Nickel–Iridium Carbonyl Clusters. Synthesis and Solid-state Structure of the Trianion $[Ir_3Ni_6(\mu\text{-}CO)_6(\mu_3\text{-}CO)_2(CO)_9]^{3-}$. The First Example of a Mixed Iridium–Nickel Carbonyl Cluster

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The dark brown $[Ir_3Ni_6(\mu\text{-}CO)_6(\mu_3\text{-}CO)_2(CO)_9]^{3-}$ trianion has been obtained by redox condensation between $[Ni(CO)_4]$ and $[Ir(CO)_4]^-$. This new mixed-metal cluster is rapidly degraded, at room temperature and atmospheric pressure, by carbon monoxide to form the $[Ni(CO)_4]$ and $[Ir(CO)_4]^-$ parent mononuclear compounds. The salt $[NMe_2(CH_2Ph)_2]_3[Ir_3Ni_6(CO)_{17}]$ crystallizes in the monoclinic space group $P2_1/c$ (no. 14) with $a = 24.295(4)$, $b = 12.765(3)$, $c = 23.898(5)$, $\beta = 113.68(1)°$, and $Z = 4$. The structure was solved by conventional Patterson and Fourier methods and refined by full-matrix least squares to a final R value of 0.032 for 6 169 independent reflections having $I > 3\sigma(I)$. The metal framework consists of a face-sharing bioctahedron, with the three iridium atoms located in the inner triangle.

The chemistry of bimetallic carbonyl clusters is currently under active investigation because of their applications as catalyst precursors of bimetallic catalysts supported on metal oxides,[1] as models for catalytic metal surfaces,[2] or as catalysts in their own right.[3–5] Moreover mixed-metal clusters often adopt unexpected geometries[6,7] and are particularly useful for studies of site reactivity and molecular dynamics.[8]

A large number of mixed-metal carbonyl clusters has been already studied and several examples of these compounds containing either iridium (with Mo,[9] W,[9,10] FeCu,[11] Fe,[12] Ru,[13] Os,[14] Co,[15,16] Rh,[15] or Pt[17]) or nickel (with Cr,[18] Mo,[18] W,[18,19] Fe,[20,21] Ru,[22,23] Os,[23,24] Co,[20,25–28] Rh,[29,30] or Pt[31,32]) are known. However, to our knowledge, there are no reports of IrNi bimetallic clusters and we wish to report here the synthesis and crystal structure of the first example of an IrNi mixed-metal carbonyl cluster, namely $[NMe_2(CH_2Ph)_2]_3[Ir_3Ni_6(CO)_{17}]$.

Results and Discussion

Synthesis and Chemical Behaviour of $[Ir_3Ni_6(CO)_{17}]^{3-}$ (**1**).—The initial attempts in which a nickel carbonyl anion such as $[Ni_6(CO)_{12}]^{2-}$ was treated with iridium compounds such as $IrCl_3·3H_2O$ or $[Ir(CO)_3Br]$ were unsuccessful, yielding invariably $[Ni_9(CO)_{18}]^{2-}$ and iridium metal. The reverse redox condensation involving iridium carbonyl anions and $[Ni(CO)_4]$ was also tested. For example, the reaction of $[Ir_6(CO)_{15}]^{2-}$ with $[Ni(CO)_4]$ in acetone was carried out, but after 48 h at room temperature no detectable transformation occurred. The trianion $[Ir_3Ni_6(CO)_{17}]^{3-}$ was ultimately obtained almost quantitatively and selectively by reacting at 60 °C in tetrahydrofuran (thf) a large excess of $[Ni(CO)_4]$ with $Na[Ir(CO)_4]$ according to the formal equation (1).

$$3\,[Ir(CO)_4]^- + 6\,[Ni(CO)_4] \underset{\text{CO, 25 °C}}{\overset{\text{N}_2\text{, 60 °C}}{\rightleftarrows}} [Ir_3Ni_6(CO)_{17}]^{3-} + 19\,CO \quad (1)$$

The reaction mixture was monitored by i.r. spectroscopy and only the starting material and the final product could be detected, without evidence of formation of any other cluster compounds. This observation is in accordance with the fact that preformed homometallic clusters do not condense to form heterometallic compounds. The reaction was carried out until the i.r. absorptions due to the $[Ir(CO)_4]^-$ anion disappeared; the crude sodium salt of the trianion was isolated after evaporation *in vacuo* of the excess of $[Ni(CO)_4]$. Other salts were obtained by metathesis of $Na_3[Ir_3Ni_6(CO)_{17}]$ with halides of different bulky cations in methanol. The tetrasubstituted ammonium or phosphonium salts are generally well soluble in acetone and acetonitrile, sparingly soluble in thf and propan-2-ol, and insoluble in non-polar solvents. Most of them can be crystallized from acetone solution by precipitation by slow diffusion of propan-2-ol.

