Hexaruthenium and Heptaruthenium Clusters Possessing μ_4-Imido Ligands

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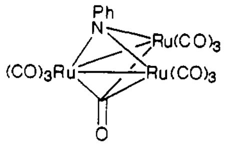
Thermolysis of the μ_3-imido cluster $Ru_3(\mu_3\text{-}NPh)(CO)_{10}$ (1) gives formation of the novel hexaruthenium cluster $Ru_6(\mu_4\text{-}NPh)_2(CO)_{15}$ (2) in high yield. Cluster 2 has been crystallographically characterized: $P2_1/c$, $a = 9.679$ (3) Å, $b = 22.638$ (7) Å, $c = 16.999$ (6) Å, $\beta = 96.03$ (3)°, $V = 3704$ Å^3, $Z = 4$, $R = 0.031$, and $R_w = 0.042$ for 5353 reflections with $F_o \geq 5\sigma(F_o)$. The cluster has a distorted pentagonal-bipyramidal core with three Ru atoms and the two nitrogen atoms forming the pentagonal plane and two Ru atoms forming the axis of the pentagonal bipyramid. The remaining Ru atom is π-coordinated to the phenyl ring of one of the μ_4-NPh ligands and is also bonded to one of the Ru atoms in the cluster core. Cluster 2 can also be prepared from the reaction of $Ru_3(CO)_{12}$ with $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ in refluxing octane. A minor product of this reaction is the heptaruthenium cluster $Ru_7(\mu_4\text{-}NPh)_2(CO)_{16}$ (3), which also forms from reacting 2 with $Ru_3(CO)_{12}$. Spectroscopic data for 3 are consistent with a structure similar to that of 2, with the added Ru atom π-coordinated to the second imido phenyl group.

Introduction

One of the most often used synthetic methods for the formation of high nuclearity metal carbonyl clusters involves thermolysis of lower nuclearity species to induce ligand loss and framework reorganization.[1,2] Although generally unpredictable as to the nuclearity and composition of the final product, many important compounds have been made via this procedure and often in high yields. In many cases, a nonmetallic element is involved in the cluster expansion process and often stabilizes unusual cluster geometries, with carbon, sulfur, and phosphorus atoms and donor ligands most typically employed.[1] However, there have been no such studies of the thermolytic behavior of clusters possessing imido (NR, nitrene) ligands. In the course of examining the carbonylation of imido clusters to produce isocyanates,[3] we investigated the thermolysis behavior of several of these clusters. Herein we describe the thermally induced reaction of $Ru_3(\mu_3\text{-}NPh)(CO)_{10}$ (1)[4] to form the hexaruthenium and heptaruthenium clusters 2 and 3, respectively, which have the unusual structures sketched below.



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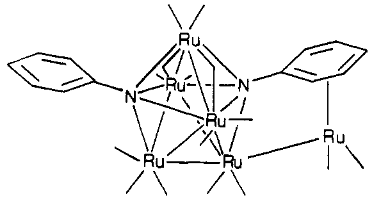
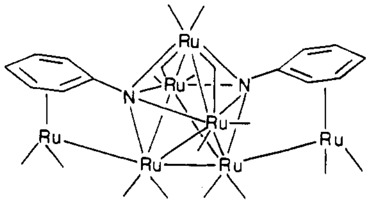


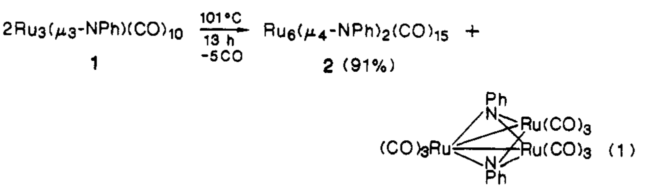
2



3

Results and Discussion

Synthesis of $Ru_6(\mu_4\text{-}NPh)_2(CO)_{15}$ (2) and $Ru_7(\mu_4\text{-}NPh)_2(CO)_{16}$ (3). When the imido cluster 1 was heated in refluxing methylcyclohexane for 13 h, it lost CO and two molecules combined to form the new hexanuclear cluster $Ru_6(\mu_4\text{-}NPh)_2(CO)_{15}$ (2; eq 1). Cluster 2 was isolated as an orange crystalline solid in high yield, and it has been spectroscopically and crystallographically characterized (Figures 1 and 2). Its IR spectrum shows the presence of both bridging and terminal CO's, and a parent ion at m/z 1208 was observed in its FD mass spectrum. Its −50 °C ^{13}C NMR spectrum shows eight separate resonances in a 1:3:1:2:2:2:2:2 intensity ratio, exactly as expected on the basis of the determined structure. An additional low-yield product of reaction 1 is the known cluster 4.[4a,c]



$$2Ru_3(\mu_3\text{-}NPh)(CO)_{10} \xrightarrow[-5CO]{101\,°C,\ 13\ h} Ru_6(\mu_4\text{-}NPh)_2(CO)_{15} + 4 \quad (1)$$

1 2 (91%) 4 (3%)

The structure of cluster 2 suggests an alternative synthesis involving the addition of a $Ru_3(CO)_6$ fragment to the bis(imido) cluster 4. Since such a fragment would logically derive from $Ru_3(CO)_{12}$, this latter species was allowed to react with 4 in refluxing octane. As shown in eq 2, this reaction did indeed give the Ru_6 cluster 2 in modest yield, but a surprising additional product was the

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(1) Vargas, M. D.; Nicholls, J. N. *Adv. Inorg. Chem. Radiochem.* **1986**, *30*, 123.

