Figure 1. An ORTEP diagram of Ru6(C)(CO)15(CN-*tert*-Bu)(μ-CO) showing 50% probability thermal-motion ellipsoids.

I
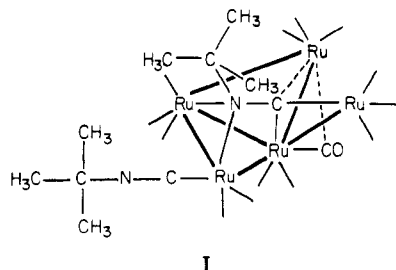
to reflux in nonane solvent for 2 h, I is converted into two new compounds. One of these, obtained in 13% yield, has been found to be the carbido cluster Ru6(C)(CO)15(CN-*t*-Bu)(μ-CO), II. This compound was characterized by X-ray crystallographic methods, and an ORTEP diagram of its structure is shown in Figure 1.[12,13] The molecule consists of an octahedral cluster of six ruthenium atoms that encapsulate a single carbido atom C(50) located in the center of the cluster. There are 15 linear terminal carbonyl ligands and one terminal isocyanide ligand distributed about the surface of the cluster as shown in the figure.[14] One carbonyl ligand, C(9)–O(9), symmetrically bridges one edge of the octahedron. Overall the structure is very similar to those of the related compounds Ru6(C)(CO)16(μ-CO)[15] and Ru6(C)(CO)15(PPh2Et)(μ-CO).[16]

The source of the carbido carbon atom was established

by an isotope labeling experiment.[17] Ru5(CO)14(^{13}CN-*t*-Bu)(μ5-^{13}CN-*t*-Bu) was prepared by using ^{13}CN-*t*-Bu and was converted into the carbido cluster as described above. Both this product and a sample prepared from unlabeled I (for comparative purposes) were investigated by mass spectral analysis. The mass spectra of both samples clearly showed the parent ion and ions corresponding to the loss of the isocyanide ligand and each of the 16 carbonyl ligands. However, the isotope distribution pattern of the parent ion of compound II prepared from the labeled isocyanide was displaced to heavier *m/e* values by 2 amu compared to that obtained from the unlabeled sample. An analysis of the relative abundances of selected isotopes indicates that the parent ion is within experimental error 100% doubly ^{13}C labeled.[17] For all ions for which the isocyanide ligand was not present, including the ion Ru6C+, the isotope patterns from the labeled sample were displaced to a higher *m/e* value by only 1 amu.

To our knowledge this is the first reported example of the abstraction of the carbon atom of an isocyanide ligand to yield a carbido cluster. The fate of the NR portion of the fragmented isocyanide ligand has not been established with certainty, but GC and GC–mass spectral analyses of the reaction solutions showed the presence of *t*-Bu N=C=O.

In studies, currently in progress, we hope to establish further details concerning the mechanism of the C–N bond rupture and the nature of the addition of the sixth ruthenium atom to the five contained in I.

(12) Crystal data: space Group *P*Ī, No. 2, *a* = 13.750 (3) Å, *b* = 15.461 (5) Å, *c* = 15.991 (8) Å, *α* = 104.51 (3)°, *β* = 102.39 (3)°, *γ* = 96.65 (2)°, *V* = 3162 (4) Å³, *M*r 1149.7, *Z* = 4, *ρ*calcd = 2.41 g/cm³. The structure was solved by direct methods (MULTAN) and refined with 5774 reflections (*F*² ≥ 3.0*σ*(*F*²)) to final values of the residuals *R*F = 0.053 and *R*wF = 0.060.

(13) Intensity data (Mo Kα) were collected on an Enraf-nonius CAD-4 automatic diffractometer by using the ω–scan technique. All calculations were performed on a Digital Equipment Corp. PDP 11/45 computer by using the Enraf-Nonius SDP program library, version 18.