In accordance with the solid-state structure (see later) the i.r. spectrum of many tetra-alkylammonium salts of (**1**), in CH_3CN solution, show absorption bands in the carbonyl stretching region at 1 967vs, 1 778m, and 1 720w cm^{-1} (see Figure 1) in the right ratio for terminal, edge and face bridging carbon monoxide groups, respectively. In contrast, the sodium salt of (**1**) is soluble in thf with an i.r. spectrum (ν_{CO} at 1 980vs, 1 790m, and 1 740ms cm^{-1}) which differs especially in the bridging region, and with the absorption bands shifted to higher wavenumbers from that of the tetra-alkylammonium salts, probably because of ion-pairing effects. However, regardless of the counter ions, all the salts of (**1**) show identical reactivity.

The trianion (**1**) is air-sensitive both in solution and in the solid state and decomposes to form $[Ni(CO)_4]$, iridium metal, and other by-products.

The $[Ir_3Ni_6(CO)_{17}]^{3-}$ trianion reacts in acetone with acids to yield a complex mixture of brown products which are presently under investigation. No appreciable thermal decomposition

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† 1,5;3,4;2,6;5,8;4,9;6,7-Hexa-μ-carbonyl-1,2,3;7,8,9-di-μ_3-carbonyl-1,2,3,4,5,6,7,8,9-nonacarbonyl-*cyclo*-hexanickeltri-iridate(3 −) (6*Ni–Ni*)(3*Ir–Ir*)(12*Ni–Ir*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

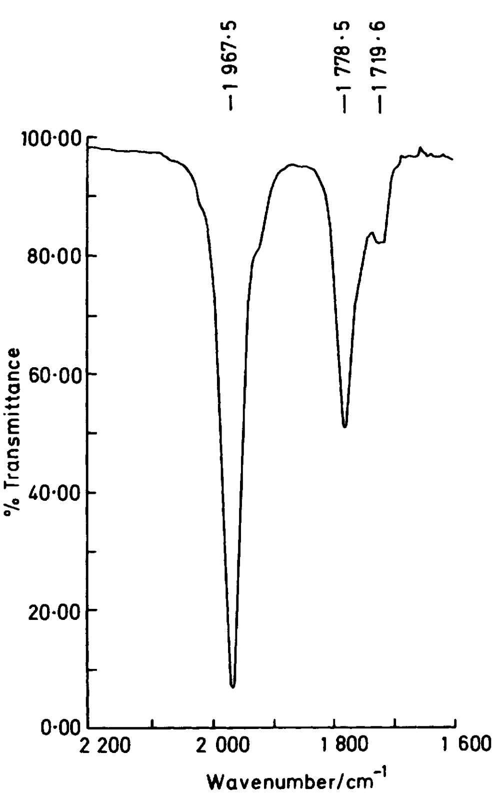

Figure 1. Infrared spectrum of $[NMe_3(CH_2Ph)]_3[Ir_3Ni_6(CO)_{17}]$ in CH_3CN

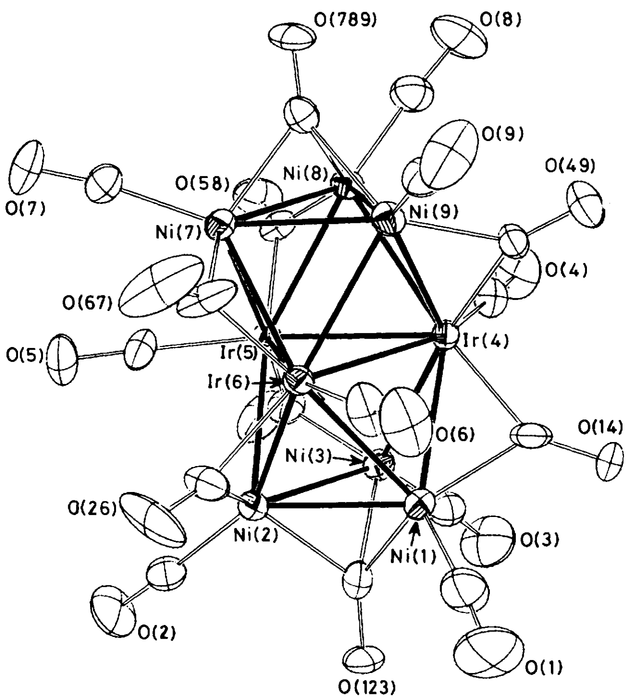

Figure 2. ORTEP drawing of $[Ir_3Ni_6(CO)_{17}]^{3-}$. Thermal ellipsoids are drawn with 30% probability