(2) Chini, P.; Longoni, G.; Albano, V. G. *Adv. Organomet. Chem.* **1976**, *14*, 285.

(3) Han, S. H.; Geoffroy, G. L.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 3426.

(4) (a) Smieja, J. A.; Gladfelter, W. L. *Inorg. Chem.* **1986**, *25*, 2667. (b) Bhaduri, S.; Gopalkrishnan, K. S.; Sheldrick, G. M.; Clegg, W.; Stalke, D. *J. Chem. Soc., Chem. Commun.* **1983**, 2339. (c) Sappa, E.; Milone, L. *J. Organomet. Chem.* **1973**, *61*, 383.

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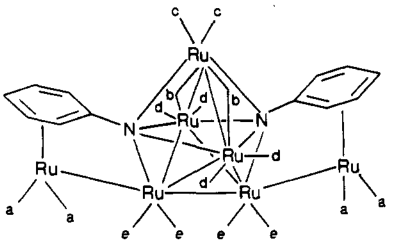
$$\underset{\mathbf{4}}{\mathrm{Ru_3(\mu_3\text{-}NPh)_2(CO)_9}} + \mathrm{Ru_3(CO)_{12}} \xrightarrow[\substack{3.5\ \mathrm{h} \\ \mathrm{octane}}]{125\ ^\circ\mathrm{C}} \underset{\mathbf{2}\ (28\%)}{\mathrm{Ru_6(\mu_4\text{-}NPh)_2(CO)_{15}}} + \underset{\mathbf{3}\ (13\%)}{\mathrm{Ru_7(\mu_4\text{-}NPh)_2(CO)_{16}}} \quad (2)$$

Ru_7 cluster **3**. Cluster **3** was isolated as a dark orange solid and was characterized by its spectroscopic properties. The observation of a parent ion at m/z 1344 in its FD mass spectrum is consistent with the formulation indicated in eq 2, and the overall similarity of its IR spectrum to that of the hexaruthenium cluster **2** implies similar metal frameworks for the two compounds. We assume that the additional Ru atom in **3** is π-coordinated to the second imido phenyl substituent, as illustrated in the drawing above. The −50 °C ^{13}C NMR spectrum of **3** is consistent with this structure as it shows five resonances in a 1:2:2:2:1 intensity ratio, exactly that expected if the assignments are as sketched below.



The structure of the heptaruthenium cluster **3** suggested that an alternative synthetic route might involve the addition of a $Ru(CO)_2$ fragment derived from $Ru_3(CO)_{12}$ to the hexaruthenium cluster **2**. An independent experiment, eq 3, showed this to be the case, with the yield of **3** substantially improved over that in eq 2.

$$\underset{\mathbf{2}}{\mathrm{Ru_6(\mu_4\text{-}NPh)_2(CO)_{15}}} + \mathrm{Ru_3(CO)_{12}} \xrightarrow[\substack{10\ \mathrm{h} \\ \mathrm{octane}}]{125\ ^\circ\mathrm{C}} \underset{\mathbf{3}\ (57\%)}{\mathrm{Ru_7(\mu_4\text{-}NPh)_2(CO)_{16}}} \quad (3)$$

Interestingly, cluster **3** is a rare example of a heptaruthenium cluster, the other three being the recently reported sulfido clusters $Ru_7(\mu_4\text{-}S)(CO)_{21}$[5a] and $Ru_7(\mu_4\text{-}S)_2(CO)_{20}$[5b] and the phosphinidene species $Ru_7(\mu_4\text{-}PPh)_2(CO)_{18}$ (**5**).[5c] It is interesting that each of the known Ru_7 clusters has tetrabridging main-group elements, but the structures of the four compounds are significantly different. Phosphinidine and imido ligands are isoelectronic, but Carty's $Ru_7(\mu_4\text{-}PPh)_2(CO)_{18}$ (**5**),[5c] with two μ_4-phosphinidene ligands has a markedly different geometry and electron count than the bis(imido) cluster **3**. The key difference between **3** and **5** is that the imido ligands in **3** bridge four Ru atoms in a butterfly arrangement whereas the phosphinidine ligands in **5** bridge planar arrays of four metals. This latter geometry, although quite common for phosphinidine ligands,[6] has never been observed for the isoelectronic imido ligands. The closest analogue of **3** is Adams' $Ru_7(\mu_4\text{-}S)_2(CO)_{20}$.[5b] This species also has a pentagonal-bipyramidal structure with three Ru atoms and two sulfur atoms forming the pentagonal plane and with a Ru atom above and a Ru atom below the plane along the axis of the pentagonal bipyramid. This atom arrangement is similar to that found in the Ru_5N_2 core of **3**. However the two clusters differ significantly in the location of the sixth and seventh Ru atoms, with these atoms bridging Ru–Ru bonds in $Ru_7(\mu_4\text{-}S)_2(CO)_{20}$.[5b]

