Synthetic and Structural Studies on Organoruthenium–Indium Complexes†

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The synthesis and X-ray crystal structure of the triruthenium–indium complex $[In\{Ru(CO)_2(\eta-C_5H_5)\}_3]$ **1** are described. Complex **1** comprises a trigonal-planar indium centre bonded to three $Ru(CO)_2(\eta-C_5H_5)$ fragments by unsupported In–Ru bonds. The magnitude of the In–Ru bond lengths are discussed with respect to π bonding *vs.* ionic bonding in this and related compounds, and the possibility of π bonding is also addressed with regard to the orientations of the $Ru(CO)_2(\eta-C_5H_5)$ fragments in **1**. The syntheses of the diruthenium complexes $[InCl\{Ru(CO)_2(\eta-C_5H_5)\}_2]$ and $[N(PPh_3)_2][InCl_2\{Ru(CO)_2(\eta-C_5H_5)\}_2]$ are also described together with the X-ray crystal structure of the former.

As part of our interest in compounds with transition-metal to main-group metal bonds, we have recently described the synthesis and structural characterisation of a range of organoiron indium and gallium complexes containing the $Fe(CO)_2(\eta-C_5H_5)$ fragment.[1–4] Herein we report synthetic and structural details on some related ruthenium compounds.

Results and Discussion

The reaction between $InCl_3$ and three equivalents of Na/K-$[Ru(CO)_2(\eta-C_5H_5)]$ afforded, after work-up, orange crystals of the triruthenium–indium complex $[In\{Ru(CO)_2(\eta-C_5H_5)\}_3]$ **1**. Compound **1** was characterised by normal spectroscopic and analytical methods (Table 1), the infrared spectrum being especially informative due to its similarity to the related compounds, $[E\{Fe(CO)_2(\eta-C_5H_5)\}_3]$ (E = Ga **2** or In **3**). A tetrahydrofuran (thf) solution infrared spectrum for **1** is shown in Fig. 1(*a*) [*cf.* ref. 3, Fig. 1(*a*) for **2** and ref. 1, Fig. (*a*) for **3**].

The precise structure of **1** was established by X-ray crystallography. Compound **1** crystallises with two molecules in the asymmetric unit and a view of molecule 1 is shown in Fig. 2. Selected bond lengths and angles are listed in Table 2 and atomic positional parameters are given in Table 3. The two crystallographically independent molecules are similar and contain a three-co-ordinate, trigonal-planar indium centre (sum of angles, 359.7° for molecule 1 and 359.8° for molecule 2) bonded to three $Ru(CO)_2(\eta-C_5H_5)$ fragments through unsupported In–Ru bonds. As such, they are analogous to other structurally characterised complexes of the general formula $[In(ML_n)_3]$.[4,5]

The In–Ru bond lengths average 2.671 Å; we are not aware of any previous such bonds for comparison. A calculated In–Ru single-bond distance based on the covalent radius of indium (1.414 Å from the structure of $[In_2\{CH(SiMe_3)_2\}_4]$[6] which contains three-co-ordinate In) and ruthenium (1.367 Å from $[Ru_2(CO)_4(\eta-C_5H_5)_2]$[7]) is 2.781 Å and so the bond lengths in **1** are apparently somewhat shortened. We made a similar comment[8] with regard to the In–Mo bond lengths in $[In\{Mo(CO)_3(\eta-C_5H_5)\}_3]$ **4** which are around 2.85–2.89 Å[5,8] compared with a calculated distance of 3.06 Å[8] and originally ascribed this presumed bond shortening[8] to the presence of π bonding between filled Mo-based d orbitals and the vacant indium 5p orbital. In subsequent extended Hückel molecular orbital calculations, however,[5] we showed that π bonding was likely to be of only minor importance in these compounds due to the large separation in energy between the In p and Mo d orbitals; in fact the bonding in compounds of the type $[In(ML_n)_3]$ is probably largely ionic and may be represented, at least in part, as $[In]^{3+}3[ML_n]^-$. Consistent with this view, particularly for **4**, is the ready dissociation which occurs in basic solvents and the low-frequency CO absorptions for the $Mo(CO)_3(\eta-C_5H_5)$ fragments due to the build up of negative charge at the Mo centre.[5] The *apparent* bond shortening in these complexes is, therefore, probably due to this degree of ionic character rather than any π bonding. In this regard, we

