

Articles

Mass Spectrometric Method for the Rapid Characterization of Transition Metal Carbonyl Cluster Reaction Mixtures

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Energy-dependent electrospray ionization mass spectrometry (EDESI-MS) has been applied to the characterization of reaction products that contain a mixture of metal carbonyl cluster anions. The technique allows rapid identification of the components and provides molecular weight (parent ion), ion composition (isotope pattern), and structural information (fragmentation pattern). The spectra are presented as a two-dimensional map of cone voltage versus mass-to-charge ratio which resolves each component of the reaction product. The EDESI-MS technique is illustrated using the reaction products obtained from the reaction of $[\text{Ru}_6\text{C}(\text{CO})_{17}]^-$ and $[\text{PPN}][\text{M}(\text{CO})_4]^-$ where $\text{M} = \text{Co}$ or Ir . The anions identified from these reactions are $[\text{Ru}_5\text{CoC}(\text{CO})_{16}]^-$, $[\text{Ru}_3\text{Co}(\text{CO})_{13}]^-$, $[\text{RuCo}_3(\text{CO})_{12}]^-$, $[\text{HRu}_4\text{Co}_2\text{C}(\text{CO})_{15}]^-$, $[\text{Ru}_5\text{IrC}(\text{CO})_{16}]^-$, $[\text{Ru}_3\text{Ir}(\text{CO})_{13}]^-$, and $[\text{RuIr}_3(\text{CO})_{12}]^-$. All the compounds have been fully characterized as their $[\text{PPN}]^+$ salts by EDESI-MS together with other methods including single-crystal X-ray diffraction for $[\text{PPN}][\text{Ru}_5\text{CoC}(\text{CO})_{16}]^-$.

Introduction

The ultimate synthetic goal in cluster chemistry must be to produce a single (predicted) compound in quantitative yield. Unfortunately, the complicated nature of the kinetics of cluster formation allows both ligand and metal core transformations to occur and the consequent formation of mixtures of products. The usual methodology used by synthetic chemists working on group 8 transition metal carbonyl clusters is first to separate the reaction products chromatographically and then analyze each in turn by spectroscopic and other methods. Fractional crystallization is commonly used to separate the components of a reaction, followed by an X-ray structural investigation if appropriate single crystals have formed. In this paper we describe a variation of electrospray mass spectrometry (ESI-MS) that allows rapid identification of products without prior purification. ESI-MS is a soft ionization technique¹ that, under normal conditions, causes little fragmentation, works well for inorganic,² organometallic,³ and cluster⁴

compounds, and can be used for rapid screening of reactions.⁵ ESI-MS has previously been used to characterize the mixture of cluster products composed of $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$, $[\text{Os}_5(\text{CO})_{16}]$, $[\text{Os}_6(\text{CO})_{18}]$, and $[\text{Os}_7(\text{CO})_{21}]$ obtained from the pyrolysis of $[\text{Os}_3(\text{CO})_{12}]$.⁶ Since these compounds are neutral, the product mixture was derivatized using methoxide ion to provide ions of the type $[\text{M} + \text{OMe}]^-$ before analysis.⁷ The technique has also been applied to a mixture of high-nuclearity osmium clusters to demonstrate their colloid-like properties⁸ and has been shown to be a useful way to monitor reaction progress in anion condensation reactions of clusters.⁹ Although ESI-MS provides the molecular weight of the

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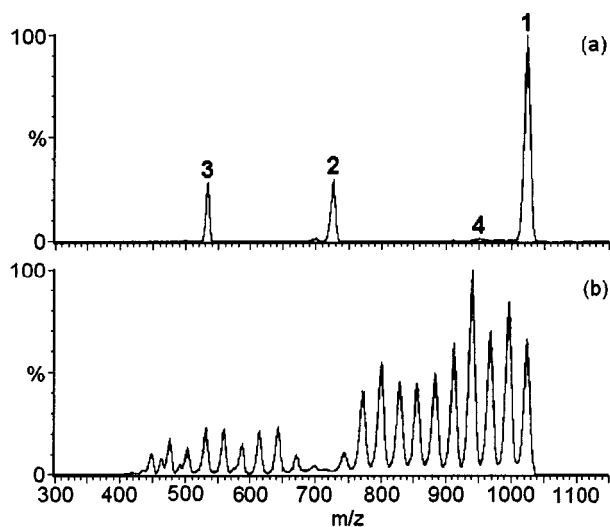