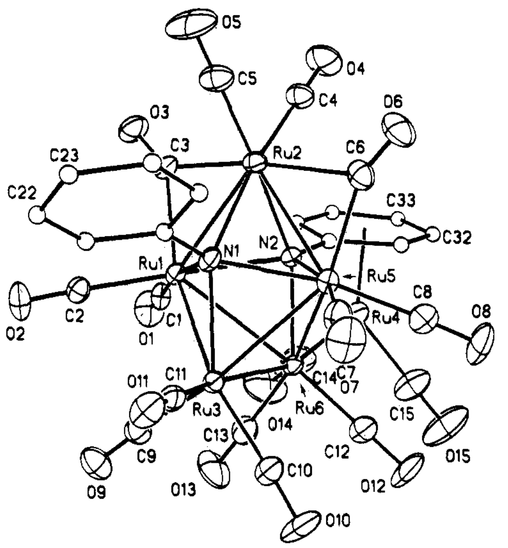


Figure 1. An ORTEP drawing of $Ru_6(\mu_4\text{-}NPh)_2(CO)_{15}$ (**2**), giving the atom numbering scheme. Thermal ellipsoids are drawn at the 40% probability level.

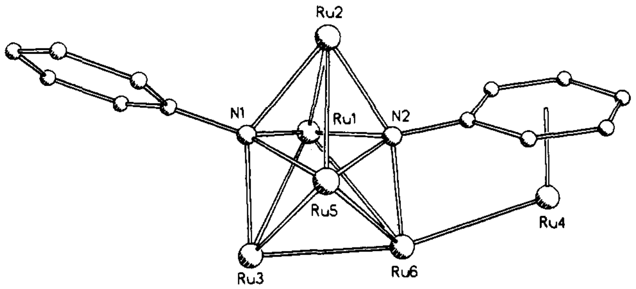


Figure 2. An ORTEP drawing of the $Ru_6(\mu\text{-}NPh)_2$ core of **2**.

Crystal and Molecular Structure of $Ru_6(\mu_4\text{-}NPh)_2(CO)_{15}$ (2). An ORTEP drawing of cluster **2** is shown in Figure 1, and Figure 2 illustrates the $Ru_6(NPh)_2$ cluster core. The cluster can be described as having an approximate pentagonal-bipyramidal core with two ruthenium atoms in the axial positions and three rutheniums and the two imido nitrogens forming the pentagonal plane. The sixth ruthenium, atom, Ru(4), is π-coordinated to one of the imido phenyl substituents and also binds to Ru(6) in the pentagonal plane. This atom Ru(4) is roughly coplanar (0.282-Å deviation) with the five atoms of the pentagonal plane which has a maximum deviation of 0.052 Å associated with N(2). As illustrated in Figure 2, the pentagonal plane is far from ideal, with the Ru(2)–N(1)–Ru(3) and Ru(2)–N(2)–Ru(6) angles of 130.5 (2)° and 152.9 (2)°, respectively, being substantially larger and the N(1)–Ru(2)–N(2) angle of 72.5 (2)° being far less than the ideal pentagonal angle of 108°, an asymmetry which is dictated by the significantly different Ru–Ru and Ru–N bond lengths.

A pentagonal bipyramid is exactly the geometry predicted by the cluster skeletal electron counting rules,[7] if

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(5) (a) Adams, R. D.; Babin, J. E.; Tosi, M. *Organometallics* **1988**, *7*, 503. (b) Adams, R. D.; Babin, J. E.; Tosi, M. *Inorg. Chem.* **1987**, *26*, 2807. (c) Gastel, F. V.; Taylor, N. J.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1049.

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(7) (a) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1980**, *18*, 1. (b) See also: Lukehart, C. M. *Fundamental Transition Metal Organometallic Chemistry*; Brooks/Cole Publishing Co.: Monterey, CA, 1985; pp 47–50 for a concise summary.

it is assumed that Ru(4) is a 2e donor to Ru(6). This is reasonable given that Ru(4) with an arene and two carbonyl ligands has an 18e count and thus must form a dative rather than a covalent bond to Ru(6). The skeletal electron pair calculation is as follows where m = the number of Ru atoms, n = the number of electrons per Ru, r = the number of CO ligands *on the cluster core*, x = the number of electrons per CO, y = the number of imido ligands, and z = the number of electrons per imido ligand:

$$P = \tfrac{1}{2}[m(n) + r(x) + y(z) + (2\text{e from Ru(4)}) - 12m]$$

$$P = \tfrac{1}{2}[5(8) + 13(2) + 2(4) + 2 - 12(5)]$$

$$P = 8 = m + y + 1 \rightarrow \text{closo pentagonal bipyramid}$$

An interesting feature of the structure of **2** concerns the distribution of the atoms within the cluster core. As Figure 2 illustrates, three ruthenium atoms and two nitrogen atoms form the pentagonal plane, and each nitrogen atom bridges four Ru atoms that are arranged in a butterfly fashion. An alternative structure that would satisfy the skeletal electron pair theory would be one with all five Ru atoms in a pentagonal plane capped with two μ_5-imido ligands above and below the plane. This structure is not adopted presumably because of the difficulty that imido ligands would have in coordinating to five metal atoms. Even coordination to four metals is rare for imido ligands, and there are only three other known examples of this coordination mode.[8] Clearly the preferred geometry is capping three metals, as in **1** and **4**. The Ru–N distances in **2** range from 2.105 to 2.245 Å. These Ru–N distances average 2.189 Å, similar to the average Ru–N distances of 2.140 and 2.199 Å for the two other known μ_4-imido clusters $Ru_4(\mu_4\text{-NR})(CO)_{11}(PhC{\equiv}CPh)$ (**6**, R = H,[8a] and **7**, R = Ph,[8b] respectively). However, the Ru–N distances in all three μ_4-imido compounds are significantly longer than the 2.053 Å average of the Ru–N distances in the μ_3-imido cluster $Ru_3(\mu_3\text{-NPh})(CO)_{10}$,[4b] again reflecting the difficulty that an imido ligand has in bridging four metals.

The nitrogen atoms in **2** are five-coordinate in a distorted square-pyramidal geometry. The other known μ_4-imido compounds of ruthenium, $Ru_4(\mu_4\text{-NR})(CO)_{11}(PhC{\equiv}CPh)$ (**6**, R = H;[8a] **7** R = Ph[8b]), have similar imido coordination geometries, except that the metal "butterflies" are considerably more flattened than that of **2**. It is interesting to note that of the three other known μ_4-imido compounds,[8] only $Fe_4(\mu_4\text{-NEt})(\mu_4\text{-EtN{=}O})(CO)_{11}$ has a *planar* arrangement of the four metals bridged by the imido ligand, although such coordination geometry is quite common for the isoelectronic phosphinidene ligand.[6] Apparently, such a geometry for Ru with normal Ru–Ru and Ru–N bond lengths would constrain the imido ligand to lie so close to the Ru_4 plane so as to have an unacceptable geometry at the nitrogen atom. It is also significant to note that each of the known μ_4-imido compounds[8] also has a bridging ligand *on the other side of the M_4 unit* which is apparently needed to stabilize this coordination mode.

The Ru–Ru distances in **2** average 2.829 Å which compares well to the average Ru–Ru distance of 2.854 Å in $Ru_3(CO)_{12}$.[9] However, the Ru–Ru distances in **2** vary considerably from a low of 2.743 to a high of 2.995 Å with no obvious pattern except that the Ru–Ru bonds spanned by a bridging CO have the shorter values. The Ru(1)···Ru(5) distance is 3.489 (1) Å, clearly outside bonding range. The bond lengths between Ru(4) and the carbon atoms of the η_6-phenyl ring of the imido ligand are almost the same within experimental error and average 2.28 Å, similar to the typical Ru–(η^6-C_6H_6) bond distance of 2.22 Å.[10]

Table I. Crystallographic Parameters for 2

formula	$Ru_6C_{30}H_{16}NO_{16}$
mol wt	1252.8
crystal system	monoclinic
space group	$P2_1/c$
a, Å	9.679 (3)
b, Å	22.638 (7)
c, Å	16.999 (6)
β, deg	96.06 (3)
V, Å^3	3704 (2)
Z	4
D(calcd),g cm^{-3}	2.247
temp, °C	23
color	deep red
size,mm	0.28 × 0.31 × 0.34
μ(Mo Kα), cm^{-1}	24.1
diffractometer	Nicolet R3m
radiatn	Mo Kα
wavelength, Å	0.71073
monochromator	graphite
scan technique	Wyckoff
scan limits, deg	$4 \le \theta \le 52$
scan speed, deg min^{-1}	var 5–20
std rflns	3 std/197 rflns
decay	~3%
data collected	7728
indpdnt data	7272
obsddata ($5\sigma(F_0)$)	5353
R(int), %	1.73
$R(F)$, %	3.12
$R(wF)$, %	4.17
GOF	0.92
Δ/σ	0.086
$\Delta(\rho)$, e Å^{-3}	0.57
N_o/N_v	11.0