occurred by refluxing a solution of the salt in CH_3CN for 8 h. The trianion is unstable to CO, being degraded quantitatively to the stable starting materials $[Ni(CO)_4]$ and $[Ir(CO)_4]^-$ within a few minutes. The reaction of (**1**) with carbon monoxide is in keeping with the instability found in most other mono- or bi-metallic nickel-containing clusters such as $[Ni_9(CO)_{18}]^{2-}$,[33] $[Ni_{38}Pt_6(CO)_{48}H_{6-n}]^{n-}$,[31] $[NiRh_6(CO)_{16}]^{2-}$,[29] or $[Co_4Ni_2(CO)_{14}]^{2-}$.[25] Differently from the above compounds, however, in the degradation of (**1**), we could not detect spectroscopically the intermediate formation of other homometallic or bimetallic complexes. This behaviour is surprising in view of the stability of several iridium and nickel clusters such as $[Ni_5(CO)_{12}]^{2-}$ [34] and $[Ir_6(CO)_{15}]^{2-}$ [35] under the same experimental conditions, and it seems conceivable that the coincidence in (**1**) between the number of negative charges and iridium atoms, together with the well known stability of both $[Ni(CO)_4]$ and $[Ir(CO)_4]^-$, could be the reason for this unexpected behaviour, previously found in the reactivity of $[Co_2Ni_{10}(CO)_{20}C]^{2-}$, where it was possible to detect, by i.r. spectroscopy, the formation of $[Co(CO)_4]^-$ and $[Ni(CO)_4]$.[28]

In keeping with this suggestion, we have found that the products obtained by treating (**1**) with acids, which are most likely to display a negative charge-to-iridium atoms ratio different from one, are also unstable under carbon monoxide and are not degraded to $[Ir(CO)_4]^-$ and $[Ni(CO)_4]$ but to different compounds presently under investigation.

Description of the Structure of $[Ir_3Ni_6(CO)_{17}]^{3-}$.—The crystal structure of $[NMe_2(CH_2Ph)_2]_3[Ir_3Ni_6(\mu\text{-}CO)_6(\mu_3\text{-}CO)_2(CO)_9]$ consists of the packing of discrete $[NMe_2(CH_2Ph)_2]^+$ and $[Ni_6Ir_3(CO)_{17}]^{3-}$ ions. There are no unusually short contact distances between the cations and trianions. Positional parameters for non-hydrogen atoms are reported in Table 1 and selected bond distances and angles in Tables 2 and 3, respectively. The metal framework of the anion $[Ir_3Ni_6(\mu\text{-}CO)_6(\mu_3\text{-}CO)_2(CO)_9]^{3-}$ is shown in Figure 2 and may be envisaged as deriving from the face condensation of two octahedral units. It can also be described as a hexagonal close-packed fragment resulting from the *aba* stacking of three almost parallel staggered triangles, the inner one being formed by iridium atoms. This is in agreement with the common trend found in mixed-metal clusters where the metal possessing the higher atomization energy preferentially occupies the site of higher metal connectivity.[31,32] The idealized symmetry of the metallic skeleton is D_{3h}, lowered to C_{3h} by the carbonyl distribution. An inspection of the metal–metal bond distances shows that the interlayer Ni–Ir bonds spanned by bridging carbonyls are shorter than the unbridged ones [average Ni–Ir(bridged) 2.599 Å, Ni–Ir(unbridged) 2.688 Å]. Within the homometallic triangles the average bond lengths are Ir–Ir 2.810, Ni–Ni 2.522 Å. The former value agrees well with the longest separations found, for instance, in octahedral iridium clusters.[36] The average Ni–Ni bonding interaction in the two outer triangles is significantly longer than those observed in the $[Ni_3(\mu\text{-}CO)_3(CO)_3]$ triangular fragments contained in the $[Ni_6(CO)_{12}]^{2-}$ [37] and $[Ni_9(CO)_{18}]^{2-}$ [38] dianions and in the series of clusters $[Ni_{12}(CO)_{21}H_n]^{(4-n)-}$ (n = 1 or 2)[39] or $[Ni_9Pt_3(CO)_{21}H]^{3-}$.[32] This is probably related to the presence in the above compounds of μ-CO groups spanning all the edges of the Ni_3 triangles instead of the single μ_3-CO group observed in (**1**).