(14) There are two independent molecules in the asymmetric crystal unit. Both molecules are essentially identical structurally. Selected bond distances (Å) for the molecule shown in the figure are as follows: Ru(1)–Ru(2) = 2.886 (1), Ru(1)–Ru(4) = 3.018 (1), Ru(1)–Ru(5) = 2.863 (1), Ru(1)–Ru(6) = 2.830 (1), Ru(2)–Ru(3) = 2.928 (1), Ru(2–Ru(5) = 2.907 (1), Ru(2)–Ru(6) = 2.912 (1), Ru(3)–Ru(4) = 2.843 (1), Ru(3–Ru(5) = 2.939 (1), Ru(3)–Ru(6) = 2.950 (1), Ru(4)–Ru(5) = 2.881 (1), Ru(4)–Ru(6) = 2.957 (1), Ru(1)–C(50) = 2.070 (8), Ru(2)–C(50) = 2.063 (8), Ru(3)–C(50) = 2.051 (8), Ru(4)–C(50) = 2.074 (8), Ru(5)–C(50) = 2.073 (8), Ru(6)–C(50) = 2.032 (8).

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(17) Labeled *tert*-butyl isocyanide was prepared by the method of Jackson et al. by using 99% enriched K^{13}CN (Merck, Sharp and Dohme).[18] Accurately calibrated mass spectra were obtained on an AEI MS-902 mass spectrometer at the University Chemical Laboratories, Cambridge, England. For the unlabeled cluster II the observed isotope distribution pattern for the parent ion is centered at *m/e* 1151. This is precisely the position calculated for this ion on the basis of the known isotopic distributions of the constituent atoms. The spectrum of II obtained from Ru5(CO)14 (^{13}CN-*t*-Bu)(μ5-^{13}CN-*t*-Bu) showed the parent ion centered at *m/e* 1153 with a distribution pattern analogous to that of unlabeled II. An analysis of the relative abundances of selected isotopes of this parent ion indicate that it is within experimental error (±5%) 100% doubly ^{13}C labeled. Isotope distribution patterns were calculated by Dr. C. E. Costello of the MIT mass spectral facility.

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Syntheses and X-ray Structure Analyses of Os3(CO)n(CH3OCONNCOOCH3) (*n* = 10–12). A Triangular Os3(CO)12X2 Structure

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Summary: The clusters Os3(CO)12-x(CH3CN)x (*x* = 1 or 2) react with dimethyl azodicarboxylate to give Os3(C-

O)$_{10}$(CH$_3$OCONNCOOCH$_3$) as the final product, which in turn transforms to Os$_3$(CO)$_{12}$(CH$_3$OCONNCOOCH$_3$) under CO pressure; the structures of both compounds have been determined by single-crystal X-ray diffraction, which shows the latter compound to be a triangular Os$_3$(CO)$_{12}$X$_2$ unit with a two-electron bridging ligand (X$_2$ = CH$_3$OCONNCOOCH$_3$) replacing one Os–Os bond.

Of the numerous compounds that have been synthesized from Os$_3$(CO)$_{12}$ or its more reactive analogues such as Os$_3$(CO)$_{11}$(CH$_3$CN), few are of the type Os$_3$(CO)$_{12}$X$_2$ [where X$_2$ corresponds to two monodentate one-electron donors or one bidentate (or η^2 two-electron donor]. In the former case (such as Os$_3$(CO)$_{12}$I$_2$) cleavage of the Os–Os bond is accompanied by rearrangement to a linear triosmium structure.[1] In the latter, the bridging bidentate ligand X$_2$ could replace an Os–Os bond, preserving a triangular arrangement of Os atoms in a triosmium dodecacarbonyl derivative, but we know of no previous example of this. An example has now been synthesized and is reported here.

Reaction of Os$_3$(CO)$_{11}$(CH$_3$CN) (1) with excess dimethyl azodicarboxylate (2) at room temperature in benzene produced an intermediate (3) which transformed to Os$_3$-(CO)$_{10}$(CH$_3$OCONNCOOCH$_3$) (4) when heated in benzene at 70 °C for 10 min. Alternatively, reaction of 2 with Os$_3$(CO)$_{10}$(CH$_3$CN)$_2$ at room temperature gave 4 quantitatively in 20 min. Compound 4 was separated on a silica