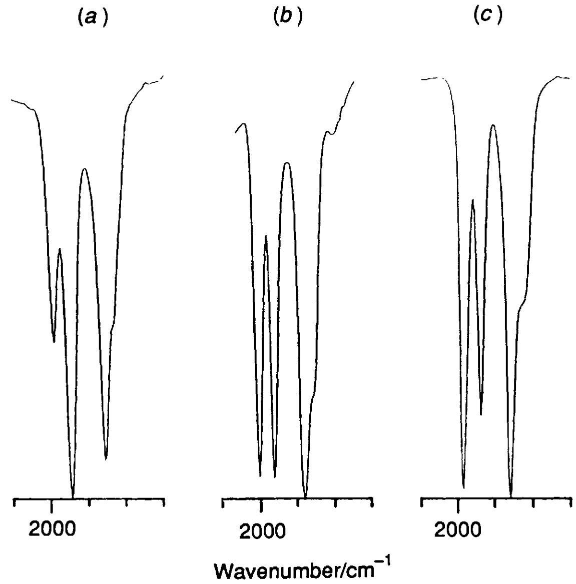

Fig. 1 Solution infrared spectra in the carbonyl stretching region obtained in thf in CaF_2 cells for complexes **1** (*a*), **6** (*b*) and **8** (*c*)

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Spectroscopic and analytical data for the complexes

Compound	$\nu(CO)$[a]/cm^{-1}	Analysis[b] (%) C	H
1 [In{Ru(CO)$_2$(η-C$_5$H$_5$)}$_3$]	1995m, 1970s, 1926s 1995m, 1970s, 1922s[c] 1997m, 1976s, 1927s[d] 1996m, 1976s, 1927s[e]	32.10 (32.30)	1.75 (1.95)
6 [InCl{Ru(CO)$_2$(η-C$_5$H$_5$)}$_2$]	2000s, 1981s, 1940s	28.95 (28.30)	1.55 (1.70)
8 [N(PPh$_3$)$_2$][InCl$_2${Ru(CO)$_2$(η-C$_5$H$_5$)}$_2$]	1994s, 1970m, 1929s	51.90 (51.40)	3.20 (3.45)[f]

[a] Measured in thf solution. [b] Calculated values in parentheses. [c] Measured in MeCN solution. [d] Measured in CH$_2$Cl$_2$ solution. [e] Measured in toluene solution. [f] Nitrogen analysis, 1.25 (1.20)%.

Table 2 Selected bond lengths (Å) and angles (°) for complex **1**

Molecule 1		Molecule 2	
In(1)–Ru(11)	2.671(1)	In(2)–Ru(12)	2.671(1)
In(1)–Ru(21)	2.685(1)	In(2)–Ru(22)	2.663(1)
In(1)–Ru(31)	2.671(1)	In(2)–Ru(32)	2.668(1)
Ru(11)–In(1)–Ru(21)	117.0(1)	Ru(12)–In(2)–Ru(22)	119.2(1)
Ru(11)–In(1)–Ru(31)	123.2(1)	Ru(12)–In(2)–Ru(32)	120.8(1)
Ru(21)–In(1)–Ru(31)	119.5(1)	Ru(22)–In(2)–Ru(32)	119.8(1)