Concluding Remarks

This study has shown that novel Ru_6 and Ru_7 imido clusters can be systematically derived from $Ru_3(\mu_3\text{-NPh})(CO)_{10}$ (**1**) and $Ru_3(\mu_3\text{-NPh})_2(CO)_9$ (**4**). Most impressive is the high yield (91%) production of the Ru_6 species **2** upon thermolysis of **1**. Seldom are thermolytic transformations of clusters observed to be as selective as that reported here. Also remarkable are the structures of the new clusters **2** and **3**, especially that of the latter with its two (arene)Ru(CO)$_2$ wings symmetrically attached to the Ru_5N_2 cluster core. It is especially significant that this latter species readily derives from the addition of a Ru(CO)$_2$ fragment to the existing Ru_6 cluster **2**. This reaction suggests that it should be possible to prepare a series of bimetallic clusters within this family with different metal atoms attached to the two sides of the cluster. Also important is the formation of **2** from the reaction of $Ru_3(\mu_3\text{-NPh})_2(CO)_9$ with $Ru_3(CO)_{12}$. This contrasts with the analogous reaction of the bis(phosphinidene) cluster $Ru_3(\mu_3\text{-PPh})_2(CO)_9$ which has been reported to give the tetranuclear species $Ru_4(\mu_4\text{-PPh})_2(CO)_{13}$ that has two phosphinidene ligands capping the opposite sides of a planar Ru_4 core.[6a] The fact that a similar μ_4-imido species does not form in the analogous reaction of $Ru_3(\mu_3\text{-NPh})_2(CO)_9$ with $Ru_3(CO)_{12}$ presumably reflects the dif-

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(8) (a) Blohm, M. L.; Gladfelter, W. L. *Organometallics* **1986**, *5*, 1049. (b) Rheingold, R. L.; Staley, D. L.; Han, S. H.; Geoffroy, G. L. *Acta Crystallogr.*, to be submitted for publication. (c) Gervasio, G.; Rossetti, R.; Stanghellini, P. L. *J. Chem. Soc., Chem. Commun.* **1977**, 387.

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(10) (a) Restivo, R. J.; Ferguson, G. *J. Chem. Soc., Chem. Commun.* **1973**, 847. (b) Schmid, H.; Ziegler, M. L. *Chem. Ber.* **1976**, *109*, 132. (c) Bennett, M. A.; Robertson, G. B.; Smith, A. K. *J. Organomet. Chem.* **1972**, *43*, C41.

Table II. Atomic Coodinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for 2

	x	y	z	U
Ru(1)	1254.1 (5)	1298.3 (2)	709.0 (3)	27.4 (1)
Ru(2)	994.3 (5)	1029.5 (2)	2260.0 (3)	32.2 (1)
Ru(3)	4200.0 (5)	1221.4 (2)	817.9 (3)	28.6 (1)
Ru(4)	1229.4 (5)	3258.5 (2)	1521.7 (3)	39.0 (2)
Ru(5)	3712.3 (5)	1412.2 (2)	2357.9 (3)	30.4 (1)
Ru(6)	3010.9 (5)	2313.1 (2)	1088.5 (3)	27.9 (1)
N(1)	2702 (5)	788 (2)	1523 (3)	31 (1)
N(2)	1773 (5)	1833 (2)	1810 (3)	27 (1)
O(1)	−378 (6)	2147 (2)	−393 (3)	67 (2)
O(2)	756 (5)	537 (2)	−747 (3)	60 (2)
O(3)	−1548 (4)	839 (2)	1072 (3)	55 (2)
O(4)	−1163 (6)	1582 (3)	3180 (4)	75 (2)
O(5)	2 (7)	−151 (2)	2802 (4)	97 (3)
O(6)	2914 (6)	973 (2)	3945 (3)	64 (2)
O(7)	6364 (5)	725 (3)	2709 (3)	72 (2)
O(8)	5346 (6)	2401 (3)	3212 (4)	78 (2)
O(9)	3695 (5)	1303 (2)	−955 (3)	60 (2)
O(10)	6715 (5)	1997 (2)	749 (4)	75 (2)
O(11)	5972 (5)	92 (2)	826 (3)	54 (2)
O(12)	5453 (5)	3093 (2)	1518 (4)	86 (3)
O(13)	3084 (8)	2695 (3)	−582 (3)	92 (3)
O(14)	508 (8)	3606 (4)	−186 (4)	112 (3)
O(15)	3339 (8)	4232 (3)	1568 (5)	123 (4)
C(1)	249 (6)	1840 (3)	37 (4)	39 (2)
C(2)	965 (6)	802 (3)	−181 (4)	37 (2)
C(3)	−409 (6)	974 (3)	1233 (4)	35 (2)
C(4)	−353 (7)	1368 (3)	2854 (4)	44 (2)
C(5)	429 (7)	281 (3)	2604 (4)	51 (2)
C(6)	2844 (7)	1116 (3)	3302 (4)	46 (2)
C(7)	5364 (7)	982 (3)	2569 (4)	48 (2)
C(8)	4684 (7)	2043 (3)	2895 (4)	48 (2)
C(9)	3850 (7)	1257 (3)	−289 (4)	42 (2)
C(10)	5741 (7)	1719 (3)	788 (4)	47 (2)
C(11)	5302 (6)	501 (3)	821 (4)	38 (2)
C(12)	4490 (7)	2803 (3)	1346 (4)	49 (2)
C(13)	3074 (8)	2554 (3)	69 (4)	52 (2)
C(14)	788 (9)	3466 (4)	458 (5)	70 (3)
C(15)	2576 (8)	3859 (3)	1551 (6)	71 (3)
C(21)	2552 (6)	−207 (3)	900 (4)	38 (2)
C(22)	2730 (7)	−810 (3)	927 (4)	45 (2)
C(23)	3221 (7)	−1083 (3)	1628 (5)	53 (3)
C(24)	3528 (8)	−743 (3)	2290 (5)	55 (3)
C(25)	3359 (7)	−131 (3)	2258 (4)	47 (2)
C(26)	2870 (6)	149 (2)	1554 (4)	33 (2)
C(31)	1615 (7)	2716 (3)	2654 (4)	40 (2)
C(32)	922 (8)	3240 (3)	2828 (4)	56 (3)
C(33)	−353 (7)	3401 (3)	2416 (4)	52 (3)
C(34)	−953 (7)	3024 (3)	1832 (4)	47 (2)
C(35)	−262 (6)	2499 (3)	1639 (4)	37 (2)
C(36)	1049 (6)	2330 (2)	2034 (3)	31 (2)
Ao	7534 (22)	776 (11)	5720 (16)	283 (15)
Ac(1)	6559 (29)	1356 (15)	4791 (14)	250 (18)
Ac(2)	6297 (76)	567 (29)	5125 (28)	619 (44)
Ac(3)	7947 (46)	258 (11)	4850 (18)	331 (24)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Selected Bond Distances (Å) and Angles (deg) for 2[a]