The trianion (**1**) possesses 17 carbonyls: nine are terminally bonded, one for each metal atom, six are edge bridging, spanning six alternating interlayer Ni–Ir bonds, and the two remaining are face bridging on the two Ni_3 faces. The average Ni–CO(terminal) and Ni–CO(face bridging) bond lengths of 1.753 and 2.009 Å are in good agreement with the separations found in other anionic nickel clusters.[34,37–39] The average Ir–CO(terminal) bond separation of 1.847 Å is in the range usually found in anionic iridium clusters.[36]

The μ-CO ligands are almost symmetrical, with average

Table 1. Final positional parameters with estimated standard deviations (e.s.d.s) in parentheses for $[NMe_2(CH_2Ph)_2]_3[Ir_3Ni_6(\mu\text{-}CO)_6(\mu_3\text{-}CO)_2(CO)_9]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ir(4)	0.261 10(2)	0.038 47(3)	0.079 43(1)	C(102)	0.987 2(6)	0.321(1)	0.068 5(6)
Ir(5)	0.302 43(2)	0.108 93(3)	−0.007 50(1)	C(103)	0.884 3(5)	0.340(1)	−0.012 5(5)
Ir(6)	0.197 94(2)	0.197 60(3)	−0.002 11(2)	C(104)	0.902 5(5)	0.349(1)	−0.064 8(5)
Ni(1)	0.157 06(5)	0.001 3(1)	−0.010 82(5)	C(105)	0.933 9(6)	0.269(1)	−0.076 5(6)
Ni(2)	0.189 54(6)	0.074 1(1)	−0.090 77(5)	C(106)	0.949 7(7)	0.277(1)	−0.1302(7)
Ni(3)	0.249 07(5)	−0.071 6(1)	−0.021 09(5)	C(107)	0.927 6(7)	0.363(1)	−0.163 6(6)
Ni(7)	0.297 81(5)	0.303 2(1)	0.034 27(5)	C(108)	0.896 6(7)	0.443(1)	−0.155 5(7)
Ni(8)	0.358 97(5)	0.161 3(1)	0.105 56(5)	C(109)	0.884 3(6)	0.432(1)	−0.104 0(6)
Ni(9)	0.266 18(5)	0.232 7(1)	0.115 20(5)	C(110)	0.899 0(5)	0.370(1)	0.093 7(5)
O(1)	0.031 5(4)	−0.035(1)	−0.041 8(5)	C(111)	0.938 0(5)	0.400(1)	0.157 4(5)
O(2)	0.182 8(5)	0.048 2(9)	−0.213 1(3)	C(112)	0.973 0(6)	0.327(1)	0.197 0(6)
O(3)	0.261 6(5)	−0.296 3(7)	−0.016 8(5)	C(113)	1.010 5(7)	0.353(1)	0.258 0(7)
O(4)	0.365 9(3)	−0.109 3(7)	0.135 6(4)	C(114)	1.011 2(6)	0.455(1)	0.276 5(6)
O(5)	0.300 7(3)	0.241 7(7)	−0.111 9(3)	C(115)	0.974 7(6)	0.524(1)	0.239 1(6)
O(6)	0.096 3(3)	0.231 8(9)	0.036 4(4)	C(116)	0.938 7(5)	0.501(1)	0.178 8(5)
O(7)	0.335 8(5)	0.468 0(8)	−0.025 3(4)	C(201)	0.751 5(5)	0.320(1)	0.267 7(5)
O(8)	0.449 0(4)	0.130 6(9)	0.227 6(4)	C(202)	0.741 9(5)	0.225(1)	0.175 6(5)
O(9)	0.211 6(4)	0.358 7(7)	0.179 3(4)	C(203)	0.811 1(5)	0.374(1)	0.208 6(5)
O(14)	0.182 2(3)	−0.133 8(7)	0.093 6(3)	C(204)	0.830 2(5)	0.478(1)	0.240 7(5)
