Inorg. Chem. **1992,** *31,* 4023–4025

A Heptaruthenium Carbonyl Cluster: Synthesis and Structural Characterization of $[PPN][HRu_7(CO)_{20}]$

Catherine E. Housecroft,*,† Arnold L. Rheingold,*,‡ and Xuejing Song†

University Chemical Laboratory, Lensfield Road,
Cambridge CB2 1EW, U.K., and Department of Chemistry,
University of Delaware, Newark, Delaware 19716

Received April 23, 1992

Introduction

Despite the wealth of ruthenium cluster chemistry, the number of fully characterized heptaruthenium carbonyl clusters remains small.[1-5] Even for osmium, heptanuclear clusters are still rare.[6-12] The known heptanuclear osmium carbonyl clusters include the simple binary or hydrido species $Os_7(CO)_{21}$,[8] $H_2Os_7(CO)_{20}$,[9] $H_2Os_7(CO)_{21}$,[6] and $H_2Os_7(CO)_{22}$.[6] No such ruthenium clusters have been reported to date although Adams et al. have used the (dimethylamino)carbyne ligand to stabilize higher nuclearity ruthenium clusters, one of which is $(\mu_6\text{-H})Ru_7(CO)_{19}(\mu\text{-CNMe}_2)$.[3] The molecular structure of this neutral compound exhibits a capped octahedral Ru_7 core, and the interstitial hydride ligand is directly located within the octahedral portion of the skeleton. During our recent studies of boron-containing ruthenium clusters, we have been investigating a variety of possible routes to synthesize Ru_xB_y species in which $x \geq 4$ and $y = 1$ or 2.[13,14] Here we report that during one such study we have isolated the non-boron-containing cluster anion $[HRu_7(CO)_{20}]^-$ (**1**) as its $[PPN]^+$ salt.

Experimental Section

General Data. All reactions were carried out by using Schlenk techniques under an atmosphere of argon. Solvents were dried over suitable reagents and freshly distilled under N_2 before use. Separations were carried out by thin-layer plate chromatography with Kieselgel 60-PF-254 (Merck). FT-NMR spectra were recorded on a Bruker WM 250 spectrometer. ^1H NMR shifts are reported with respect to δ 0 for Me_4Si; downfield chemical shifts are positive. Infrared spectra were recorded on a Perkin-Elmer FT 1710 spectrophotometer. FAB mass spectra were recorded on a Kratos MS 902 instrument. $[PPN][Ru_3(CO)_9BH_4]$ was prepared as previously reported.[13] $[PPN]^+$ = bis(triphenylphosphine)-nitrogen(1+).

Synthesis of [PPN][1]. $Ru_3(CO)_{12}$ (0.153 g, 0.24 mmol) was dissolved in CH_2Cl_2 (50 mL) and $MeNO_2$ (5 mL), and the solution was cooled to −78 °C. Me_3NO (0.036 g, 0.48 mmol) was dissolved in $MeNO_2$ (5 mL), and the solution was added dropwise to that containing the $Ru_3(CO)_{12}$. A yellow-orange suspension was obtained. This was allowed to warm to room temperature and was stirred for 1 h. Solvent was removed, and the solid residue was redissolved in acetone (10 mL). To this was added a solution of $[PPN][Ru_3(CO)_9BH_4]$ (0.10 mmol) in acetone (10 mL), and the mixture was stirred at room temperature for 1.5 h. Solvent was removed and the products were separated by TLC, eluting with CH_2Cl_2–hexane (2:1). $[PPN][HRu_7(CO)_{20}]$ ([PPN][**1**]) was collected as the third (dark red-brown) fraction in ≈5% yield. The first (pale yellow) fraction consisted mainly of $H_4Ru_4(CO)_{12}$; the second (orange) fraction consisted of $[PPN][(\mu_6\text{-H})Ru_6(CO)_{18}]$[19,20] (≈20%) with a trace amount of $[PPN][H_2Ru_6(CO)_{18}B]$;[14] the fourth fraction (brown) consisted of $[PPN][Ru_6(CO)_{17}B]$[15] in ≈10% yield.