(a) Ru–Ru			
Ru(1)–Ru(2)	2.743 (1)	Ru(3)–Ru(5)	2.743 (1)
Ru(1)–Ru(3)	2.843 (1)	Ru(3)–Ru(6)	2.785 (1)
Ru(1)–Ru(6)	2.890 (1)	Ru(4)–Ru(6)	2.892 (1)
Ru(2)–Ru(5)	2.758 (1)	Ru(5)–Ru(6)	2.995 (1)
(b) Ru–N			
N(1)–Ru(1)	2.191 (4)	N(2)–Ru(1)	2.241 (4)
N(1)–Ru(2)	2.245 (5)	N(2)–Ru(2)	2.141 (4)
N(1)–Ru(3)	2.206 (5)	N(2)–Ru(5)	2.221 (4)
N(1)–Ru(5)	2.161 (4)	N(2)–Ru(6)	2.105 (5)
(c) Ru–CO, Terminal			
Ru(1)–C(1)	1.877 (6)	Ru(4)–C(14)	1.873 (9)
Ru(1)–C(2)	1.882 (6)	Ru(4)–C(15)	1.881 (8)
Ru(2)–C(4)	1.894 (7)	Ru(5)–C(7)	1.874 (7)
Ru(2)–C(5)	1.891 (7)	Ru(5)–C(8)	1.890 (7)
Ru(3)–C(9)	1.878 (6)	Ru(6)–C(12)	1.827 (6)
Ru(3)–C(10)	1.874 (6)	Ru(6)–C(13)	1.823 (7)
Ru(3)–C(11)	1.948 (6)		
(d) Ru–CO, Bridging			
Ru(1)–C(3)	2.056 (6)	Ru(2)–C(6)	2.390 (7)
Ru(2)–C(3)	2.100 (6)	Ru(5)–C(6)	2.004 (7)
(e) Other Distances			
N(1)–C(26)	1.457 (7)	Ru(5)–CNT(31–36)	1.793 (5)
N(2)–C(36)	1.399 (7)		
(f) Ru–Ru–Ru			
Ru(2)–Ru(1)–Ru(3)	96.71 (6)	Ru(2)–Ru(5)–Ru(6)	91.61 (7)
Ru(2)–Ru(1)–Ru(6)	94.18 (7)	Ru(3)–Ru(5)–Ru(6)	57.88 (6)
Ru(3)–Ru(1)–Ru(6)	58.10 (6)	Ru(1)–Ru(6)–Ru(3)	60.06 (6)
Ru(1)–Ru(2)–Ru(5)	78.69 (6)	Ru(1)–Ru(6)–Ru(4)	107.00 (6)
Ru(1)–Ru(3)–Ru(5)	77.31 (6)	Ru(1)–Ru(6)–Ru(5)	72.67 (6)
Ru(1)–Ru(3)–Ru(6)	61.77 (7)	Ru(3)–Ru(6)–Ru(4)	165.21 (6)
Ru(5)–Ru(3)–Ru(6)	65.62 (6)	Ru(3)–Ru(6)–Ru(5)	56.53 (7)
Ru(2)–Ru(5)–Ru(3)	98.70 (6)	Ru(4)–Ru(6)–Ru(5)	114.63 (6)
(g) Ru–N–Ru			
Ru(1)–N(1)–Ru(2)	76.4 (1)	Ru(1)–N(2)–Ru(2)	77.5 (1)
Ru(1)–N(1)–Ru(3)	80.6 (2)	Ru(1)–N(2)–Ru(5)	102.9 (2)
Ru(1)–N(1)–Ru(5)	106.6 (2)	Ru(1)–N(2)–Ru(6)	83.3 (2)
Ru(2)–N(1)–Ru(3)	139.5 (2)	Ru(2)–N(2)–Ru(5)	78.4 (1
Ru(2)–N(1)–Ru(5)	77.5 (2)	Ru(2)–N(2)–Ru(6)	152.9 (2)
Ru(3)–N(1)–Ru(5)	77.8 (1)	Ru(5)–N(2)–Ru(6)	87.6 (2)
(h) Bridging CO			
Ru(1)–C(3)–Ru(2)	82.6 (2)	Ru(2)–C(6)–Ru(5)	77.2 (2)
Ru(1)–C(3)–O(3)	140.2 (5)	Ru(2)–C(6)–O(6)	130.9 (6)
Ru(2)–C(3)–O(3)	137.2 (5)	Ru(5)–C(6)–O(6)	151.5 (6)
(i) All Terminal OC–Ru–CO Angles = 90 ± 6°			
(j) All Terminal Ru–C–O Angles = 177 ± 2°			
(k) CNT–Ru–CO			
CNT–Ru(4)–C(14)	134.3 (5)	CNT–Ru(4)–Ru(6)	98.7 (2)
CNT–Ru(4)–C(15)	136.1 (5)		