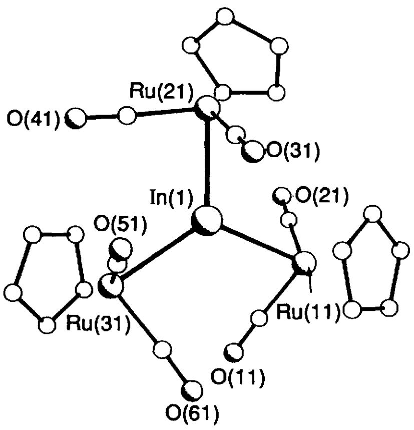

Fig. 2 A view of the molecular structure of molecule 1 of compound **1** showing the atom numbering scheme. Hydrogen atoms omitted for clarity

note a recent and comprehensive discussion of this matter (*i.e.* π bonding *vs.* ionic character as a reason for *apparent* bond shortening) by Power and co-workers[9] whilst dealing with the observed Al–O and Ga–O bond lengths in three-co-ordinate aluminium and gallium alkoxides. As a final point regarding bond distances, we note that the In–Mo bonds in **4** are about 0.2 Å longer than the In–Ru bonds in **1**. *Part* of this difference is almost certainly steric in origin (the covalent radii of Mo and Ru are unlikely to differ by more than about 0.02 Å). In **4** there are close intramolecular contacts between some of the carbonyl oxygens and the hydrogens on the C$_5$H$_5$ rings of adjacent Mo(CO)$_3$(η-C$_5$H$_5$) fragments.[5] These close contacts, which are absent in **1**, undoubtedly lead to a lengthening of the In–Mo bonds. However, we note that In–Mo bond lengths are generally about 2.85 ± 0.03 Å[5,8] with the exception of that in [InCl$_3${Mo(CO)$_3$(η-C$_5$H$_5$)}]$^-$ [8] (2.739 Å) which, although significantly shorter, is still longer than the In–Ru bonds in **1**.

One of the reasons that we were tempted to postulate π bonding in **4** was that the orientations of the Mo(CO)$_3$(η-C$_5$H$_5$) fragments with respect to the InMo$_3$ plane were such as to maximise any such interaction.[5,8] If π bonding were important in **1** then we might expect a similar orientational preference for the Ru(CO)$_2$(η-C$_5$H$_5$) fragment as it has been shown by Hoffmann and co-workers[10] that the better π-donor orbital in the M(CO)$_2$(C$_5$H$_5$) moiety is the one which lies orthogonal to the fragment symmetry plane. Thus in order to maximise π bonding between Ru and the vacant In 5p orbital, the symmetry planes of the Ru fragments would have to be coplanar with the InRu$_3$ plane such that the angle between the In–Ru–C$_5$H$_5$ centroid and InRu$_3$ planes be 0°. In **1** the relevant angles for the two independent molecules are Ru(11) 68.8, Ru(21) 45.0, Ru(31) 75.5 and Ru(12) 71.7, Ru(22) 47.9, Ru(32) 77.9°. On this basis it is clear that there is little orientational preference as a result of electronic factors and thus, by implication, that π-bonding effects are relatively unimportant.

Finally, it is instructive to compare the structure of **1** with the related and isoelectronic compounds [Ga{Fe(CO)$_2$(η-C$_5$H$_5$)}$_3$] **2**[3] and [Te{Mn(CO)$_2$(η-C$_5$H$_5$)}$_3$] **5**.[11] Compound **2**, whilst not isomorphous with **1**, is nearly isostructural and has interplanar angles, defined as for **1**, of 73.5, 57.9 and 73.7°. For complex **5**, however, the angles are quite different: 84.9, 16.6 and 16.4° (see ref. 3 for a prior discussion of this point and relevant diagrams). The latter two angles are not too far from the idealised value of 0° which would maximise any π bonding and the third would enable an interaction between the second orbital of π symmetry on the Mn(CO)$_2$(η-C$_5$H$_5$) fragment, albeit the one of lower energy.[10] These data indicate that π bonding *may* be more important in the tellurium complex but this should not be unexpected in view of the greater electronegativity of tellurium *vs.* indium or gallium and hence the closer match in energy between the 5p orbital and the transition-metal based orbitals. We have already commented on the similarity of the solution infrared spectra of **1** and **3** (**2** is also similar). The reported infrared spectrum for **5** is rather different [ν(CO) (Et$_2$O) 1998m, 1992m(sh), 1940s, 1928vs, 1909m, 1886w] and indicates that these conformational differences may be maintained in solution.