Figure 1. (a) Negative-ion ESI mass spectrum of a mixture of the clusters **1**, **2**, **3**, and **4**, cone voltage 15 V; (b) the negative-ion ESI mass spectrum of the same mixture of clusters, cone voltage 75 V.

various components, attempts to extract structural information by inducing fragmentation often result in highly complicated spectra. In this work, using the products obtained from the reaction between $[\text{Ru}_6\text{C}(\text{CO})_{17}]$ and $[\text{PPN}][\text{M}(\text{CO})_4]$ (where $\text{M} = \text{Co}$ or Ir and $\text{PPN} = \text{bis}\{\text{triphenylphosphino}\}\text{iminium}$) we demonstrate a new technique that gives a complete fragmentation pattern for each of the components of a product mixture.

Results and Discussion

The reaction of $[\text{Ru}_6\text{C}(\text{CO})_{17}]$ and $[\text{PPN}][\text{Co}(\text{CO})_4]$ in tetrahydrofuran affords a mixture of cluster anions as evidenced by spot TLC. The reaction may be monitored by IR spectroscopy, and the single $\nu(\text{CO})$ peak due to $[\text{Co}(\text{CO})_4]^-$ disappears completely after about an hour, as do those attributable to $[\text{Ru}_6\text{C}(\text{CO})_{17}]$. The new peaks are shifted to lower wavenumbers, indicating the formation of anionic species. However, a characteristic of the IR spectra of carbonyl cluster compounds is that they may contain fewer bands than predicted by group theory and as such very little can be drawn from the IR spectra regarding structure or symmetry.¹⁰ Fortunately, ESI mass spectrometry also allows rapid and direct analysis of reaction solutions, and the information provided on each component is immediately useful. The negative-ion ESI mass spectrum of the postreaction solution shows that in this case a number of compounds are obtained, and provided a sufficiently low cone voltage is used, a single peak envelope is obtained for each component (Figure 1a). The resulting m/z values and isotope patterns allow tentative assignment of the four main components as $[\text{Ru}_5\text{CoC}(\text{CO})_{16}]^-$, **1**, $[\text{Ru}_3\text{Co}(\text{CO})_{13}]^-$, **2** (the small peak next to **2** is due to early loss of CO, i.e., $[\text{Ru}_3\text{Co}(\text{CO})_{12}]^-$), $[\text{RuCo}_3(\text{CO})_{12}]^-$, **3**, and $[\text{HRu}_4\text{Co}_2\text{C}(\text{CO})_{15}]^-$, **4**. However, increasing the cone voltage in order to induce fragmentation results in a more complicated spectrum (Figure 1b), and establishing the

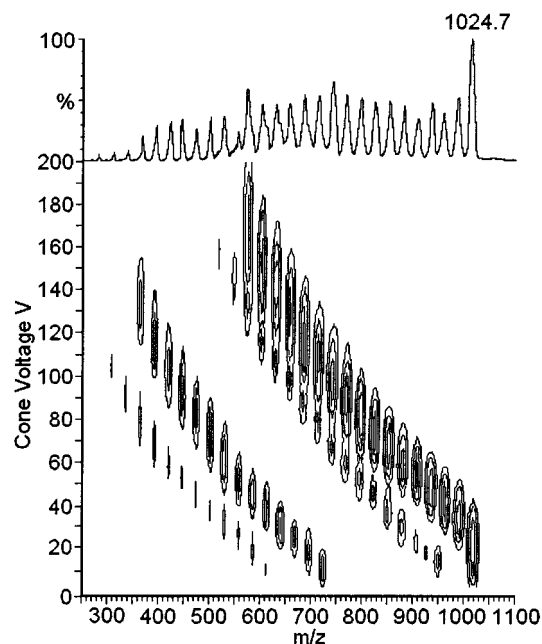


Figure 2. Negative-ion EDESI mass spectrum of a mixture of **1**, **2**, **3**, and **4**.

origin of the fragment ion is not a trivial task. However, analyzing the mixture using energy-dependent ESI-MS (EDESI-MS)¹¹ provides a complete picture of the fragmentation pattern of each component and confirms the original assignment, as demonstrated in Figure 2.