O(26)	0.115 6(5)	0.259 4(8)	−0.128 5(4)	C(205)	0.817 3(5)	0.573(1)	0.209 6(5)
O(35)	0.344 7(3)	−0.070 5(7)	−0.062 1(3)	C(206)	0.837 1(6)	0.664(1)	0.241 7(6)
O(49)	0.276 6(3)	0.082 3(7)	0.209 3(3)	C(207)	0.870 1(6)	0.663(1)	0.301 8(6)
O(58)	0.437 9(3)	0.091 4(7)	0.049 5(3)	C(208)	0.886 6(6)	0.572(1)	0.335 3(6)
O(67)	0.194 1(4)	0.432 8(7)	−0.009 9(7)	C(209)	0.865 1(5)	0.476(1)	0.302 7(5)
O(123)	0.131 1(4)	−0.130 9(6)	−0.119 2(3)	C(210)	0.700 3(5)	0.406 8(9)	0.166 7(5)
O(789)	0.372 9(3)	0.377 6(6)	0.157 4(3)	C(211)	0.637 2(4)	0.375(1)	0.157 7(4)
C(1)	0.081 4(5)	−0.020(1)	−0.026 5(5)	C(212)	0.613 1(5)	0.411(1)	0.197 0(5)
C(2)	0.181 7(5)	0.061 3(9)	−0.166 9(5)	C(213)	0.552 8(6)	0.386(1)	0.185 6(6)
C(3)	0.258 1(5)	−0.207 1(9)	−0.016 5(4)	C(214)	0.519 8(6)	0.325(1)	0.135 5(6)
C(4)	0.324 9(4)	−0.053 7(9)	0.113 3(4)	C(215)	0.543 8(6)	0.288(1)	0.098 0(6)
C(5)	0.301 2(4)	0.192 7(9)	−0.071 2(4)	C(216)	0.603 6(5)	0.312(1)	0.107 8(5)
C(6)	0.134 8(4)	0.212(1)	0.021 2(5)	C(301)	0.381 6(5)	0.330(1)	0.304 2(5)
C(7)	0.324 0(5)	0.406 0(9)	0.001 6(5)	C(302)	0.475 9(5)	0.411(1)	0.316 1(5)
C(8)	0.415 6(5)	0.143(1)	0.178 3(5)	C(303)	0.400 2(5)	0.518(1)	0.334 4(5)
C(9)	0.235 0(5)	0.311(1)	0.155 4(5)	C(304)	0.370 3(5)	0.560 7(9)	0.271 6(4)
C(14)	0.196 7(4)	−0.060(1)	0.070 7(4)	C(305)	0.404 5(6)	0.621(1)	0.247 6(6)
C(26)	0.151 3(5)	0.207(1)	−0.091 4(5)	C(306)	0.377 1(6)	0.660(1)	0.189 2(6)
C(35)	0.316 3(5)	−0.028 1(9)	−0.040 0(4)	C(307)	0.320 2(6)	0.640(1)	0.155 3(6)
C(49)	0.268 8(4)	0.101 0(8)	0.158 7(4)	C(308)	0.285 4(6)	0.582(1)	0.175 7(6)
C(58)	0.389 8(4)	0.110 6(8)	0.048 0(4)	C(309)	0.309 9(5)	0.544(1)	0.235 4(5)
C(67)	0.215 4(5)	0.348(1)	−0.000 1(7)	C(310)	0.454 7(5)	0.381(1)	0.408 5(5)
C(123)	0.162 4(5)	−0.066 7(9)	−0.081 8(4)	C(311)	0.483 2(5)	0.275(1)	0.422 3(5)
C(789)	0.343 0(4)	0.314 5(9)	0.123 5(4)	C(312)	0.450 9(5)	0.188(1)	0.423 5(5)
N(1)	0.928 9(3)	0.382 3(7)	0.047 6(3)	C(313)	0.476 7(6)	0.087(1)	0.433 1(6)
N(2)	0.750 1(4)	0.331 0(7)	0.204 3(3)	C(314)	0.533 6(6)	0.076(1)	0.441 2(6)
N(3)	0.427 6(3)	0.409 8(7)	0.339 5(3)	C(315)	0.568 7(6)	0.165(1)	0.442 9(6)
C(101)	0.942 8(5)	0.494(1)	0.042 8(5)	C(316)	0.542 8(6)	0.263(1)	0.434 0(5)

values for Ni–C and Ir–C bond distances of 1.938 and 1.979 Å, respectively.