[PPN][**1**]: 250-MHz ^1H NMR ($(CD_3)_2CO$, 298 K) δ +7.7–7.5 (m, *Ph*); IR (CH_2Cl_2, cm^{-1}) 2083 w, 2048 s, 2028 vs, 2020 vs, 2005 sh; FAB-MS (in 3-NBA matrix) m/z 1270 (P^- with 8 CO losses observed).

Crystallographic Determination for [PPN][1]

Crystallographic data are given in Table I. X-ray data were collected using a Siemens P4 diffractometer [Mo Kα radiation (λ = 0.710 73 Å); 2θ range 4–50°, ω scans, 13 119 reflections collected; $h = \pm 18$, $k = \pm 18$, $l = +19$] at 298 K for a dark red block-shaped crystal (0.32 × 0.36 × 0.38 mm). The data were empirically corrected for absorption effects. The structure was solved by direct methods and refined by full-matrix least-squares refinement on 589 parameters. The interstitial hydrogen atom was not located, and the remaining hydrogen atoms were fixed using a riding model. All non-hydrogen atoms were refined anisotropically; $R(F)$ = 4.15% for 8326 observed reflections ($F_o > 4\sigma|F_o|$).

Results and Discussion

The triruthenaborane anion $[Ru_3(CO)_9BH_4]^-$ consists of a trimetal-supported monoborane unit, and we have recently shown that this cluster provides a convenient precursor from which to synthesize higher nuclearity boron-containing clusters.[13] The reaction of $[Ru_3(CO)_9BH_4]^-$ with $Ru_3(CO)_{10}(NCMe)_2$[16] appeared to be a logical method of generating the borido cluster $[Ru_6(CO)_{17}B]^-$, an anion previously reported both by us[17] and by Shore et al.[15] In the course of this study, details of which will be reported separately, we noted the formation of the non-boron-containing anionic cluster $[(\mu_6\text{-H})Ru_6(CO)_{18}]^-$.[19,20] When the acetonitrile used in the preparation[16] of $Ru_3(CO)_{10}(NCMe)_2$ was replaced by nitromethane, another non-boron-containing cluster anion, **1**, was produced in approximately 5% yield. **1** was isolated as its $[PPN]^+$ salt. The anion was characterized in its negative FAB mass spectrum by a parent envelope at m/z 1270, which corresponds closely to a formulation of $(^{101}Ru)_7(^{12}C)_{20}(^{16}O)_{20}$ (calcd m/z = 1267).

Suitable crystals of [PPN][**1**] were grown from CH_2Cl_2 layered with hexane. The molecular structure of anion **1** is shown in Figure 1, and bond distances and angles describing the heptaruthenium cage are given in Table III. The results of the X-ray diffraction study confirm that **1** is a monoanion and consists of a monocapped octahedral core with composition "$Ru_7(CO)_{20}$"; as such, **1** appeared to be the first binary heptaruthenium carbonyl cluster. The Ru_7 core consists of condensed octahedral (86 valence electrons (ve)) and tetrahedral (60 ve) units sharing one face (48 ve in common), giving an overall valence electron requirement of 98. This implies that anion **1** possesses one hy-

---

† University Chemical Laboratory.

‡ University of Delaware.

(1) Van Gastel, F.; Taylor, N. J.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1049.

(2) Adams, R. D.; Babin, J. E.; Tasi, M. *Organometallics* **1988**, *7*, 503.

(3) Adams, R. D.; Babin, J. T.; Tanner, M. *Organometallics* **1988**, *7*, 2027.

(4) Frediani, P.; Bianchi, M.; Salvani, A.; Piancenti, F.; Ianelli, S.; Nardelli, M. *J. Chem. Soc., Dalton Trans.* **1990**, 1705.

(5) Edwards, K. J.; Field, J. S.; Haines, R. J.; Mulla, F. *J. Organomet. Chem.* **1991**, *402*, 113.

(6) Johnson, B. F. G.; Lewis, J.; McPartlin, M.; Morris, J.; Powell, G. L.; Raithby, P. R.; Vargas, M. D. *J. Chem. Soc., Chem. Commun.* **1986**, 429.

(7) Adams, R. D.; Foust, D. F.; Mathur, P. *Organometallics* **1983**, *2*, 990.

(8) Eady, C. R.; Johnson, B. F. G.; Lewis, J.; Mason, R.; Hitchcock, P. B.; Thomas, K. M. *J. Chem. Soc., Chem. Commun.* **1977**, 385.