An EDESI mass spectrum is generated by combining spectra collected across the full range of cone voltages and presenting them in a map format. The y -axis represents the cone voltage (hence fragmentation energy increases as the map is ascended). The x -axis displays the mass-to-charge ratio. The contours display the relative intensity of the various cross-peaks, and the "traditional" spectrum that appears at the top of the map comprises a combination of all the individual spectra recorded at different cone voltages. It is this representation of the data in map form that allows compounds **1–4** (Scheme 1) to be fully distinguished.

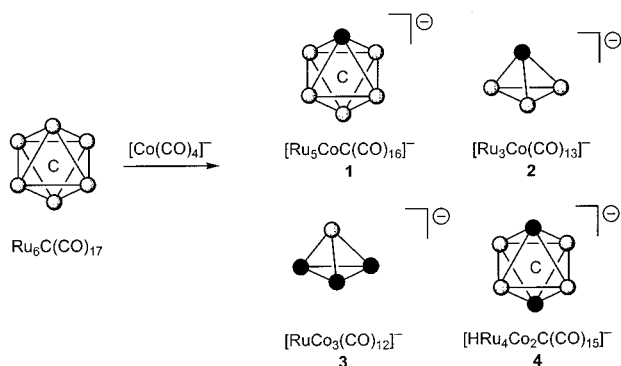
Each series of peaks correspond to a species with a charge of -1 , and each peak in their respective series is $vz.$ ca. 28 mass units apart, corresponding to the sequential loss of carbonyl ligands. At lower cone voltages, V (fragmentation energy), the only peaks observed are those corresponding to the intact parent ions (fully ligated), e.g., $[\text{Ru}_5\text{CoC}(\text{CO})_{16}]^-$ or $[\text{RuCo}_3(\text{CO})_{12}]^-$. Upon increasing the cone voltage, carbonyl ligands are stripped from the metal core, which in turn provides structural information for each cluster species.¹² All the cluster species examined undergo fragmentation to the naked core, e.g., at ca. 576.4 Da $[\text{Ru}_5\text{CoC}]^-$ and ca. 362.3 Da $[\text{Ru}_3\text{Co}]$, a loss of 16 and 13 carbonyl ligands, respectively.

The technique employed to examine pure compounds has been described previously.⁹ However, EDESI mass

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Scheme 1. Products Obtained from the Reaction of $[\text{Ru}_6\text{C}(\text{CO})_{17}]$ and $[\text{PPN}][\text{Co}(\text{CO})_4]^a$


^a The structure of **4** is not known with certainty, the two Co-centers could lie adjacent to each other in the octahedral framework, and the location of the hydride is also unknown.

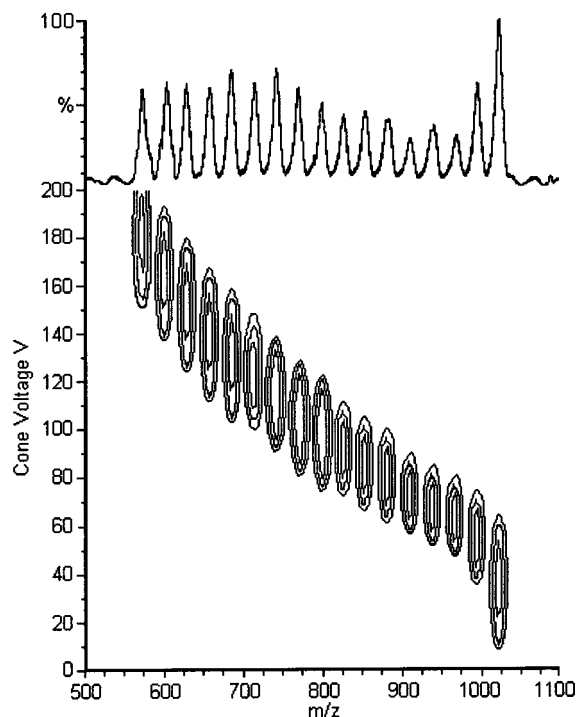


Figure 3. Negative-ion EDESI mass spectrum of pure **1**.