Several other enneanuclear carbonyl clusters formed by a stacking of triangles are known, *i.e.* $[Ni_9(CO)_{18}]^{2-}$,[38] $[Pt_9(CO)_{18}]^{2-}$,[40] $[Rh_9(CO)_{19}]^{3-}$,[41] and $[PtRh_8(CO)_{19}]^{2-}$,[42] but the different twisting of these triangular subunits gives rise to different structures: face-sharing bioctahedra for $[Rh_9(CO)_{19}]^{3-}$[41] and $[PtRh_8(CO)_{19}]^{2-}$,[42] face-sharing trigonal prisms in $[Pt_9(CO)_{18}]^{2-}$,[40] and face-sharing trigonal antiprism and trigonal prism for $[Ni_9(CO)_{18}]^{2-}$.[38] Consistently, for these clusters, the number of cluster valence electrons (c.v.e.) ranges from 122 in $[Rh_9(CO)_{19}]^{3-}$ and $[PtRh_8(CO)_{19}]^{2-}$ to 128 in $[Ni_9(CO)_{18}]^{2-}$ and $[Pt_9(CO)_{18}]^{2-}$. Trianion (**1**) and $[Rh_9(CO)_{19}]^{3-}$ have the same metal core, nevertheless they possess a different number of c.v.e. (124 *versus* 122 respectively). The value for $[Rh_9(CO)_{19}]^{2-}$ and $[PtRh_8(CO)_{19}]^{2-}$ is in agreement with the general rule of $6N + 7$ valence orbitals[43] for clusters derived by fragmentation of a close-packed lattice. However for this particular arrangement topological electron counting,[44] polyhedral skeletal electron pair[45] theories, and molecular orbital calculations[43] on a naked metal cluster, predict 124 c.v.e., as found in (**1**) and in the recently characterized $[Ir_9(CO)_{20}]^{3-}$.[46] The same discrepancy was previously observed in the case of $[Rh_{12}(CO)_{25}H_2]$[47] and $[Ir_{12}(CO)_{26}]^{2-}$,[48] two clusters having closely related structures composed by three face-sharing octahedra.

Experimental

All the reactions were carried out under a nitrogen atmosphere with standard Schlenk-tube techniques. All solvents were dried and freshly distilled under nitrogen before use. $[Ir_4(CO)_{12}]$ was prepared by reductive carbonylation of $K_2[IrCl_6]$ in 2-methoxyethanol.[49] An approximately 0.5 mol dm^{-3} solution

Table 2. Relevant bond distances (Å) with e.s.d.s in parentheses for $[Ir_3Ni_6(\mu\text{-}CO)_6(\mu_3\text{-}CO)_2(CO)_9]^{3-}$

Ni(1)–Ni(2)	2.520(2)	Ni(1)–C(1)	1.743(14)
Ni(1)–Ni(3)	2.522(2)	Ni(2)–C(2)	1.759(12)
Ni(2)–Ni(3)	2.527(2)	Ni(3)–C(3)	1.742(13)
Ni(1)–Ir(4)	2.624(1)	Ni(7)–C(7)	1.770(13)
Ni(1)–Ir(6)	2.673(1)	Ni(8)–C(8)	1.746(13)
Ni(2)–Ir(5)	2.701(1)	Ni(9)–C(9)	1.759(12)
Ni(2)–Ir(6)	2.583(1)	Ir(4)–C(4)	1.853(13)
Ni(3)–Ir(4)	2.696(1)	Ir(5)–C(5)	1.851(11)
Ni(3)–Ir(5)	2.600(1)	Ir(6)–C(6)	1.839(11)
Ir(4)–Ir(5)	2.794(1)	Ni(1)–C(14)	1.954(12)
Ir(4)–Ir(6)	2.806(1)	Ir(4)–C(14)	1.948(12)
Ir(5)–Ir(6)	2.829(1)	Ni(2)–C(26)	1.927(13)
Ir(4)–Ni(8)	2.704(1)	Ir(6)–C(26)	1.976(11)
Ir(4)–Ni(9)	2.609(1)	Ni(3)–C(35)	1.942(11)
Ir(5)–Ni(7)	2.692(1)	Ir(5)–C(35)	1.996(11)
Ir(5)–Ni(8)	2.579(1)	Ir(4)–C(49)	1.993(10)
Ir(6)–Ni(7)	2.601(1)	Ni(9)–C(49)	1.964(11)
Ir(6)–Ni(9)	2.660(1)	Ir(5)–C(58)	2.002(11)
Ni(7)–Ni(8)	2.521(2)	Ni(8)–C(58)	1.923(10)
Ni(7)–Ni(9)	2.517(2)	Ir(6)–C(67)	1.960(14)
Ni(8)–Ni(9)	2.526(2)	Ni(7)–C(67)	1.919(13)
Ni(1)–C(123)	1.955(12)	C(7)–O(7)	1.128(13)
Ni(2)–C(123)	1.955(12)	C(8)–O(8)	1.141(13)
Ni(3)–C(123)	2.022(12)	C(9)–O(9)	1.127(13)
Ni(7)–C(789)	1.973(11)	C(14)–O(14)	1.216(13)
Ni(8)–C(789)	2.072(12)	C(26)–O(26)	1.172(13)
Ni(9)–C(789)	2.078(11)	C(35)–O(35)	1.158(12)
C(1)–O(1)	1.133(14)	C(49)–O(49)	1.171(11)
C(2)–O(2)	1.128(13)	C(58)–O(58)	1.179(11)
C(3)–O(3)	1.141(13)	C(67)–O(67)	1.185(15)
C(4)–O(4)	1.163(12)	C(123)–O(123)	1.226(13)
C(5)–O(5)	1.151(12)	C(789)–O(789)	1.166(12)
C(6)–O(6)	1.161(13)		

