

Synthesis and Molecular Structure of Bis(acetonitrilecuprio)carbidohexadecacarbonylhexaurthenium, [(CH₃CN)₂Cu₂Ru₆C(CO)₁₆], a Bimetallic Carbido Carbonyl Cluster Containing a Copper-Copper Bond

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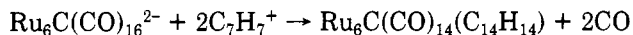
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The reaction of (Et₄N)₂Ru₆C(CO)₁₆, **1**, with Cu(MeCN)₄BF₄ in acetone gives (MeCN)₂Cu₂Ru₆C(CO)₁₆, **2**, in 77% yield. The crystal structure of **2** has been determined. The molecule crystallizes in the triclinic space group *P* $\bar{1}$ with *a* = 10.122 (2) Å, *b* = 16.364 (2) Å, *c* = 9.874 (2) Å, α = 97.34 (1)°, β = 96.58 (2)°, γ = 77.89 (1)°, *V* = 1580 Å³, and *Z* = 2. Data were collected on an Enraf-Nonius CAD 4 automatic diffractometer, and the structure was solved by using a combination of Patterson and direct methods and Fourier techniques. All atoms were refined with anisotropic thermal parameters, and least-squares refinement converged when residuals of *R*₁ = 0.033 and *R*₂ = 0.051 were reached. The cluster comprises a distorted octahedral Ru₆C core, capped by two directly bonded, nonbridged copper atoms. One copper atom caps a trigonal Ru₃ face, the second a CuRu₂ face, with a copper-copper distance of 2.693 (1) Å.

Introduction

As part of our continuing synthetic, structural and catalytic studies in carbido carbonyl cluster chemistry, we recently reported the oxidative fragmentation of the octahedral iron cluster dianion Fe₆C(CO)₁₆²⁻ by reaction with tropylium bromide in methanol, yielding Fe₄(CO)₁₂-CCO₂CH₃⁻. This organometallic cluster was formed as consequence of the reactivity of the cluster bond carbon atom, exposed when two iron atom vertices were removed from the encapsulating Fe₆ polyhedron of the dianion. The novelty of this fragmentation caused us to examine other carbido carbonyl clusters in a similar manner.

The high-yield synthesis of Ru₆C(CO)₁₆²⁻ from Ru₃(C-O)₁₂, which we reported earlier² enabled us to attempt the extension of this work to a second row carbide-containing cluster. However, we observed that tropylium bromide oxidation of the hexaruthenium dianion resulted not in cluster fragmentation but in the formation of an adduct between the Ru₆C core and the bitropyl produced in the redox reaction.^{3,4}



Although this has led us to the facile synthesis of organometallic Ru₆C clusters by oxidation of the dianion in the presence of organic ligands,⁵ the fragmentation of the cluster eluded us.

We have attempted to achieve our goal by the oxidation of Ru₆C(CO)₁₆²⁻ by using inorganic cations. This paper reports our observation of the formation of a bimetallic carbido carbonyl cluster by the reaction of cupric (or cuprous) ion with the dianion, in which the Ru₆C core has again remained intact. The product, (CH₃CN)₂Cu₂Ru₆C(CO)₁₆, **2**, was synthesized most readily by reaction of Cu(CH₃CN)₄⁺BF₄⁻ with (Et₄N)₂Ru₆C(CO)₁₆, **1**, in acetone. Initially we had reacted Cu²⁺ salts **1**, but elemental analysis revealed a Cu/Ru ratio of 1:3, so direct reaction with a cuprous salt suggested itself as a more rational synthesis. A similar synthesis of an analogous rhodium-copper cluster (CH₃CN)₂Cu₂Rh₂C(CO)₁₅ was recently reported⁶ by Chini

and co-workers, and it was consideration of then unpublished data on this system⁷ which led us to understand the nature of our initial observations in the ruthenium case and to recognize the unusual aspects of the structure of **2**, in which the two copper atoms are bonded to each other. This is in contrast to their positions on opposite faces of the trigonal prismatic Rh₆C core in the Cu₂Rh₆C cluster and appears to have implications for the comparative strengths of Cu-Rh and Cu-Ru bonds.

Experimental Section

All solvents were dried and, when necessary, distilled by the usual methods. (Et₄N)₂Ru₆C(CO)₁₆ was prepared by reaction of Ru₃(CO)₁₂ with NaMn(CO)₅ in refluxing diglyme, as described previously.² Cu(CH₃CN)₄BF₄ was prepared by addition of HBF₄ (48%) to an acetonitrile suspensions of cuprous oxide.⁸ All transfers and manipulations were performed in an atmosphere of dry nitrogen.

Synthesis of (CH₃CN)₂Cu₂Ru₆C(CO)₁₆. (Et₄N)₂Ru₆C(CO)₁₆ (1.33 g, 1.0 mmol) was dissolved in dry acetone (50 mL), giving a bright red solution to which was added a solution of Cu(CH₃CN)₄BF₄ (0.75 g, 2.0 mmol) in acetone (20 mL). The reaction solution immediately darkened, and the infrared absorbance of the dianion were replaced by new bands at 2070 (m), 2030 (s), 1998 (sh), 1948 (sh), and 1850 (br) cm⁻¹ in methylene chloride solutions of evaporated aliquots of the reaction mixture. The acetone was removed under reduced pressure and the residue washed with water and dried in vacuo. Extraction into methylene chloride produced a deep red solution which, when diluted with hexane and slowly evaporated yielded the product as a dark red crystalline solid (0.98 g, 77%). Satisfactory elemental analysis was obtained (Cu/Ru = 2:6.02). ¹H NMR (60 MHz, CD₂Cl₂, 30

(1) Bradley, J. S.; Ansell, G. B.; Hill, E. W. *J. Am. Chem. Soc.* **1979**, *101*, 7417.