[a] CNT is the center of the η^6-C_6H_6 ring defined by carbon atoms C(31)–C(36).

ficulty that imido ligands have in assuming μ_4-bridging positions over a planar arrangement of four Ru atoms.

Experimental Section

The reagents $Ru_3(CO)_{12}$,[11] $Ru_3(\mu_3\text{-}NPh)(CO)_{10}$,[4] and $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$[4] were prepared by literature procedures. All solvents used were dried by standard methods, and all manipulations were conducted under N_2 by using standard Schlenk techniques. Instruments used in this research have been previously described.[12]

Synthesis of $Ru_6(\mu_4\text{-}NPh)_2(CO)_{15}$ (2). A 100-mL Schlenk flask was charged with 1 (110 mg, 0.163 mmol) to which was added 40 mL of dry methylcyclohexane. The solution was refluxed under N_2 with stirring for 13 h, during which time the yellow solution became dark red. After cooling to room temperature, the solvent was removed on a rotary evaporator and the residue was chromatographed on silica gel with hexane as the initial eluent but with the gradual addition of CH_2Cl_2 to a final concentration of 30%. This gave first a small orange band of $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ (4, 4 mg, 3%) followed by a dark orange band of $Ru_6(\mu_4\text{-}NPh)_2(CO)_{15}$ (2, 90 mg, 91%). 2: IR (CH_2Cl_2) ν_{CO} 2076 (s), 2043 (sh), 2033 (vs), 2002 (w), 1987 (m), 1844 (w, br) cm^{-1}; MS (FD), *m/z* 1208 (M^+, ^{101}Ru); ^{13}C NMR (THF, −50 °C) δ 192.92, 193.70, 197.52, 199.37, 199.63, 200.95, 235.20 (1:3:1:2:2:2:2:2 intensity ratio). Anal. Calcd for $C_{27}H_{10}O_{15}N_2Ru_6\cdot CH_2Cl_2$: C, 25.79; H, 0.93. Found: C, 25.52; H, 0.96.

Reaction of $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ (4) with $Ru_3(CO)_{12}$. A solution of 4 (50 mg, 0.068 mmol) and $Ru_3(CO)_{12}$ (60 mg, 0.094 mmol) in octane (40 mL) was refluxed for 3.5 h under N_2 to give

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[11] 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.

[12] Morrison, E. D.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1985**, *107*, 3541.

a dark red solution. After the solution was cooled to room temperature, the solvent was removed on a rotary evaporator followed by chromatography on silica gel. With hexane as eluent, a yellow band of unreacted $Ru_3(CO)_{12}$ (22 mg) was eluted followed by an orange band of unreacted **4** (28 mg) and a yellow band of an uncharacterized species (10 mg). When the polarity of the eluent was changed by the gradual addition of CH_2Cl_2, an orange band of **2** (10 mg, 28% based on consumed **4**) eluted when hexane/CH_2Cl_2 = 7:3 and a yellow band of **3** (5 mg, 13%) eluted at hexane/CH_2Cl_2 = 2:3 from which **4** was isolated as a dark orange solid by solvent evaporation. **3**: IR (CH_2Cl_2) ν_{CO} 2058 (w), 2033 (vs), 2017 (s), 1977 (m), 1956 (w), 1831 (w, br) cm^{-1}; MS (FD), *m/z* 1344 (M^+, ^{102}Ru); ^{13}C NMR (THF, −50 °C) δ 196.08, 201.47, 201.62, 202.62, 235.26, (1:2:2:2:1 intensity ratio). Anal. Calcd for $C_{28}H_{10}O_{16}N_2Ru_6$: C, 25.00; H, 0.74. Found: C, 25.26; H, 0.63.