The complex [InCl{Ru(CO)$_2$(η-C$_5$H$_5$)}$_2$] **6** was prepared from the reaction between InCl$_3$ and 2 equivalents of Na/K[Ru(CO)$_2$(η-C$_5$H$_5$)] in thf solution. Analytical and spectroscopic data for **6** are presented in Table 1 and are consistent with the formula given. In particular, we note the similarity between the infrared spectrum of **6** [Fig. 1(*b*)] and that of the related iron complex [InCl{Fe(CO)$_2$(η-C$_5$H$_5$)}$_2$] **7** [see ref. 2, Fig. 1(*a*)].[2] The structure of **6** was confirmed by X-ray crystallography the results of which are shown in Fig. 3. Selected bond lengths and angles are given in Table 4 and atomic positional parameters are presented in Table 5. Crystals of **6** are isomorphous with **7** and contain centrosymmetric, chloro-bridged dimeric molecules. The In–Ru bond distances are 2.6278(5) and 2.6300(4) Å, which are slightly shorter than those found in **1**, but in all other respects, the description given for the structure of **7** in ref. 2 is adequate and will not be repeated here. One point which was made in ref. 2 concerned the conformations about the In–Fe bonds of **7** and a comparison was made with the isoelectronic manganese–bismuth complex, [{BiCl[Mn(CO)$_2$(η-C$_5$H$_5$)]$_2$}$_2$]. Possible electronic reasons were suggested but a closer look at space-filling models of all

Table 3 Atomic coordinates (× 10^4) for complex **1**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Molecule 1				Molecule 2			
In(1)	934.3(3)	2 300.4(2)	8 026.3(2)	In(2)	2 863.0(3)	7 573.8(2)	6 999.8(2)
Ru(11)	2 180.7(3)	2 352.2(3)	6 639.3(2)	Ru(12)	4 165.6(3)	7 627.5(3)	8 299.9(2)
Ru(21)	−1 735.7(3)	3 065.2(3)	7 809.1(2)	Ru(22)	759.9(4)	7 011.9(3)	7 258.7(2)
Ru(31)	2 196.4(3)	1 734.7(3)	9 555.7(2)	Ru(32)	3 759.6(3)	7 920.8(3)	5 485.1(2)
O(11)	4 640(4)	716(4)	7 790(3)	O(12)	5 152(5)	9 108(3)	6 964(3)
O(21)	1 273(4)	659(3)	6 500(2)	O(22)	1 714(4)	9 436(3)	8 365(2)
O(31)	−1 343(5)	5 089(3)	7 569(4)	O(32)	2 843(5)	4 785(3)	7 854(3)
O(41)	−1 707(4)	2 628(5)	9 681(3)	O(42)	636(5)	7 095(5)	5 460(2)
O(51)	566(4)	3 972(3)	9 452(3)	O(52)	3 960(6)	5 701(3)	5 690(3)
O(61)	4 330(4)	2 454(3)	8 710(2)	O(62)	6 503(4)	7 035(5)	6 391(3)
C(11)	3 674(5)	1 338(4)	7 360(3)	C(12)	4 749(5)	8 560(4)	7 476(3)
C(21)	1 611(5)	1 296(4)	6 572(3)	C(22)	2 638(5)	8 758(4)	8 322(3)
C(31)	−1 476(5)	4 321(4)	7 646(4)	C(32)	2 062(6)	5 658(4)	7 608(3)
C(41)	−1 691(5)	2 796(5)	8 968(3)	C(42)	704(6)	7 064(5)	6 143(3)
C(51)	1 184(5)	3 117(4)	9 482(3)	C(52)	3 894(6)	6 538(4)	5 625(3)
C(61)	3 493(4)	2 206(3)	9 012(3)	C(62)	5 430(5)	7 357(5)	6 074(3)
C(71)	1 280(6)	4 129(4)	6 359(3)	C(72)	4 920(6)	5 821(4)	8 724(3)
C(81)	2 652(5)	3 828(4)	6 308(3)	C(82)	6 019(5)	6 126(4)	8 705(3)
C(91)	2 969(6)	3 442(5)	5 629(3)	C(92)	5 911(6)	6 623(5)	9 319(3)
C(101)	1 782(6)	3 480(4)	5 277(3)	C(102)	4 747(6)	6 637(5)	9 685(3)
C(111)	732(5)	3 895(4)	5 723(3)	C(112)	4 117(5)	6 149(4)	9 314(3)
C(121)	−1 688(5)	1 754(4)	7 344(3)	C(122)	−242(5)	8 452(4)	7 650(3)
C(131)	−1 797(5)	2 664(4)	6 630(3)	C(132)	233(5)	7 519(4)	8 380(3)
C(141)	−3 014(6)	3 476(5)	6 602(3)	C(142)	−452(6)	6 867(4)	8 367(3)
C(151)	−3 687(5)	3 103(5)	7 292(3)	C(152)	−1 349(5)	7 374(5)	7 617(3)
C(161)	−2 869(6)	2 052(5)	7 751(3)	C(162)	−1 201(5)	8 335(4)	7 170(3)
C(171)	2 952(5)	−51(3)	9 889(3)	C(172)	3 148(6)	9 702(5)	5 053(3)
C(181)	1 557(5)	314(3)	9 890(3)	C(182)	1 972(5)	9 477(4)	5 094(3)
C(191)	1 245(5)	765(4)	10 522(3)	C(192)	1 987(5)	8 970(4)	4 505(3)
C(201)	2 438(5)	668(4)	10 933(3)	C(202)	3 157(5)	8 899(4)	4 077(3)
C(211)	3 492(4)	160(3)	10 532(3)	C(212)	3 850(6)	9 348(5)	4 446(3)