spectrometry is most useful, aiding the synthetic chemist to rapidly assign reaction products and allowing reactions to be tuned to give the desired product in high yield. The reaction described here was carried out on a low scale over a range of different time intervals and then analyzed by EDESI-MS in order to maximize the formation of each product. The products were then purified chromatographically and reanalyzed by EDESI-MS. The EDESI mass spectrum of **1** is shown in Figure 3 for comparison purposes with the spectrum of **1** recorded in the postreaction mixture shown in Figure 2. The two spectra are essentially identical, illustrating the reliability of the technique.

The mechanism for the formation of **1–4** from this reaction is unclear. Compounds related to **1** in which a square pyramidal Ru_5C core is capped by a different metal to form a heteronuclear octahedron have been reported with the metals Cr, Mo, W,¹³ Rh,¹⁴ and Pt.¹⁵ However, these compounds are not made from $[\text{Ru}_6\text{C}(\text{CO})_{17}]$, but from the reaction of Ru_5C precursors with

appropriate mononuclear complexes. Mononuclear ruthenium fragments can also be used to introduce different ligands into the system, and this has been widely examined for various $[\text{Ru-arene}]$ fragments.¹⁶ In contrast, $[\text{Ru}_5\text{C}(\text{CO})_{14}]^{2-}$ and $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$ react with $[\text{Pd}(\text{C}_6\text{Ph}_4)(\text{NCMe})_2]^{2+}$ to form $[\text{Ru}_5\text{C}(\text{CO})_{13}(\text{C}_6\text{Ph}_4)]$ and $[\text{Ru}_6\text{C}(\text{CO})_{15}(\text{C}_6\text{Ph}_4)]$, respectively, in which the ligand transfer, rather than metal atom capping, takes place.¹⁷

The reaction of $[\text{Ru}_5\text{C}(\text{CO})_{15}]$ with $[\text{PPN}][\text{Co}(\text{CO})_4]$ affords **1** in quantitative yield without forming the additional side products observed in the reaction commencing with $[\text{Ru}_6\text{C}(\text{CO})_{17}]$.¹⁸ Since $[\text{Ru}_6\text{C}(\text{CO})_{17}]$ is converted to $[\text{Ru}_5\text{C}(\text{CO})_{15}]$ in a carbonylative decomposition reaction under high pressures of CO,¹⁹ it is not unreasonable to assume that in the absence of CO **1** is formed in a stepwise decapping/recapping process. Compound **4**, in which two cobalt and four ruthenium atoms presumably make up an octahedral core (as it has 86 CVEs), is isolated only in trace quantities. It is not an unreasonable product to observe given previous studies which show that under high CO pressures the heteronuclear cluster $[\text{Ru}_5\text{RhC}(\text{CO})_{14}(\text{C}_5\text{H}_5)]$ undergoes decapping to give a square-pyramidal Ru_4RhC -centered cluster²⁰ and is therefore susceptible to further capping. During the proposed stepwise decapping/recapping processes the mononuclear ruthenium fragments generated are also able to condense with the cobalt species to form the tetranuclear clusters **2** and **3**. Both of these species can be made by more rational methods.²¹

Compounds **1** and **4** are new, and the structure of **1** has been established in the solid state using X-ray diffraction analysis. The structure of **1** is illustrated in Figure 4, and selected bond parameters are given in Table 1. The metal core is composed of one cobalt and five ruthenium atoms, forming a distorted octahedron. The carbide carbon atom occupies the octahedral interstice and is at a distance of 1.881(4) Å from the cobalt atom, compared to an average $\text{Ru-C}_{\text{interstitial}}$ distance of 2.04 Å. As all the Co–Ru distances are shorter than the Ru–Ru distances, the cobalt apex is compressed toward the center of the octahedron. Fourteen of the carbonyls are terminal, with two bridging carbonyls. Three of the ruthenium atoms, forming a triangular face, have three terminal carbonyl ligands each; the remaining two ruthenium atoms have two terminal