3

4

5
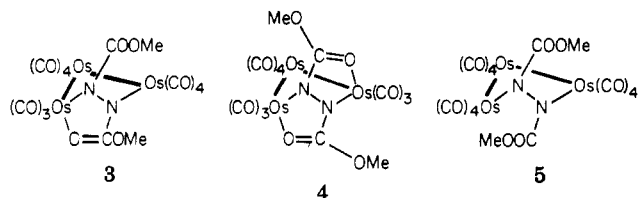
gel column using 1:1 hexane–benzene (50% yield) and crystallized from hexane as yellow, air-stable crystals, mp 104 °C. Its spectroscopic properties were as follows: mass spectrum, m/z 1002 (based on ^{192}Os, by fast atom bombardment); IR 2104 (w), 2078 (s), 2050 (s), 2005 (vs), 1996 (w), 1982 (w), 1972 (w) cm^{-1} (hexane), 1518 (w), 1484 (w) cm^{-1} (C$_2$Cl$_4$); ^{1}H NMR (CDCl$_3$) δ 3.86 (s). An X-ray structure analysis[2] revealed the molecular structure shown in Figure 1. The dimethyl azodicarboxylate ligand spans one edge of the triosmium cluster that has been elongated to a nonbonding distance of 4.161 (1) Å. It is clear from an examination of N–N, N–C, and C–O bond lengths that the ligand is acting as a chelating substituted hydrazide rather than a diazene and supplies six electrons to the cluster. The N–N bond length (1.439 (9) Å) is exactly that expected for a single bond, compared with ca. 1.23 Å for a double bond,[3] and is similar to the value (1.436 Å) ob-
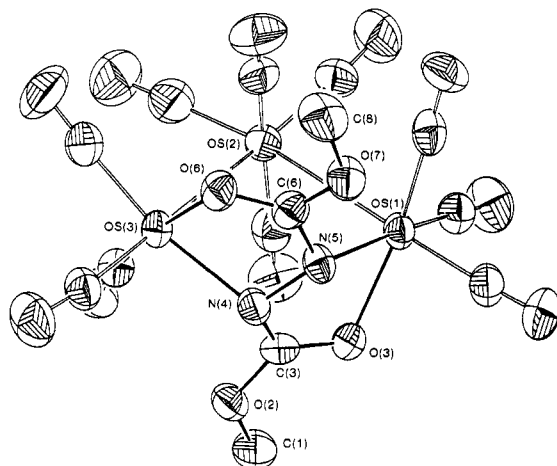
Figure 1. The structure of Os$_3$(CO)$_{10}$(CH$_3$OCONNCOOCH$_3$) (4). Selected bond lengths (Å) and angles (deg) are Os(1)–Os(2) = 2.964 (1), Os(2)–Os(3) = 2.970 (1), Os(1)···Os(3) = 4.161 (1), Os(1)–N(5) = 2.120 (6), N(4)–N(5) = 1.439 (9), N(4)–C(3) = 1.302 (10), C-(3)–O(3) = 1.281 (9), Os(1)–O(3) = 2.144 (5), Os(3)–N(4) = 2.128 (6), N(5)–C(6) = 1.338 (10), C(6)–O(6) = 1.253 (9), Os(3)–O(6) = 2.144 (6), Os(1)–Os(2)–Os(3) = 89.06 (2).

served in the dibenzoylhydrazine ligand in a copper(II) complex.[4] The N–C distance (1.338 (10) Å) is close to the single-bond value and compares with the N–C distance in the copper complex[4] and in the arylformamido complex HOs$_3$(CO)$_{10}$(ArNCHO).[5] The C–O distance is that expected for a coordinated carbonyl group by comparison with similar distances in the above two complexes and Os$_5$C(CO)$_{14}$(COOMe).[6] The coordinated hydrazido ligand may therefore be represented by A, and the bond lengths

A
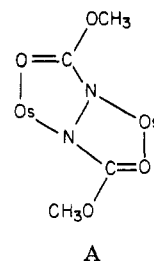
(especially N–N and N–C) contrast with those found for five-membered chelating aroylazo ligands[7] in structures of type B. Binuclear chelation similar to A in ligands such

B
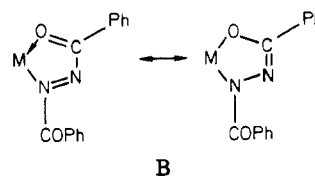
as PhCONNCOPh has been identified before,[8] and the observed bond parameters are reasonably similar.