(9) Ditzel, E. J.; Holden, D.; Johnson, B. F. G.; Lewis, J.; Saunders, A.; Taylor, M. J. *J. Chem. Soc., Chem. Commun.* **1982**, 1373.

(10) Johnson, B. F. G.; Lewis, J.; Lunniss, J. A.; Braga, D.; Grepioni, F. *J. Chem. Soc., Chem. Commun.* **1988**, 973.

(11) Amoroso, A. J.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Wong, W.-T. *J. Chem. Soc., Chem. Commun.* **1990**, 1208.

(12) Johnson, B. F. G.; Lewis, J.; Lunniss, J.; Braga, D.; Grepioni, F. *J. Organomet. Chem.* **1991**, *401*, C46.

(13) Draper, S. M.; Housecroft, C. E.; Keep, A. K.; Matthews, D. M.; Song, X.; Rheingold, A. L. *J. Organomet. Chem.* **1992**, *423*, 241.

(14) Housecroft, C. E.; Matthews, D. M.; Song, X.; Rheingold, *J. Chem. Soc., Chem. Commun.* **1992**, 842.

(15) Hong, F.-E.; Coffy, T. J.; McCarthy, D. A.; Shore, S. G. *Inorg. Chem.* **1989**, *28*, 3284.

(16) Drake, S. R.; Khattar, R. In *Organometallic Syntheses*; King, R. B., Eisch, J. J., Eds.; Elsevier: Amsterdam, 1988; Vol. 4, p 234.

(17) Chipperfield, A. K.; Housecroft, C. E.; Raithby, P. R. *Organometallics* **1990**, *9*, 479.

(18) Duer, M. D.; Wales, D. J. *Polyhedron* **1991**, *10*, 1748 and references therein.

(19) Eady, C. R.; Johnson, B. F. G.; Lewis, J.; Malatesta, M. C.; Machin, P.; McPartlin, M. *J. Chem. Soc., Chem. Commun.* **1976**, 945.

(20) Eady, C. R.; Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; Malatesta, M. C.; McPartlin, M.; Nelson, W. J. H. *J. Chem. Soc., Dalton Trans.* **1980**, 383.

0020-1669/92/1331-4023$03.00/0

Table I. Crystallographic Data for [PPN][$HRu_7(CO)_{20}$] ([PPN][**1**])

chem formula	$C_{56}H_{31}NO_{20}P_2Ru_7$	*T*, K	298
fw	1807.2	λ, Å	0.710 73
a, Å	14.3170 (29)	space group	$P\bar{1}$
b, Å	14.4298 (29)	*Z*	2
c, Å	14.6340 (28)	D_x, g cm^{-3}	2.005
α, deg	91.651 (16)	μ, cm^{-1}	18.47
β, deg	92.028 (16)	R^a	0.0415
γ, deg	97.705 (16)	$R_w{}^b$	0.0499
V, Å^3	2992.3 (10)		

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F)$.

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for [$HRu_7(CO)_{20}$]$^-$ (**1**)