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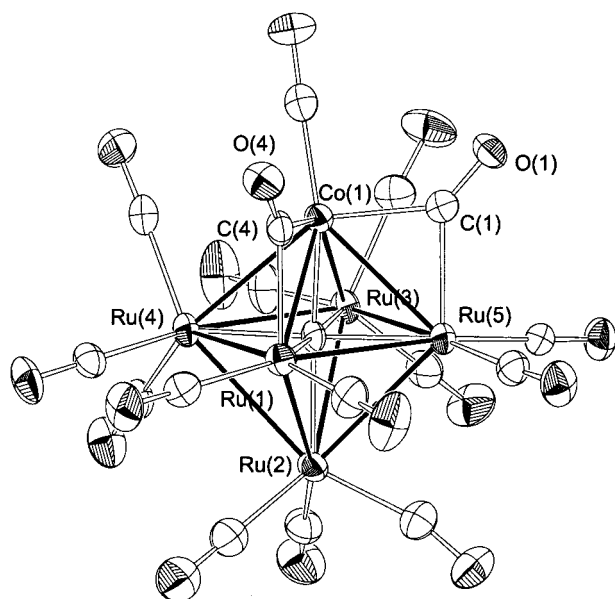


Figure 4. X-ray crystal structure of the anion **1**. The counteranion [PPN]⁺ is not shown.

Table 1. Selected Bonded Distances (Å) and Angles (deg) for the Anion 1

Co(1)–Ru(1)	2.6399(7)	Co(1)–C(4)	1.967(5)
Co(1)–Ru(3)	2.8539(6)	Ru(1)–Ru(4)	2.9232(5)
Co(1)–Ru(5)	2.6615(6)	Ru(1)–Ru(2)	2.9453(5)
Co(1)–Ru(4)	2.8699(7)	Ru(3)–C(12)	1.904(5)
Co(1)–C(5)	1.784(5)	Ru(5)–C(2)	1.861(5)
Co(1)–C(1)	1.946(5)	O(1)–C(1)	1.158(5)
Co(1)–C(100)	1.881(4)	O(6)–C(6)	1.121(5)
C(1)–Co(1)–Ru(5)	50.26(13)	Ru(1)–Co(1)–Ru(5)	67.136(17)
Ru(5)–Co(1)–Ru(3)	62.512(15)	Ru(4)–Ru(1)–Ru(5)	88.546(13)
Co(1)–C(100)–Ru(2)	176.5(3)	Ru(1)–C(100)–Ru(3)	177.3(2)

carbonyl ligands each and share a bridging carbonyl ligand with the cobalt. The cobalt atom has just one terminal carbonyl ligand.

In a reaction related to the one described above, [Ru₆C(CO)₁₇] and [PPN][Ir(CO)₄] were refluxed in thf to afford [Ru₅IrC(CO)₁₆][−], **5**, [Ru₃Ir(CO)₁₃][−], **6**, and [Ru₃Ir(CO)₁₂][−], **7**, as evidenced by spot TLC and EDESI-MS. As observed for the cobalt example, EDESI-MS allowed the components of the mixture to be separated, providing molecular weight and other structural information. We believe the reaction mechanism for their formation is identical to the cobalt example with the only difference being the absence of the hypothetical cluster [HRu₄Ir₂C(CO)₁₅][−]. Since **4** was isolated only in trace amounts, the absence of an iridium analogue is not surprising. The negative-ion EDESI mass spectrum of the product mixture from the reaction, including compounds **5**, **6**, and **7**, is shown in Figure 5.