Reaction of $Ru_6(\mu_4\text{-}NPh)_2(CO)_{15}$ (2) with $Ru_3(CO)_{12}$. A solution of **2** (60 mg, 0.050 mmol) and $Ru_3(CO)_{12}$ (30 mg, 0.047 mmol) in octane (40 mL) was refluxed for 10 h under N_2 to give a dark red solution. After the solution was cooled to room temperature the solvent was removed by rotary evaporation. Column chromatographic separation (SiO_2, hexane/CH_2Cl_2 eluent with a gradual increase in CH_2Cl_2 from 0% to 50%) gave a yellow band of $Ru_3(CO)_{12}$ (2 mg) followed by a trace amount of an unidentified dark yellow band and then a yellow band of **3**. The latter was isolated in 57% yield (25 mg) by solvent evaporation.

X-ray Diffraction Study of $Ru_6(\mu_4\text{-}NPH)_2(CO)_{15}\cdot CH_3C(=O)CH_3$ (2). Table I contains the crystal and refinement parameters for **2**. A deep red crystal of **2** was grown from acetone and mounted on a glass fiber. Systematic absences in the diffraction data uniquely defined the space group, $P2_1/c$. The unit cell parameters were obtained from the least-squares fit of the angular settings of 25 reflections (21° ≤ 2θ ≤ 26°). An empirical correction for absorption was applied to the reflection data (216 Ψ-scan data; six-parameter, pseudoellipsoid model, T_{max}/T_{min} = 0.430/0.338). The merging *R* factor for the Ψ-scan data was reduced from 4.4% to 1.6%. Corrections were also applied for a linear 3% decay in standard reflection intensity.

The six Ru atoms were located by an interpreted Patterson routine; the remaining non-hydrogen atoms were located from subsequent difference Fourier syntheses. A thermally active and/or partially disordered molecule of acetone was found cocrystallizing with **2**. Occupancy refinement of the acetone molecule suggested possible substoichiometric occupancy [sof = 0.78 (1)] (*D*(calcd) was determined by assuming a sof of 1.0). All non-hydrogen atoms were anisotropically refined, and all hydrogen atoms were treated as idealized, updated isotropic contributions (*d*(CH) = 0.96 Å). SHELXTL (5.1) software was used for all computations (Nicolet Corp., Madison, WI).

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Supplementary Material Available: Tables of isotropic thermal parameters, complete bond lengths and angles, and calculated hydrogen atom positions (7 pages); a listing of structure factors (32 pages). Ordering information is given on any current masthead page.

Tris(η^5-cyclopentadienyl)(μ_3-alkylidyne)trinickel Clusters: Preparation, Characterization, and Molecular Structure

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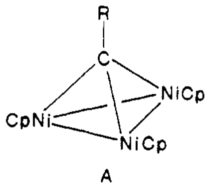
Tris(η^5-cyclopentadienyl)(μ_3-alkylidyne)trinickel clusters $(CpNi)_3(\mu_3\text{-}CR)$ (R = CH_3 (**1**), C_2H_5 (**5**), $CH(CH_3)_2$ (**6**)) with a tetrahedral Ni_3–(μ_3-C) core have been synthesized by reaction of nickelocene (Cp_2Ni) with methyl- or vinyllithium (to give **1**), with $BrMgCH{=}CHCH_3$ (to give **5**), or with $BrMgCH{=}C(CH_3)_2$ (to give **6**). CpNiCp* (Cp* = C_5Me_5) reacts with methyllithium unselectively to give a mixture of $(Cp_nCp^*_{3-n}Ni_3)CCH_3$ (**2**–**4**) with *n* = 2, 1, and 0, respectively. The molecular structure of **1** has been determined by single-crystal X-ray techniques. Crystal data: *a* = 11.684 (3) Å, *b* = 14.142 (2) Å, *c* = 9.361 (2) Å; *V* = 1546.8 Å^3; *T* = 293 K; orthorhombic; *Pnma*; *Z* = 4, D_{calcd} = 1.71 g cm^{-3}; λ(Mo Kα) = 0.71069 Å; final *R* = 0.032 (*wR* = 0.033) for 1567 unique observed reflections.

Although, the (μ_3-alkylidyne)tricobalt clusters have been investigated in detail, the analogous (μ_3-alkylidyne)trinickel compounds have received little attention. Ustynyuk et al.[1] obtained $(\eta^5\text{-}CpNi)_3CPh$ from the reaction of nickelocene with benzylmagnesium halide and proposed structure A (R = Ph) on the basis of ^1H NMR, MS, and IR data.



A

Similar reactions of Cp_2Ni with neopentyl- or ((trimethylsilyl)methyl)lithium have been used by Booth and Casey[2] to prepare the clusters $(CpNi)_3CR$ (R = CMe_3, $SiMe_3$). Recently, Vahrenkamp et al.[3] described the preparation and the molecular structure of a trinickel cluster A (R = CO_2Me). In none of these reactions does R contain α-hydrogen atoms. Reactions of Cp_2Ni with RCH_2M (M = Li, MgX), in which R contains α-H atoms (R = Me, Et, Pr), result in the decomposition of the unstable $CpNiCH_2R$ intermediate mainly via β-H elimination, and no (μ_3-alkylidyne)trinickel clusters of the

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