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(2) Compound 4, Os$_3$(CO)$_{10}$(C$_4$H$_6$N$_2$O$_4$): *M* 996.80, triclinic, space group P$\bar{1}$, *a* = 8.608 (1) Å, *b* = 9.412 (1) Å, *c* = 14.326 (3) Å, α = 104.50 (1)°, β = 97.90 (1)°, γ = 103.29 (1)°, *V* = 1069.6 Å^3, *Z* = 2, D_{calcd} = 3.095 g cm^{-3}, μ = 189.10 cm^{-1}; crystal 0.21 mm × 0.17 mm × 0.07 mm, Picker FACS-1, Mo Kα (graphite monochromated), $2\theta_{max}$ = 50°, θ–2θ scan, no. of reflections = 3779, observed reflections (*I* > 2.3σ(*I*)) = 3328, R_F = 0.030, R_{wF} = 0.038, absorption corrected with all non-hydrogen atoms anisotropic. Compound 5, Os$_3$(CO)$_{12}$(C$_4$H$_6$N$_2$O$_4$): *M* 1052.82, monoclinic, space group P2$_1$/c, *a* = 12.136 (2) Å, *b* = 12.298 (2) Å, *c* = 16.027 (3) Å, β = 91.37(1)°, *V* = 2391.3 Å^3, *Z* = 4, D_{calcd} = 2.924 g cm^{-3}, μ = 169.30 cm^{-1}; crystal 0.12 mm × 0.11 mm × 0.27 mm, Picker FACS-1, Mo Kα (graphite monochromated), $2\theta_{max}$ = 50°, θ–2θ scan, no. of reflections = 4235, observed reflections (*I* > 2.3σ(*I*)) = 3359, R_F = 0.021, R_{wF} = 0.028, absorption corrected with all non-hydrogen atoms anisotropic.

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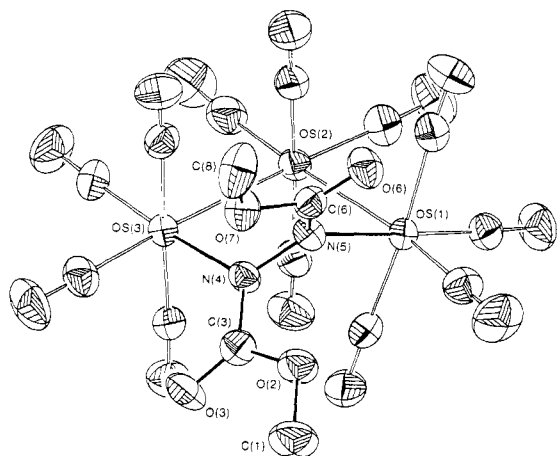
Figure 2. The structure of Os$_3$(CO)$_{12}$(CH$_3$OCONNCOOCH$_3$) (5). Selected bond lengths (Å) and angles (deg) are Os(1)-Os(2) = 2.967 (1), Os(2)-Os(3) = 3.008 (1), Os(1)···Os(3) = 4.198 (1), Os(1)-N(5) = 2.095 (5), N(4)-N(5) = 1.411 (7), N(4)-C(3) = 1.351 (8), C-(3)-O(3) = 1.220 (8), Os(3)-N(4) = 2.092 (5), N(5)-C(6) = 1.336 (8), C(6)-O(6) = 1.226 (8), Os(1)-Os(2)-Os(3) = 89.27 (2).

