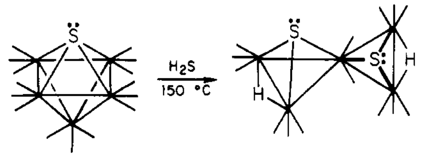
When refluxed in nonane solvent under an atmosphere of H_2S, II adds 1 mol of H_2S and eliminates 1 mol of CO to form the new compound IV in 94% yield.[15]



II

IV

The structure of IV was determined by X-ray crystallographic methods, and an ORTEP diagram of the molecule is shown in Figure 1.[16,17] The molecule consists of a "bow-tie" cluster of five metal atoms arranged in the form of two triangular Os_3 groupings which share the central metal atom Os(1).[18] Each triosmium group contains a triply bridging sulfido ligand and one bridging hydride ligand. The Os–Os and Os–S internuclear separations are similar to those in $H_2Os_3(CO)_9(\mu_3\text{-}S)$.[19] The elongated exterior Os–Os bonds Os(2)–Os(3) = 2.891 (1) Å and Os(4)–Os(5) = 2.885 (1) Å probably contain the bridging hydride ligands. Overall, the molecule has C_2 symmetry (not crystallographically imposed); thus, the hydride ligands are equivalent. The Os_5 bow tie is not planar but is twisted to give a dihedral angle of 56.3° between the Os(1), Os(2), Os(3) and Os(1), Os(4), Os(5) planes. The cluster compounds $Os_5(CO)_{19}$ and $Os_5(CO)_{16}[P(OMe)_3]_3$ contain bow-tie structures in which the dihedral angles between the Os_3 triangles are 21.2° and 24.8°, respectively.[20]

As in the reaction with I, the H_2S molecule in this reaction is converted into one triply bridging sulfido ligand and two hydride ligands which collectively donate six electrons to the cluster. However, due to the loss of the one CO ligand, the net increase in the number of cluster electrons is only four, and the conversion of II into IV results in the cleavage of only two metal–metal bonds. It is significant that the opening up of these closo clusters by H_2S does not lead to their degradation. In contrast, Lewis et al. have recently reported that the cluster $Os_6(CO)_{20}$ is converted into $H_2Os_3(CO)_9(\mu_3\text{-}S)$ upon reaction with H_2S.[21] Further studies on the addition of H_2S to *closo*-metal carbonyl clusters are in progress.

Acknowledgment. This work was supported by the National Science Foundation and the Alfred P. Sloan Foundation through a fellowship to R.D.A. NMR studies were supported by Grant no. CHE-7916210 to the Northeast Regional NSF-NMR Facility from the National Science Foundation. We wish to thank Engelhard Industries for a loan of osmium tetroxide.

Registry No. I, 82080-90-8; II, 86456-36-2; III, 72314-28-4; IV, 86456-37-3; $H_2Os_3(CO)_9(\mu_3\text{-}S)$, 38979-82-7.

Supplementary Material Available: Tables of structure factor amplitudes fractional atomic coordinates, bond distances, and bond angles (17 pages). Ordering information is given on any current masthead page.

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(15) IR (hexane solvent): δ(CO) 2090 (vs), 2086 (s, sh), 2027 (s, sh), 2024 (s), 2013 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ −19.44 (s).

(16) Crystal data: space group $P\bar{1}$, No. 2; a = 9.147 (5) Å, b = 9.913 (4) Å, c = 14.920 (5) Å, α = 86.75 (3)°, β = 89.14 (4)°, γ = 70.09 (4)°, M_r 1409.3, Z = 2, ρ_{calcd} = 3.69 g/cm^3. The structure was solved by the heavy-atom method. After correcting for absorption (μ = 251.9 cm^{-1}, for Mo Kα), full-matrix least-squares refinement (3672 reflections, $F^2 \geq 3.0\sigma(F^2)$, $2\theta \leq 50°$) yielded the final residuals R_F = 0.055 and R_{wF} = 0.056.[17]

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

(18) Selected internuclear distances (Å) and angles (deg) are as follows: Os(1)–Os(2) = 2.836 (1), Os(1)–Os(3) = 2.830 (1), Os(1)–Os(4) = 2.809 (1), Os(1)–Os(5) = 2.795 (1), Os(2)–Os(3) = 2.891 (1), Os(4)Os(5) = 2.885 (1); Os(2)–Os(1)–Os(3) = 61.38 (2), Os(1)–Os(2)–Os(3) = 59.21 (2), Os(1)–Os(3)–Os(2) = 59.41 (2); Os(4)–Os(1)–Os(5) = 61.98 (2), Os(1)–Os(4)–Os(5) = 58.78 (2), Os(1)–Os(5)–Os(4) = 59.24 (2), Os(2)–Os(1)–Os(4) = 138.06 (3), Os(2)–Os(1)–Os(5) = 139.67 (3), Os(3)–Os(1)–Os(4) = 157.89 (3), Os(3)–Os(1)–Os(5) = 111.82 (3), S(1)–Os(1)–S(2) = 90.16 (14).