Table 3. Selected angles (°) with e.s.d.s in parentheses for $[Ir_3Ni_6(\mu\text{-}CO)_6(\mu_3\text{-}CO)_2(CO)_9]^{3-}$

Ni(1)–Ni(2)–Ni(3)	59.97(5)	Ni(7)–C(7)–O(7)	172.2(12)
Ni(2)–Ni(3)–Ni(1)	59.86(5)	Ni(8)–C(8)–O(8)	174.5(11)
Ni(3)–Ni(1)–Ni(2)	60.17(5)	Ni(9)–C(9)–O(9)	175.6(12)
Ir(4)–Ir(5)–Ir(6)	59.87(1)	Ni(1)–C(14)–Ir(4)	84.5(5)
Ir(5)–Ir(6)–Ir(4)	59.45(1)	Ni(2)–C(26)–Ir(6)	82.8(5)
Ir(6)–Ir(4)–Ir(5)	60.68(1)	Ni(3)–C(35)–Ir(5)	82.6(4)
Ni(7)–Ni(8)–Ni(9)	59.82(5)	Ir(4)–C(49)–Ni(9)	82.5(4)
Ni(8)–Ni(9)–Ni(7)	59.99(5)	Ir(5)–C(58)–Ni(8)	82.1(4)
Ni(9)–Ni(7)–Ni(8)	60.19(5)	Ir(6)–C(67)–Ni(7)	84.2(6)
Ni(1)–C(1)–O(1)	174.0(14)	Ni(1)–C(123)–Ni(2)	80.2(5)
Ni(2)–C(2)–O(2)	172.5(13)	Ni(1)–C(123)–Ni(3)	78.7(4)
Ni(3)–C(3)–O(3)	176.2(13)	Ni(2)–C(123)–Ni(3)	78.9(4)
Ir(4)–C(4)–O(4)	178.1(10)	Ni(7)–C(789)–Ni(8)	77.1(4)
Ir(5)–C(5)–O(5)	177.5(10)	Ni(7)–C(789)–Ni(9)	76.8(4)
Ir(6)–C(6)–O(6)	172.9(14)	Ni(8)–C(789)–Ni(9)	75.0(4)

Table 4. Crystal data and intensity collection parameters

Compound	$[NMe_2(CH_2Ph)_2]_3[Ir_3Ni_6(CO)_{17}]$
Formula	$C_{65}H_{60}Ir_3N_3Ni_6O_{17}$
M	2 084.07
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	24.295(4)
b/Å	12.765(3)
c/Å	23.898(5)
β/°	113.68(1)
U/Å^3	6 787(5)
Z	4
D_c/g cm^{-3}	2.039
F(000)	4 024
μ(Mo-K_α)/cm^{-1}	75.37
Min. transmission factor	0.58
ω scan width/°	1.2 + 0.35 tan θ
θ range/°	3—25
Octants of reciprocal space explored	$\pm h, +k, +l$
Measured reflections	11 861
Unique observed reflections with $I > 3\sigma(I)$	6 169
Final R and R'[a]	0.032, 0.037
No. of variables	592
E.s.d.[b]	1.079