	x	*y*	*z*	*U*(eq)
Ru(1)	6450 (1)	2912 (1)	7055 (1)	49 (1)
Ru(2)	4480 (1)	2893 (1)	7096 (1)	41 (1)
Ru(3)	4391 (1)	1350 (1)	8268 (1)	36 (1)
Ru(4)	6353 (1)	1404 (1)	8223 (1)	43 (1)
Ru(5)	5197 (1)	1223 (1)	6531 (1)	42 (1)
Ru(6)	5540 (1)	3076 (1)	8798 (1)	41 (1)
Ru(7)	3534 (1)	2912 (1)	8689 (1)	45 (1)
O(1)	8306 (4)	2356 (5)	7879 (4)	79 (3)
O(2)	7573 (5)	2592 (7)	5406 (5)	126 (4)
O(3)	7509 (5)	4829 (5)	7559 (5)	107 (3)
O(4)	5502 (4)	4001 (4)	5592 (4)	72 (2)
O(5)	2876 (4)	2075 (4)	5792 (4)	77 (2)
O(6)	3728 (6)	4746 (5)	6965 (5)	107 (3)
O(7)	2389 (4)	648 (4)	7564 (4)	60 (2)
O(8)	4110 (5)	765 (4)	10233 (3)	73 (2)
O(9)	4865 (4)	−640 (3)	7989 (3)	60 (2)
O(10)	6685 (4)	1337 (4)	10265 (4)	73 (2)
O(11)	7417 (5)	−241 (5)	8026 (4)	91 (3)
O(12)	5350 (5)	1904 (5)	4604 (4)	82 (3)
O(13)	6557 (5)	−163 (5)	6101 (4)	93 (3)
O(14)	3452 (5)	−133 (4)	5919 (4)	79 (2)
O(15)	5504 (5)	5158 (4)	8620 (6)	98 (3)
O(16)	5073 (4)	2861 (4)	10811 (4)	74 (2)
O(17)	7559 (4)	3650 (4)	9552 (4)	70 (2)
O(18)	2821 (4)	2304 (5)	10531 (4)	76 (2)
O(19)	3425 (5)	4910 (4)	9280 (4)	82 (3)
O(20)	1613 (4)	2727 (5)	7724 (4)	85 (3)
C(1)	7488 (5)	2233 (5)	7798 (5)	55 (3)
C(2)	7151 (6)	2713 (7)	6025 (6)	76 (4)
C(3)	7108 (6)	4117 (6)	7351 (6)	68 (3)
C(4)	5459 (5)	3528 (5)	6209 (5)	52 (3)
C(5)	3506 (6)	2372 (5)	6279 (5)	54 (3)
C(6)	4021 (6)	4063 (6)	7095 (6)	65 (3)
C(7)	3139 (5)	931 (5)	7832 (5)	47 (2)
C(8)	4209 (5)	1019 (5)	9511 (5)	49 (2)
C(9)	4835 (5)	153 (5)	8038 (5)	49 (2)
C(10)	6554 (5)	1370 (5)	9499 (5)	51 (3)
C(11)	7004 (6)	370 (6)	8070 (5)	58 (3)
C(12)	5326 (6)	1667 (6)	5341 (5)	59 (3)
C(13)	6079 (7)	372 (6)	6301 (5)	63 (3)
C(14)	4084 (6)	388 (6)	6161 (5)	55 (3)
C(15)	5460 (5)	4357 (6)	8662 (6)	60 (3)
C(16)	5189 (5)	2921 (5)	10047 (5)	51 (3)
C(17)	6830 (5)	3394 (5)	9236 (5)	53 (3)
C(18)	3109 (5)	2524 (5)	9850 (6)	54 (3)
C(19)	3474 (6)	4167 (5)	9042 (5)	55 (3)
C(20)	2332 (6)	2776 (6)	8104 (5)	58 (3)

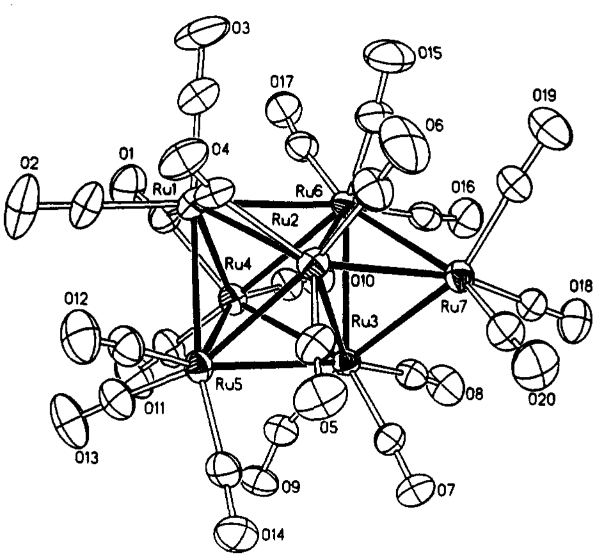

Figure 1. Molecular structure of anion **1**.