Figure 5 shows features similar to Figure 2. All the species present are well-separated in the two-dimensional map, whereas the summation of the fragmentation data is impossible to deconvolute. Compound **5** dominates the spectrum, just as **1** does in the cobalt example. It is stripped of all 16 carbonyl ligands down to an [Ru₅IrC][−] core. Like **1**, this requires very high cone voltages to remove all of the ligands. [Ru₃Ir(CO)₁₃][−], **6**, like its cobalt analogue **2**, is stripped of all its ligands by a cone voltage of 140 V. Above 160 V even the intensity of the cross-peak due to the completely stripped cluster, [Ru₃Ir][−], has dropped away to nothing, but there

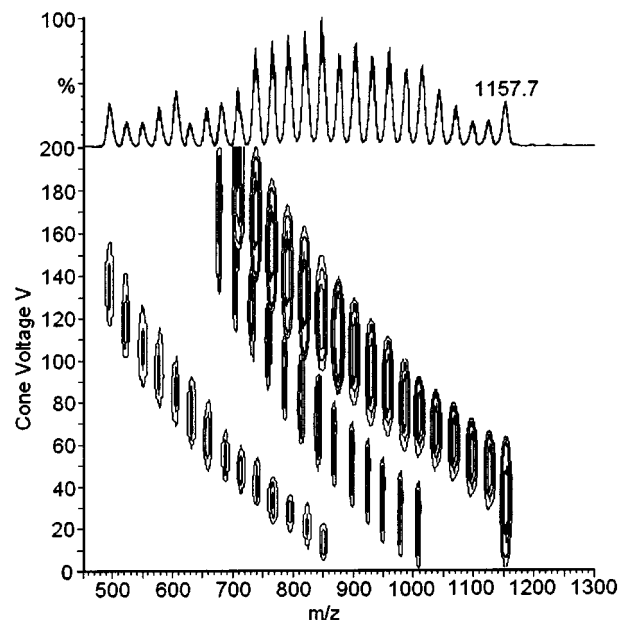


Figure 5. Negative-ion EDESI mass spectrum of a mixture of **5**, **6**, and **7**.

is no evidence for fragmentation of the metal core. [Ru₃Ir(CO)₁₂][−], **7**, shows an appreciably higher intensity than did its cobalt analogue **3** in Figure 2. The cone voltage required to remove the carbonyl ligands is much higher for **7** than for **3**, indicative of the relatively stronger M–CO bonds for the third-row transition metal. The absence of an iridium analogue of **4** is immediately apparent (the parent ion for [HRu₄Ir₂C(CO)₁₅][−] should appear at a higher mass-to-charge ratio than **4**, at around 1220 *m/z*). Both **6** and **7** are known compounds and can be made by more rational methods.²²

Concluding Remarks

The application of EDESI-MS provides a fast and simple method for the characterization of mixtures of compounds obtained from reactions. The technique allows rapid identification of the components, and in addition to providing molecular weight (parent ion) and ion composition (isotope pattern), it also provides structural information (fragmentation patterns) viewed as a two-dimensional map of cone voltage versus mass-to-charge ratio. The method can easily be extended to identify neutral species by the addition of a suitable derivatization agent; such agents have been critically assessed previously.^{5,6} We anticipate that the EDESI technique will also find uses in other areas of organometallic and inorganic chemistry.

Experimental Section

All reactions were carried out under a nitrogen atmosphere. [Ru₆C(CO)₁₇],²³ [PPN][Co(CO)₄],²⁴ and [PPN][Ir(CO)₄]²⁵ were prepared by literature procedures.

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Table 2. Crystallographic Data for 1

