with **6** and **7**, these slowly lose THF. Satisfactory microanalytical data were therefore not obtained.

All compounds were obtained in high yield (>70%), such yields being reported by Mays et al.⁸

X-ray Crystallographic Studies. Crystals of **2** were stable in air, but those of **6** and **8** were sealed under dinitrogen in Lindemann glass capillaries for diffraction studies. All measurements were made at room temperature (295 K) on a Siemens AED2 diffractometer with graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). Cell parameters were obtained by least-squares refinement from 2θ values of 32 reflections ($20 < 2\theta < 25^\circ$) measured on both sides of the direct beam to minimize systematic errors. Intensity data were collected in an ω/θ scan mode with on-line profile fitting.¹⁷ Three standard reflections showed no significant variation in intensity for **2** and **8**, but for **6** a rapid decrease was observed: data were collected at high speed (measurements completed in under 24 h), with no symmetry-equivalent reflections included, and were corrected for decay on the basis of the standard reflection intensities, which declined to ca. 45% of their initial values.

Semiempirical absorption corrections were applied, based on sets of equivalent reflections measured at a range of azimuthal angles.¹⁸ Extinction was treated by refinement of an isotropic factor x such that $F_c' = F_c / (1 + xF_c^2 / \sin 2\theta)^{1/4}$. The structures were solved by heavy-atom methods and refined by blocked-cascade least squares to minimize $\sum w\Delta^2$, with $\Delta = |F_o| - |F_c|$. The weighting scheme was $w^{-1} = \sigma_c^2(F) + A_1 + A_2G + A_3G^2 + A_4S + A_5S^2 + A_6GS$ ($G = F_o/F_{\text{max}}$, $S = \sin \theta / \sin \theta_{\text{max}}$) with A_n derived from an analysis of variance and $\sigma_c(F)$ from counting statistics only.¹⁹ Hydrogen atoms were included with the following constraints: C-H = 0.96 \AA , H-C-H = 109.5° for THF, H's placed on ring angle external bisectors for Cp, $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, where U_{eq} is the equivalent isotropic thermal parameter. Anisotropic thermal parameters were refined for all non-H atoms. Scattering factors were taken from ref 20.

Details of the data collection and structure determination are given in Table VIII.

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funds.

Registry No. 2, 37206-38-5; 5, 37206-39-6; 6, 114942-22-2; 7, 114942-26-6; 8, 114942-24-4; 9, 114942-28-8; Na[Mo(CO)₃(η⁵-C₅H₅)], 12107-35-6; InCl₃, 10025-82-8; Na[W(CO)₃(η⁵-C₅H₅)], 12107-36-7.

Supplementary Material Available: Tables S1-S12, listing complete bond lengths and angles, anisotropic thermal parameters, and hydrogen atom parameters (11 pages); tables of observed and calculated structure factors and esd's (54 pages). Ordering information is given on any current masthead page.

Contribution from the Institut de Chimie, Université de Neuchâtel, CH-2000 Neuchâtel, Switzerland, Laboratorium für Elektronenmikroskopie, Universität Bern, CH-3000 Bern 9, Switzerland, and Department of Chemistry, Monash University, Clayton, Victoria 3168, Australia

Hydrolytic Trimer of Chromium(III). Synthesis through Chromite Cleavage and Use in the Preparation of the "Active" Trimer Hydroxide