[a] $R = \Sigma(F_o - k|F_c|)/\Sigma F_o$, $R' = [\Sigma w(F_o - k|F_c|)^2/\Sigma w F_o^2]^{\frac{1}{2}}$. [b] E.s.d. in observation of unit weight $= [\Sigma w(F_o - k|F_c|)^2/(\text{n.o.} - \text{n.v.})]^{\frac{1}{2}}$, n.o. = number of observations, n.v. = number of variables.

of Na[Ir(CO)$_4$] was obtained by suspending [Ir$_4$(CO)$_{12}$] (1.1 g) and a Na (0.5 g) dispersion in vaseline oil in tetrahydrofuran (thf) (40 cm^3) and stirring under CO for 48 h, to give an approximate 50% yield. The suspension was then allowed to settle for 12 h and the clear solution used without any attempt to isolate the sodium salt as a solid material.

Infrared spectra were recorded on a Perkin-Elmer 781 grating spectrophotometer (calibrated with polystyrene film) and on a Nicolet MX-1FT IR instrument, using calcium fluoride cells previously purged with N_2.

Preparation of $[Ir_3Ni_6(CO)_{17}]^{3-}$ (**1**).—In a 100-cm^3 round-bottomed flask equipped with a condenser cooled at −30 °C was placed [Ni(CO)$_4$] (2 cm^3), thf (30 cm^3), and the solution of Na[Ir(CO)$_4$] (20 cm^3). The mixture was then heated at 60 °C under a light stream of nitrogen. Within a few minutes the colour of the solution became yellow-brown, then dark brown. After heating for 4 h, all the $[Ir(CO)_4]^-$ had reacted. The solvent was evacuated and the residue dissolved in CH_3OH (30 cm^3) and precipitated by adding a water solution (15 cm^3) containing [NPr$^n_4$]Br (2.0 g). The microcrystalline precipitate was filtered off, washed with isopropyl alcohol, and dried *in vacuo*. Yield: 0.59 g {90% on $[Ir(CO)_4]^-$} as $[NPr^n_4]^+$ salt, after crystallization from acetone and propan-2-ol.

Several salts with different counter ions including $[NEt_4]^+$, $[NMe_4]^+$, $[N(PPh_3)_2]^+$, $[AsPh_4]^+$, $[NMe_2(CH_2Ph)_2]^+$ were similarly prepared in comparable yields.

Crystals of $[NMe_2(CH_2Ph)_2]_3[Ir_3Ni_6(CO)_{17}]$, suitable for *X*-ray analysis were obtained by layering the methanolic solution of the sodium salt (5 cm^3) with a 5% solution of $[NMe_2(CH_2Ph)_2]Cl$ (10 cm^3) in propan-2-ol. A large number of different crystals with different cations were unsuccessfully tested for the *X*-ray analysis and eventually the salt containing the $[NMe_2(CH_2Ph)_2]^+$ cation gave crystals of good quality for data collection.

Crystal Structure Determination.—A well shaped prismatic crystal of $[NMe_2(CH_2Ph)_2]_3[Ir_3Ni_6(CO)_{17}]$ (dark brown, dimensions 0.12 × 0.19 × 0.23 mm) was used for data collection. Intensity data were collected on an Enraf-Nonius CAD-4 automated diffractometer by the ω-scan technique, using Mo-K_α radiation (λ = 0.710 73 Å) with a graphite monochromator in the incident beam. Crystal data together with some experimental details are summarized in Table 4. Standard CAD-4 centring, indexing, and data collection programs were used; a periodic remeasurement of three standard reflections revealed a decay of *ca.* 10% during the data collection. The structure was solved by conventional Patterson and Fourier methods and refined by full-matrix least squares, the minimized function being $\Sigma w(F_o - k|F_c|)^2$. Weights were assigned according to the formula $w = \sigma^{-2}(F_o)$, where $\sigma(F_o) = \sigma(F_o^2)/2F_o$, $\sigma(F_o^2) = [\sigma^2(I) + (iI)^2]^{\frac{1}{2}}/Lp$ and *i*, the ignorance factor, was equal to 0.04.

The final difference Fourier map showed only peaks not exceeding 0.9 e $Å^{-3}$ near to the metal atoms. Absorption correction was performed with the empirical method described in ref. 50. Scattering factors and anomalous dispersion coefficients were taken from ref. 51. All the computations were performed on a PDP 11/34 computer using the SDP package of crystallographic programs.[52]

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