Compound **4** reacted quantitatively with CO (1500 psi, room temperature, 12 h) to form **5**, formulated as Os$_3$(C-O)$_{12}$(CH$_3$OCONNCOOCH$_3$) on the basis of its mass (*m/z* 1058, based on ^{192}Os, fast atom bombardment), IR (2123 (s), 2075 (s), 2062 (s), 2026 (m), 1995 (mw) cm^{-1} (hexane), 1633 (m), 1433 (mw) cm^{-1} (C$_2$Cl$_4$)), and NMR (δ 3.64 in CDCl$_3$). It crystallized from CH$_2$Cl$_2$-hexane as yellow air-stable crystals, mp 126 °C, the structure of which 2).[2] (Figure 2).[2] In relation to compound **4** compound **5** is derived by the replacement of the two ligating methoxycarbonyl groups by carbon monoxide. The organic ligand thus is now a two-electron donor bridging hydrazido group, consistent with retention of the long N-N bond (1.41 Å) and the nonbonding Os···Os distance of 4.198 Å. Compound **5** is therefore a unique example of a 50-electron Os$_3$(CO)$_{12}$X$_2$ type of cluster that retains a triangular disposition of Os atoms.

The intermediate **3** formulated as Os$_3$(CO)$_{11}$(CH$_3$OCO-NNCOOCH$_3$) could be isolated by stopping the reaction of **1** with **2** at 10 °C after 1.5 h, followed by flash chromatography on cellulose with hexane-benzene (1:1) as eluent. Due to a tendency to transform to **4** on attempted crystallization, no X-ray structure is available, but it is assigned the structure illustrated from spectroscopic evidence. The ^{1}H NMR exhibits two sharp singlets of equal intensity at δ 3.64 and 3.82, readily assigned to the methyls of the free and coordinated methoxycarbonyl groups respectively by comparison with **4** and **5**. The IR also shows the absorptions of the free and complexed carbonyls of these groups, again by comparison with **4** and **5**: IR 2134 (mw), 2095 (s), 2060 (s, br), 2040 (sh), 2020 (m), 2007 (s, br) cm^{-1} (benzene), 1658 (mw), 1530 (mw), 1472 (mw) cm^{-1} (C$_2$Cl$_4$). Furthermore **3** takes up CO under very mild conditions (1 atm, 0 °C, CH$_2$Cl$_2$) to give **5** quantitatively. The course of the reaction of **1** with excess **2** could be followed conveniently by ^{1}H NMR in CDCl$_3$ at 10 °C. The signal at 2.76 ppm due to the CH$_3$CN ligand in **1** decreased, with a corresponding smooth increase in the signals at 3.64 and 3.82 ppm due to formation of **3** alone and at 1.98 ppm (free CH$_3$CN). After the disappearance of **1** the temperature was raised to 35 °C, and this produced a smooth decrease in the signals of **3** and an increase in a new signal at 3.87 ppm due to **4**. At 60 °C a small amount of **5** was detected, probably due to uptake by **3** of CO released from decomposition.

Mechanism of Hydroboration of Alkenes by Dibromoborane–Methyl Sulfide. Remarkable Catalysis of the Reaction by Small Quantities of Boron Tribromide

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Summary: The hydroboration of alkenes with BHBr$_2$·SMe$_2$ proceeds by a prior dissociation of the reagent followed by the reaction of BHBr$_2$ with the alkene to give RBBr$_2$, which then forms a complex with Me$_2$S formed in the dissociation step. In conformity with this mechanism, the reaction is remarkably catalyzed by small quantities of BBr$_3$.

Since their discovery,[2] the haloborane–methyl sulfide complexes have found extensive use in organic synthesis,[3-5] but the mechanism of their reaction with alkenes is not yet well understood.

In the past, we have established that 9-BBN·Lewis base complexes hydroborate alkenes by the dissociation mechanism.[6] For example, excess Me$_3$N represses the rate of hydroboration of 2-methyl-1-pentene by 9-BBN·NMe$_3$ complex significantly, indicating that the complex dissociates into 9-BBN and Me$_3$N prior to hydroboration. It is also known that the ease of hydroboration by BH$_3$·Lewis base complexes increases with decreasing stability of the complex.[7,8] Consequently, we were led to think that haloborane–methyl sulfide complexes also will hydroborate alkenes by a prior dissociation of the complex into the free borane. In fact, addition of 1 equiv of methyl sulfide significantly retards the rate of hydroboration of alkenes and alkynes by BHBr$_2$·SMe$_2$[9] and thexylchloroborane–methyl sulfide.[5b]

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