empirical formula	C ₅₃ H ₃₀ CoNO ₁₆ P ₂ Ru ₅
fw	1563.00
temperature	180(2) K
wavelength	0.71070 Å
cryst syst	orthorhombic
space group	P2 ₁ 2 ₁ 2 ₁
unit cell dimens	<i>a</i> = 15.1650(3) Å <i>b</i> = 17.1310(2) Å <i>c</i> = 20.9410(3) Å
volume	5440.30(15) Å ³
<i>Z</i>	4
density (calcd)	1.908 Mg/m ³
abs coeff	1.779 mm ⁻¹
<i>F</i> (000)	3040
cryst size (mm)	0.16 × 0.13 × 0.05
θ range for data collection	3.52–27.48°
index ranges	–19 ≤ <i>h</i> ≤ 19, –22 ≤ <i>k</i> ≤ 22, –26 ≤ <i>l</i> ≤ 27
no. of reflns collected	51 546
no. of ind reflns	12397 (<i>R</i> _{int} = 0.0676)
abs corr	multiscan
max. and min. transmn	0.934 and 1.115
no. of data/restraints/params	12397/0/702
goodness-of-fit on <i>F</i> ²	1.009
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0350, w <i>R</i> 2 = 0.0601
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0541, <i>R</i> 2 = 0.0658
absolute structure param	0.010(16)
largest diff peak and hole	0.498 and –0.648 e Å ⁻³

Reaction of [Ru₆C(CO)₁₇] and [PPN][Co(CO)₄]. To a tetrahydrofuran (20 mL) solution of [Ru₆C(CO)₁₇] (50 mg, 0.046 mmol) was added a tetrahydrofuran (10 mL) solution of [PPN][Co(CO)₄] (32.4 mg, 0.046 mmol). The solution was refluxed for 3 h. The resulting deep red solution was allowed to cool and evaporated to dryness. The solution was dissolved in the minimum amount of CH₂Cl₂ and chromatographed (silica) using acetone/hexane (50:50) as eluant. The major product, [PPN][Ru₅CoC(CO)₁₆] (**1**), was crystallized as dark red needles by vapor diffusion of pentane into a dichloromethane solution at 4 °C (52 mg, 0.033 mmol, 62%). IR (CH₂Cl₂): ν(CO) 2053w, 2019vs, 1995sh, 1827vw cm⁻¹. The spectroscopic characteristics of compounds **2** and **3** matched literature values. Compound **4** was not isolated in sufficient quantity after chromatography to characterize except by mass spectrometry.

Reaction of Ru₆C(CO)₁₇ and [PPN][Ir(CO)₄]. To a tetrahydrofuran (20 mL) solution of [Ru₆C(CO)₁₇] (50 mg, 0.046 mmol) was added a tetrahydrofuran (10 mL) solution of [PPN][Ir(CO)₄] (39 mg, 0.046 mmol). The solution was refluxed for 3 h. The resulting deep red solution was allowed to cool and evaporated to dryness. The solution was dissolved in the minimum amount of CH₂Cl₂ and chromatographed (silica) using acetone/hexane (50:50) as eluant. The major product [PPN][Ru₅IrC(CO)₁₆] (**5**) was crystallized as red/orange needles by vapor diffusion of pentane into a dichloromethane solution at 4 °C (39 mg, 0.021 mmol, 50%). IR (CH₂Cl₂): ν(CO) 2047w, 2015vs, 1990sh, 1808vw cm⁻¹. The spectroscopic characteristics of compounds **6** and **7** matched literature values.

Mass Spectrometry Instrumentation. ESI and EDESI mass spectra were collected using a Micromass Quattro LC instrument in negative-ion mode, with dichloromethane as the mobile phase. The nebulizer tip was at 3100 V and 90 °C, and nitrogen was used as the bath gas. Samples were introduced directly to the source at 4 μL min⁻¹ via a syringe pump. The cone voltage was ramped from 0 to 200 V for the EDESI spectrum.

X-ray Diffraction Study. Single crystals of [PPN][Ru₅CoC(CO)₁₆] were crystallized from pentane/dichloromethane, mounted in inert oil, and transferred to the cold gas stream of the diffractometer. The structure was solved using direct methods and refined by full-matrix least-squares on *F*². Key data for the determination are listed in Table 2.

Acknowledgment. We would like to thank the Royal Society for a University Research Fellowship (P.J.D.), Newnham and Trinity Colleges, Cambridge, for a college lectureship (J.S.M.), and the EPSRC and ICI for funding (A.K.H.).

Supporting Information Available: Tables of bond distances, angles, positional parameters, anisotropic thermal parameters, and hydrogen atom coordinates of **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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