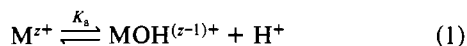
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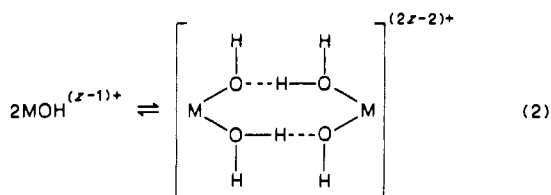
Acidification of chromite solutions, prepared by addition of OH⁻ to Cr³⁺ (pH >13), generates a homogeneous mixture containing several oligomers, which in acid are slowly cleaved into monomer, dimer, and trimer. After 27 h of acid cleavage the hydrolytic trimer (65% of total Cr) predominates over the monomer (15%), dimer (16%), and higher oligomers (4%). The greater stability of the trimer compared with that of the other oligomers is interpreted in terms of a compact structure. Alkalinization of the trimer, Cr₃(μ-OH)₄(OH)₂³⁺, results in the formation of a finely dispersed light green precipitate of the "active" trimer hydroxide. Chromium and thermogravimetric analyses are consistent with the composition [Cr₃(μ-OH)₄(OH)₂(OH₂)₄]·4H₂O. Dissolution in acid regenerates >90% of the original trimer, the difference being made up of hexamer and higher oligomers that, in acid, cleave back into trimer. This suggests that the hydroxide consists predominantly of unaltered trimer units. The IR spectrum indicates that these units are linked through H-bonds of ca. 2.9 Å. X-ray powder diffraction patterns and electron micrographs were also recorded. In aqueous suspension, "active" trimer hydroxide is readily transformed into higher oligomers. The aging profile exhibits minima at pH 5.5-5.7 and 11-11.8 and a distinct maximum at pH ≈8.2. For pH ≤8.2, the aging profile closely resembles that of the "active" dimer hydroxide although the "active" trimer hydroxide ages more rapidly. For pH >8.2, a reduction in aging rate, at present unique to this hydroxide, is observed. The aging process is proposed to occur predominantly through the release of trimer into solution and polymerization in solution, followed by adsorption of polynuclears onto the surface of the solid "active" hydroxide phase.

Introduction

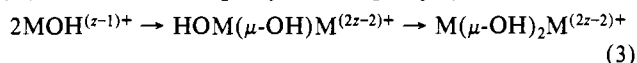
The precipitation of metal hydroxides may be envisaged to result from a combination of the following processes (H₂O ligands are omitted for clarity):⁴⁻⁷ (i) deprotonation of the aqua ions



(ii) intermolecular association of conjugate bases through H-bonding

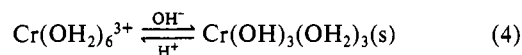


(iii) substitution of H₂O by OH⁻ to give polynuclears



For labile metal centers, such as Fe(III), the H-bonded forms (eq 2) are expected to have only transient existence since deprotonation (eq 1) leads, initially, to the rapid formation of the hydrolytic dimer (eq 3)⁵ followed by further substitution to give species of increasingly higher nuclearity and eventually to the precipitation of metal hydroxides. Since many different species coexist in solution at the same time, hydrolytic polymerization proceeds by a complicated mechanism and, as a consequence, these initial precipitates are usually amorphous. Such hydroxides, however, are often metastable, leading to the formation of microcrystalline phases when aged in contact with the mother liquor.^{5,6}

For kinetically inert metal centers, such as Cr(III), substitution rates are many orders of magnitude slower than either deprotonation (eq 1) or association (eq 2) reactions. Furthermore, in dilute Cr³⁺ solutions, the concentration of H-bonding aggregates (eq 2) is likely to be small since this type of stabilization cannot compete with the more efficient H-bonding interactions between the solvent and the deprotonated metal ion.⁷ While the Cr(bpy)₂(OH)(OH₂)²⁺ complex is not a true aqua ion, three phase vapor tensiometry studies have demonstrated the concentration-dependent nature of different intermolecular H-bonding interactions. Thus, for [Cr(III)] < 5 × 10⁻⁴ M monomeric Cr(bpy)₂(OH)(OH₂)²⁺ predominates while for [Cr(III)] > 0.1 M significant amounts of the dimer (bpy)₂Cr(H₃O₂)₂Cr(bpy)₂⁴⁺, corresponding to eq 2 above, are present. A classical example of H-bonding aggregation in the solid state is the "active" monomer hydroxide,⁸ which forms upon alkalinization of Cr³⁺ to pH >5 (eq 4). This hydroxide has a layer structure in which Cr(III)



octahedra are linked solely through H-bonding between OH⁻ and H₂O ligands of adjacent metal centers. As a foreseeable consequence of this structure, acidification of this hydroxide leads to

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