Table III. Selected Bond Distances and Angles for [$HRu_7(CO)_{20}$]$^-$ (**1**)

(a) Bond Distances (Å)

Ru(1)–Ru(2)	2.819 (1)	Ru(1)–Ru(4)	2.798 (1)
Ru(1)–Ru(5)	2.893 (1)	Ru(1)–Ru(6)	2.924 (1)
Ru(2)–Ru(3)	2.842 (1)	Ru(2)–Ru(5)	2.855 (1)
Ru(2)–Ru(6)	2.857 (1)	Ru(2)–Ru(7)	2.739 (1)
Ru(3)–Ru(4)	2.803 (1)	Ru(3)–Ru(5)	2.840 (1)
Ru(3)–Ru(6)	2.865 (1)	Ru(3)–Ru(7)	2.771 (1)
Ru(4)–Ru(5)	2.915 (1)	Ru(4)–Ru(6)	2.930 (1)
Ru(6)–Ru(7)	2.847 (1)		

(b) Bond Angles (deg)

Ru(2)–Ru(1)–Ru(4)	90.7 (1)	Ru(2)–Ru(1)–Ru(5)	60.0 (1)
Ru(4)–Ru(1)–Ru(5)	61.6 (1)	Ru(2)–Ru(1)–Ru(6)	59.6 (1)
Ru(4)–Ru(1)–Ru(6)	61.6 (1)	Ru(5)–Ru(1)–Ru(6)	91.7 (1)
Ru(1)–Ru(2)–Ru(3)	89.0 (1)	Ru(1)–Ru(2)–Ru(5)	61.3 (1)
Ru(3)–Ru(2)–Ru(5)	59.8 (1)	Ru(1)–Ru(2)–Ru(6)	62.0 (1)
Ru(3)–Ru(2)–Ru(6)	60.4 (1)	Ru(5)–Ru(2)–Ru(6)	93.9 (1)
Ru(1)–Ru(2)–Ru(7)	123.0 (1)	Ru(3)–Ru(2)–Ru(7)	59.5 (1)
Ru(5)–Ru(2)–Ru(7)	119.0 (1)	Ru(6)–Ru(2)–Ru(7)	61.1 (1)
Ru(2)–Ru(3)–Ru(4)	90.1 (1)	Ru(2)–Ru(3)–Ru(5)	60.3 (1)
Ru(4)–Ru(3)–Ru(5)	62.2 (1)	Ru(2)–Ru(3)–Ru(6)	60.1 (1)
Ru(4)–Ru(3)–Ru(6)	62.3 (1)	Ru(5)–Ru(3)–Ru(6)	94.0 (1)
Ru(2)–Ru(3)–Ru(7)	58.4 (1)	Ru(4)–Ru(3)–Ru(7)	122.8 (1)
Ru(5)–Ru(3)–Ru(7)	118.4 (1)	Ru(6)–Ru(3)–Ru(7)	60.7 (1)
Ru(1)–Ru(4)–Ru(3)	90.2 (1)	Ru(1)–Ru(4)–Ru(5)	60.8 (1)
Ru(3)–Ru(4)–Ru(5)	59.5 (1)	Ru(1)–Ru(4)–Ru(6)	61.3 (1)
Ru(3)–Ru(4)–Ru(6)	59.9 (1)	Ru(5)–Ru(4)–Ru(6)	91.1 (1)
Ru(1)–Ru(5)–Ru(2)	58.7 (1)	Ru(1)–Ru(5)–Ru(3)	87.6 (1)
Ru(2)–Ru(5)–Ru(3)	59.9 (1)	Ru(1)–Ru(5)–Ru(4)	57.6 (1)
Ru(2)–Ru(5)–Ru(4)	87.6 (1)	Ru(3)–Ru(5)–Ru(4)	58.3 (1)
Ru(1)–Ru(6)–Ru(2)	58.4 (1)	Ru(1)–Ru(6)–Ru(3)	86.5 (1)
Ru(2)–Ru(6)–Ru(3)	59.6 (1)	Ru(1)–Ru(6)–Ru(4)	57.1 (1)
Ru(2)–Ru(6)–Ru(4)	87.3 (1)	Ru(3)–Ru(6)–Ru(4)	57.8 (1)
Ru(1)–Ru(6)–Ru(7)	115.6 (1)	Ru(2)–Ru(6)–Ru(7)	57.4 (1)
Ru(3)–Ru(6)–Ru(7)	58.0 (1)	Ru(4)–Ru(6)–Ru(7)	115.7 (1)
Ru(2)–Ru(7)–Ru(3)	62.1 (1)	Ru(2)–Ru(7)–Ru(6)	61.5 (1)
Ru(3)–Ru(7)–Ru(6)	61.3 (1)		

dride ligand (see below). The core structure of **1** is similar to that detailed for (μ_6-H)$Ru_7(CO)_{19}$(μ-$CNMe_2$).[3]