Table 4 Selected bond lengths (Å) and angles (°) for complex **6**

In(1)–Ru(1)	2.6278(5)	In(1)–Ru(2)	2.6300(4)
In(1)–Cl(1)	2.5967(9)	In(1)–Cl(1a)	2.7094(9)
Ru(1)–In(1)–Ru(2)	131.23(2)	Ru(1)–In(1)–Cl(1a)	105.79(2)
Ru(1)–In(1)–Cl(1)	112.80(2)	Ru(2)–In(1)–Cl(1a)	101.87(2)
Ru(2)–In(1)–Cl(1)	110.79(2)	Cl(1)–In(1)–Cl(1a)	80.52(3)
In(1)–Cl(1)–In(1a)	99.48(3)		

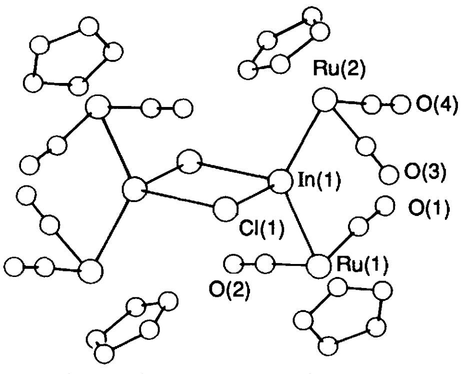

Fig. 3 A view of the molecular structure of compound **6** showing the atom numbering scheme. Hydrogen atoms omitted for clarity

three structures indicates that the observed conformations may well be the ones which allow the most efficient packing of the M(CO)$_2$(η-C$_5$H$_5$) fragments about the E$_2$X$_2$ core.

In ref. 2 we reported an alternative preparation of **7** from InCl and [Fe$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$]. The corresponding reaction between InCl and [Ru$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$], however, did not afford measurable amounts of **6**; rather we observed only unreacted starting material and traces of [RuCl(CO)$_2$(η-C$_5$H$_5$)]. This is consistent with an observation we have made before whereby indium monohalide insertion reactions into M–M bonds occur most readily for first-row transition metals and become progressively more difficult for second- and third-row metals.[12] This presumably reflects the increasing strength of M–M bonds as transition-metal triads are descended.