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Activation of Heteronuclear Triple Bonds by Cluster Compounds. The Cleavage of the C–N Triple Bond of an Isocyanide Ligand by a Ruthenium Cluster

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Summary: Pyrolysis of the compound $Ru_5(CO)_{14}(CN\text{-}t\text{-}Bu)(\mu_5\text{-}CN\text{-}t\text{-}Bu)$, I, in nonane solvent for 2 h leads to formation of the hexaruthenium carbide cluster $Ru_6(C)(CO)_{15}(CN\text{-}t\text{-}Bu)(\mu\text{-}CO)$, II.

Considerable attention has been focused on the nature of the activation of small molecules by transition-metal cluster compounds.[1-3] It has been suggested that the reduction of triple bonds will be facilitated by multinuclear coordination interactions.[4] The activation of carbon monoxide, in particular, is a problem of great interest and importance,[5,6] and it has been shown that certain carbido clusters can be made by the abstraction of carbon from carbonyl ligands. However, the importance of polynuclear coordination in the activation of the ligand has not been ascertained.[7-9]

Herein we report the synthesis of a hexaruthenium carbido cluster in which the carbide carbon atom was abstracted from an isocyanide ligand and the importance of polynuclear coordination of the isocyanide ligand is strongly implied.

The compound $Ru_5(CO)_{14}(CN\text{-}t\text{-}Bu)(\mu_5\text{-}CN\text{-}t\text{-}Bu)$, I, was recently synthesized by Bruce et al. and shown to contain a quintuply bridging isocyanide ligand.[11] When heated

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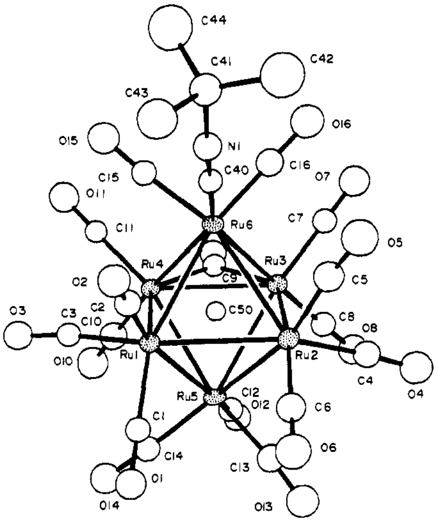
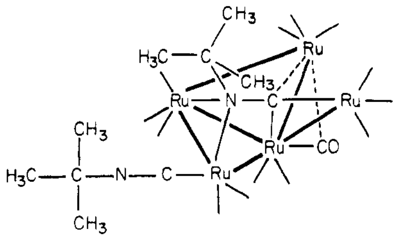


Figure 1. An ORTEP diagram of $Ru_6(C)(CO)_{15}(CN\text{-}tert\text{-}Bu)(\mu\text{-}CO)$ showing 50% probability thermal-motion ellipsoids.



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 $Ru_6(C)(CO)_{15}(CN\text{-}t\text{-}Bu)(\mu\text{-}CO)$, 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 $Ru_6(C)(CO)_{16}(\mu\text{-}CO)$[15] and $Ru_6(C)(CO)_{15}(PPh_2Et)(\mu\text{-}CO)$.[16]

The source of the carbido carbon atom was established by an isotope labeling experiment.[17] $Ru_5(CO)_{14}(^{13}CN\text{-}t\text{-}Bu)(\mu_5\text{-}^{13}CN\text{-}t\text{-}Bu)$ was prepared by using $^{13}CN\text{-}t\text{-}Bu$ 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 Ru_6C^+, 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.

Acknowledgment. This work was supported by the Office of Basic Energy Sciences of the U.S. Department of Energy under Contract No. DE-AC02-78ER04900 and the Alfred P. Sloan Foundation through a fellowship to R.D.A. We wish to thank Dr. B. F. G. Johnson of the University Chemical Laboratories, Cambridge, England, for obtaining the mass spectra for us.

Registry No. I, 86497-02-1; II, 86480-62-8; Ru, 7440-18-8.

Supplementary Material Available: Tables of final fractional atomic coordinates, thermal parameters, bond distances and angles, and structure factor amplitudes (35 pages). Ordering information is given on any current masthead page.

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(12) Crystal data: space Group $P\bar{1}$, No. 2, $a = 13.750$ (3) Å, $b = 15.461$ (5) Å, $c = 15.991$ (8) Å, $\alpha = 104.51$ (3)°, $\beta = 102.39$ (3)°, $\gamma = 96.65$ (2)°, $V = 3162$ (4) Å^3, M_r 1149.7, $Z = 4$, $\rho_{calcd} = 2.41$ g/cm^3. The structure was solved by direct methods (MULTAN) and refined with 5774 reflections ($F^2 \geq 3.0\sigma(F^2)$) to final values of the residuals $R_F = 0.053$ and $R_{wF} = 0.060$.

(13) Intensity data (Mo K$\bar{\alpha}$) 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 mas 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 $Ru_5(CO)_{14}$ $(^{13}CN\text{-}t\text{-}Bu)(\mu_5\text{-}^{13}CN\text{-}t\text{-}Bu)$ 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 $Os_3(CO)_n(CH_3OCONNCOOCH_3)$ (n = 10–12). A Triangular $Os_3(CO)_{12}X_2$ Structure

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Summary: The clusters $Os_3(CO)_{12-x}(CH_3CN)_x$ (x = 1 or 2) react with dimethyl azodicarboxylate to give Os$_3$(C-