The mean Ru–Ru distance within the octahedral part of the metal cage is 2.862 Å in **1**, compared to 2.858 Å in (μ_6-H)$Ru_7(CO)_{19}$(μ-$CNMe_2$)[3] and 2.875 and 2.877 Å, respectively, for the two crystalline modifications of [(μ_6-H)$Ru_6(CO)_{18}$]$^-$.[20] The edges from the octahedron to the capping atom, Ru(7), are relatively short (Table III); so too are edges Ru(1)–Ru(2) and Ru(1)–Ru(4), which are symmetrically bridged by carbonyl ligands with Ru(1)–C(4) = 2.147 (8) Å, Ru(2)–C(4) = 2.084 (7) Å, Ru(1)–C(1) = 2.166 (8) Å, Ru(4)–C(1) = 2.012 (7) Å, ∠Ru(2)–C(4)–O(4) = 140.6 (6)°, ∠Ru(1)–C(4)–O(4) = 135.8 (6)°, ∠Ru(1)–C(1)–O(1) = 134.4 (6)°, and ∠Ru(4)–C(1)–O(1) = 141.6 (7)°. Each of the atoms Ru(7), Ru(6), Ru(3), and Ru(5) carries three terminal carbonyl ligands, while Ru(1), Ru(2), and Ru(4) each bear two.

The hydride ligand was not located directly from the X-ray structural determination, and an inspection of the molecular structure indicates that there is no obvious site available for its location on the outside of the Ru_7 skeleton. In keeping with this fact, we did not observe a high-field resonance in the ^{1}H NMR spectrum of a solution of **1**. Comparison with (μ_6-H)$Ru_7(CO)_{19}$(μ-$CNMe_2$)[3] and [(μ_6-H)$Ru_6(CO)_{18}$]$^-$ [19,20] suggested the possibility of an interstitial hydride in **1**, for which a downfield ^{1}H NMR shift would be expected:[18] $(\mu_6\text{-H})\mathrm{Ru}_7(\mathrm{CO})_{19}(\mu\text{-CNMe}_2)$, δ +11.42;[3] $[(\mu_6\text{-H})\mathrm{Ru}_6(\mathrm{CO})_{18}]^-$, δ +16.41 ($\mathrm{CD_2Cl_2}$)[19–21] or +16.57 (acetone-d_6).[22] With a delay time of 30 s, a sharp signal at δ +16.53 (acetone-d_6) was resolved for **1**. However, we are not convinced that this is not due to a contaminant of $[(\mu_6\text{-H})\mathrm{Ru}_6(\mathrm{CO})_{18}]^-$ in the sample of **1**.[23] No other hydride signal has been observed. Thus, we propose that **1** exhibits an interstitial hydride ligand which resides within the octahedral portion of the Ru_7 cage but have been unable to confirm its ^{1}H NMR spectroscopic characteristics.

Acknowledgements are made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research, to the Isaac Newton Trust for a grant to X.S., to the NSF for a grant to purchase a diffractometer at the University of Delaware, and to Johnson-Matthey for loans of $\mathrm{RuCl_3}$. We also thank Dorn M. Matthews for obtaining the NMR spectral data.

Supplementary Material Available: Tables of crystal and refinement data, atomic coordinates, bond distances and angles, thermal parameters, and H atom fractional coordinates (12 pages). Ordering information is given on any current masthead page.

---

(21) Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; McPartlin, M.; Nelson, W. J. H.; Rouse, K. D. *J. Chem. Soc., Chem. Commun.* **1980**, 295.

(22) Housecroft, C. E.; Matthews, D. M. Unpublished observation.

(23) We have only been able to obtain small samples of **1**. A contaminant of $[(\mu_6\text{-H})\mathrm{Ru}_6(\mathrm{CO})_{18}]^-$ in a sample of **1** is difficult to identify by IR spectroscopy, since $[(\mu_6\text{-H})\mathrm{Ru}_6(\mathrm{CO})_{18}]^-$ is characterized almost exclusively by a strong absorption at 2020 cm^{-1}, coincident with a strong absorption in the spectrum of **1**.