The reaction between **6** and [N(PPh$_3$)$_2$]Cl afforded the ionic complex [N(PPh$_3$)$_2$][InCl$_2${Ru(CO)$_2$(η-C$_5$H$_5$)}$_2$] **8** which also parallels the chemistry observed for the analogous iron complexes.[2] Data for **8** are given in Table 1 and Fig. 1(*c*).

Experimental

General Considerations.—All experiments were performed under an atmosphere of 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 on a Nicolet 20 SXB FTIR spectrophotometer and microanalytical data were obtained at the University of Newcastle. Proton NMR spectra were obtained on a Bruker WP 200 spectrometer operating at 200.13 MHz referenced to SiMe$_4$. The complex [Ru$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$] was prepared according to the method of Doherty and Knox,[13] all other reagents were procured commercially and used without further purification.

Analytical and infrared data for all new complexes are given in Table 1.

Preparations.—[In{Ru(CO)$_2$(η-C$_5$H$_5$)}$_3$] **1**. A stirred solution of Na/K[Ru(CO)$_2$(η-C$_5$H$_5$)], derived from a NaK alloy (1:1) (0.3 cm^3) reduction of [Ru$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$] (0.364 g, 0.819 mmol), in thf (20 cm^3) was cooled to 0 °C and maintained at this temperature. To this was added a solution of InCl$_3$ (0.121 g, 0.546 mmol) in thf (10 cm^3) over a period of a few minutes with continuous stirring. The resulting turbid, dark yellow-

Table 5 Atomic coordinates ($\times 10^4$) for complex **6**

Atom	*x*	*y*	*z*
In(1)	5 200.7(4)	6 141.9(2)	6 677.4(2)
Ru(1)	3 765.9(4)	8 628.6(3)	7 171.5(2)
Ru(2)	6 077.0(4)	4 635.2(3)	8 023.1(2)
Cl(1)	7 390.1(13)	5 469.1(8)	4 785.1(7)
O(1)	6 763(4)	9 601(3)	9 026(2)
O(2)	6 634(4)	9 106(3)	5 370(2)
O(3)	1 953(5)	5 484(4)	8 966(3)
O(4)	7 787(5)	7 079(3)	9 765(2)
C(1)	5 690(5)	9 179(4)	8 300(3)
C(2)	5 553(5)	8 902(3)	6 051(3)
C(3)	3 534(6)	5 159(4)	8 608(3)
C(4)	7 108(6)	6 177(4)	9 076(3)
C(11)	966(7)	9 673(6)	6 914(5)
C(12)	1 231(6)	9 934(5)	8 104(5)
C(13)	1 117(6)	8 693(5)	8 357(4)
C(14)	787(6)	7 663(4)	7 352(4)
C(15)	723(7)	8 246(5)	6 447(4)
C(21)	5 604(7)	2 418(4)	7 123(4)
C(22)	6 564(8)	2 528(4)	8 176(4)
C(23)	8 399(8)	3 117(4)	8 135(4)
C(24)	8 641(7)	3 381(4)	7 042(4)
C(25)	6 878(7)	2 935(4)	6 418(3)
H(11)	1 129(91)	10 170(60)	6 586(51)
H(12)	1 344(104)	10 786(72)	8 564(61)
H(13)	1 193(75)	8 526(50)	9 176(44)
H(14)	536(85)	6 688(60)	7 263(49)
H(15)	602(68)	7 897(44)	5 892(38)
H(21)	4 137(67)	2 144(44)	6 937(36)
H(22)	6 044(60)	2 273(40)	8 706(34)
H(23)	9 274(68)	3 283(44)	8 714(39)
H(24)	9 736(82)	3 805(54)	6 759(45)
H(25)	6 582(65)	2 971(43)	5 617(38)

brown reaction solution was allowed to warm to room temperature and stirring was continued for a further 1.5 h. Removal of the thf by vacuum gave an oily yellow-brown residue which was extracted in CH_2Cl_2 (30 cm^3) and filtered through Celite. The resulting dark orange filtrate was reduced in volume to about 5 cm^3 and layered with hexanes (30 cm^3). Solvent diffusion over a period of days at −30 °C afforded orange block-like crystals of **1** (65%). Crystals suitable for X-ray diffraction were obtained by solvent diffusion from 1,2-dichloroethane–hexane mixtures at −30 °C. ^1H NMR ([$^2H_6$]-acetone): δ 5.31 (C_5H_5). Mass spectrum: *m/z* 781 [In{Ru(CO)$_2$(η-C_5H_5)}$_3$, *P*], 753 (*P* − CO), 725 (*P* − 2CO), 697 (*P* − 3CO), 669 (*P* − 4CO), 641 (*P* − 5CO), 613 (*P* − 6CO), 560 [*P* − Ru(CO)$_2$(η-C_5H_5)], 531 [*P* − Ru(CO)$_2$(η-C_5H_5) − CO], 503 [*P* − Ru(CO)$_2$(η-C_5H_5) − 2CO] and 475 [*P* − Ru(CO)$_2$(η-C_5H_5) − 3CO].

[InCl{Ru(CO)$_2$(η-C_5H_5)}$_2$] **6**. A stirred solution of Na/K-[Ru(CO)$_2$(η-C_5H_5)] derived from a NaK alloy (1 : 1) (0.3 cm^3) reduction of [$Ru_2(CO)_4$(η-C_5H_5)$_2$] (0.299 g, 0.673 mmol) in thf (20 cm^3) was cooled to 0 °C and maintained at this temperature. To this was added a solution of $InCl_3$ (0.149 g, 0.673 mmol) in thf (10 cm^3) over a period of a few minutes with continuous stirring. The yellow-brown reaction solution was allowed to warm to room temperature and stir for a further 1.5 h. Removal of the thf by vacuum afforded an oily yellow-brown residue which was extracted with thf (20 cm^3) and filtered through Celite. The resulting dark yellow filtrate was reduced in volume to about 5 cm^3 and hexane (30 cm^3) was layered over this. Solvent diffusion over a period of days at −30 °C afforded yellow block-like crystals of **6** (50%). ^1H NMR ([$^2H_6$]acetone): δ 5.41 (C_5H_5). Mass spectrum: *m/z* 596 [InCl{Ru(CO)$_2$(η-C_5H_5)}$_2$, *P*], 561 (*P* − Cl) and 345 [*P* − Cl − Ru(CO)$_2$(η-C_5H_5)].

On *some* occasions we isolated small amounts of darker yellow crystals from this reaction which gave an infrared spectrum similar to **6** but with values at 2000s, 1979s, 1939s, 1927s cm^{-1}. It is likely, based on what we have observed before, that this is the ionic material Na/K[InCl$_2${Ru(CO)$_2$(η-C_5H_5)}$_2$].[8,14]

The diruthenium iodide complex [InI{Ru(CO)$_2$(η-C_5H_5)}$_2$] can also be prepared in an exactly analogous manner to **6** using InI_3, albeit with lower recrystallised yields of about 20% [ν(CO) 2002s, 1982m, 1944s cm^{-1}].

[N(PPh$_3$)$_2$][InCl$_2${Ru(CO)$_2$(η-C_5H_5)}$_2$] **8**. A yellow solution of **6** (0.069 g, 0.116 mmol) in thf (10 cm^3) was stirred with [N(PPh$_3$)$_2$]Cl (0.067 g, 0.116 mmol) until all the white solid had dissolved. The thf was then removed by vacuum and the residue redissolved in CH_2Cl_2 (4 cm^3) affording a yellow solution over which Et_2O (25 cm^3) was layered. Solvent diffusion over a period of days at −30 °C afforded pale yellow crystals of **8** (80%). ^1H NMR ([$^2H_6$]acetone): δ 7.85–7.52 (m, 30 H, PPh$_3$) and 5.26 (s, 10 H, C_5H_5).

X-Ray Crystallographic Studies.—Crystal data for compound **1**. $C_{21}H_{15}InO_6Ru_3$, M_r = 781.4, triclinic, space group $P\bar{1}$, a = 10.844(1), b = 14.364(2), c = 16.876(2) Å, α = 70.384(8), β = 88.808(8), γ = 68.889(8)°, U = 2295.1(4) Å^3, Z = 4, D_c = 2.261 g cm^{-3}, F(000) = 1480, μ(Mo-Kα) = 29.13 cm^{-1}, λ = 0.710 73 Å.

Data collection and reduction. Siemens R3m/V diffractometer with graphite monochromator, crystal size 0.28 × 0.32 × 0.38 mm, T = 200 K, 2θ range 4.0–52.0°. Index ranges: h 0 to 13, k −16 to 17, l −20 to 20, ω scan mode, variable scan speed; 2.93 to 29.30° min^{-1} in ω, scan range 1.20°; background measurement at beginning and end of scan, each for 25.0% of total scan time, two standard reflections measured every 100 reflections. Of 9066 measured unique reflections, 8084 with $F > 6.0\sigma(F)$ were used in structure determination. Data were corrected for Lorentz and polarisation effects and also for absorption (face-indexed numerical, transmission factors 0.3997–0.5287).

Structure solution and refinement.[15] The structure was solved by direct methods and refined by full-matrix, least squares minimizing the quantity $\Sigma w(F_o - F_c)^2$ and with a weighting scheme, $w^{-1} = \sigma^2(F) + 0.0014F^2$. Anisotropic thermal parameters were refined for all non-hydrogen atoms, hydrogen atoms were constrained on ring angle external bisectors with an isotropically refined thermal parameter. Refinement converged to give R = 0.0279, R' = 0.0499, S = 1.18 for 589 parameters, largest and mean Δ/σ 0.029, 0.002. In the final refinement the maximum and minimum difference peaks were 0.81 and −1.12 e Å^{-3} respectively.

Crystal data for compound **6**. $C_{14}H_{10}ClInO_4Ru_2$, M_r = 594.70, triclinic, space group $P\bar{1}$, a = 6.746(1), b = 10.271(1), c = 12.053(1) Å, α = 107.12(1), β = 88.31(1), γ = 90.23(1)°, U = 797.8 Å^3, Z = 2, D_c = 2.475 g cm^{-3}, F(000) = 524, μ(Mo-Kα) = 34.29 cm^{-1}, λ = 0.710 73 Å.

Data collection and reduction. Enraf-Nonius CAD4F diffractometer with graphite monochromator, crystal size 0.25 × 0.10 × 0.32 mm, T = 203 K, 2θ range 3.5–60.0°. Index ranges: h −9 to 9, k −14 to 14, l 0 to 14, ω scan mode, scan width 1.20–2.30° ω, scan speed 1.70–5.00° min^{-1}, typical half-height peak width 0.15° ω, two standard reflections measured 25 times, 3% fluctuation. 2773 Unique reflections with $I > 3.0\sigma(I)$ were used in structure determination. Data were corrected for Lorentz and polarisation effects and also for absorption (DIFABS,[16] transmission factors 0.38–0.71).

Structure solution and refinement. The structure was solved by automated Patterson analysis (PHASE) and refined by full-matrix, least squares minimizing the quantity $\Sigma w(F_o - F_c)^2$ and with a weighting scheme, $w^{-1} = \sigma^2(I) + 0.0009I^2$. Anisotropic thermal parameters were refined for all non-hydrogen atoms, hydrogen atoms were refined isotropically. Refinement converged to give R = 0.022, R' = 0.023, S = 0.99 for data to parameter ratio of 11.55, largest Δ/σ 0.01, isotropic extinction parameter $g = 0.07(1) \times 10^{-4}$ mm. In the final refinement the maximum difference peak was 0.71 e Å^{-3} close to the indium atom.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

We thank the SERC for a studentship (L. M. C.) and N. C. N. and T. B. M. thank the Royal Society and Natural Sciences and Engineering Research Council (Canada) for additional supporting funds. N. C. N. also thanks Johnson Matthey for a loan of $RuCl_3$ and Professor S. A. R. Knox for assistance with the preparation of $[Ru_3(CO)_{12}]$.

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Received 24th July 1992; *Paper* 2/03962A