(2) Bradley, J. S.; Ansell, G. B.; Hill, E. W. *J. Organomet. Chem.* **1980**, *184* C33.

(3) Bradley, J. S.; Ansell, G. B. ACS/CSJ Chemical Congress; Honolulu, Hawaii, 1979; Inorganic Abstract 506.

(4) Ansell, G. B.; Bradley, J. S. *Acta Crystallogr. Sect. B* **1980**, *B36*, 1930.

(5) Bradley, J. S.; Yang, G., unpublished data.

(6) Albano, V. G.; Braga, D.; Martinengo, S.; Chini, P.; Sansoni, M.; Strumolo, D.; *J. Chem. Soc., Dalton Trans.* **1980**, 52.

(7) Personal communication from P. Chini.

(8) *Inorg. Synth.* **1900**, *19*, 90.

* Corporate Research Science Laboratories.

† Analytical and Information Division.

Table I

| A. Crystal Data | |
|-----------------------|------------------------------|
| formula | $Ru_6Cu_2C_{21}H_6N_2O_{16}$ |
| space group | $P\bar{1}$ |
| lattice const (23 °C) | |
| <i>a</i> | 10.122 (2) Å |
| <i>b</i> | 16.364 (2) Å |
| <i>c</i> | 9.874 (2) Å |
| α | 97.34 (1)° |
| β | 96.58 (2)° |
| γ | 77.89 (1)° |
| <i>V</i> | 1580 Å ³ |
| <i>Z</i> | 2 |
| mol wt | 1276 |
| ρ_{calcd} | 2.68 g cm ⁻³ |
| abs corrn | |
| μ | 41.65 cm ⁻¹ |
| type | psi scans |
| max/min values | 0.89–1.00 |

B. Data Collection

| | |
|----------------------------|------------------------------------|
| diffractometer | Enraf-Nonius CAD 4 |
| radiation | Mo K α 0.710 73 Å |
| monochromator | graphite |
| scan range | 0° < 2 θ < 55° |
| scan type | θ -2 θ |
| scan speed | 2-20°/min |
| reflectns examined | 7481 |
| reflectns independent | 7220 |
| reflectns obsd | 6215 |
| criterion | $I > 3\sigma(I)$ |
| stability, check reflectns | 3% linear decrease over experiment |

°C): δ 2.30. ¹³C NMR (22.5 MHz, THF-*d*₈, 30 °C): 458, 207 ppm. IR (CH₂Cl₂) 2070 (m), 2030 (s), 1998 (sh), 1948 (sh), 1850 (m, br) cm⁻¹.

Crystals suitable for X-ray diffraction were grown by slow evaporation of a methylene chloride/hexane solution over a period of 3 weeks. Data were collected⁹ on a prism 0.25 × 0.25 × 0.25 mm sealed in a Lindemann capillary in contact with the mother liquor from which it was grown. Table I contains a summary of the crystallographic data and the experimental conditions under which they were obtained. The metal atoms were located by a combination of Patterson and direct methods,¹⁰ and the remaining nonhydrogen atoms located by difference Fourier techniques. All atoms were refined with anisotropic thermal parameters. Least-squares refinement converged when residuals of $R_1 = 0.033$ and $R_2 = 0.051$ were reached. Atomic coordinates are listed in

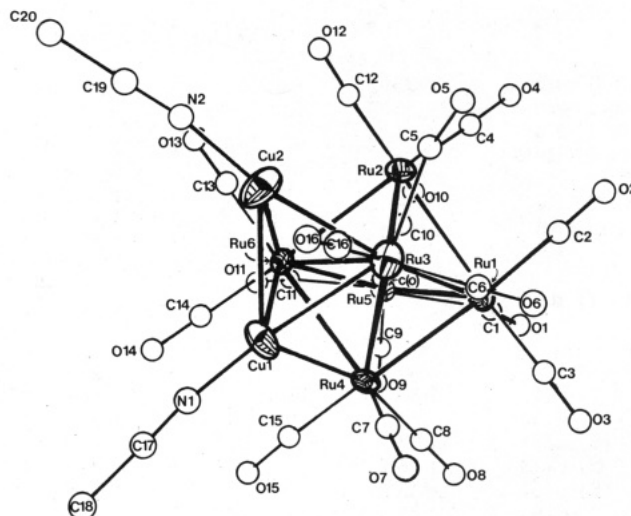
Figure 1. Structure of $(MeCNCu)_2Ru_6C(CO)_{16}$.

Table II, bond lengths in Table III and relevant angles in Table IV.

Discussion

The molecule (Figure 1) comprises a distorted octahedron of ruthenium atoms encapsulating a carbon atom and capped by two adjacent copper atoms, each bearing one acetonitrile ligand.

The Ru_6C unit, with a mean Ru–Ru distance of 2.89 ± 0.18 Å, is distorted from the regular octahedral array found for the dianion in $(Me_4N)_2Ru_6C(CO)_{16}$ in which the mean Ru–Ru distance is 2.89 ± 0.04 Å (averaged over the two independent clusters in the unit cell).¹¹ In the Cu_2Ru_6C cluster the Ru–Ru bonds range from 2.798 (1) to 3.072 (1) Å and reflect the widely differing environments available for the ruthenium atoms. The longest such bond, Ru(3)–Ru(6), is that most perturbed by the presence of the two copper atoms, being the only Ru–Ru bond shared by the two confacial tetrahedra Ru(3)(4)(6)Cu(1) and Ru(3)(6)Cu(1)(2), and the angles within these tetrahedra reflect this elongation (Table IV).

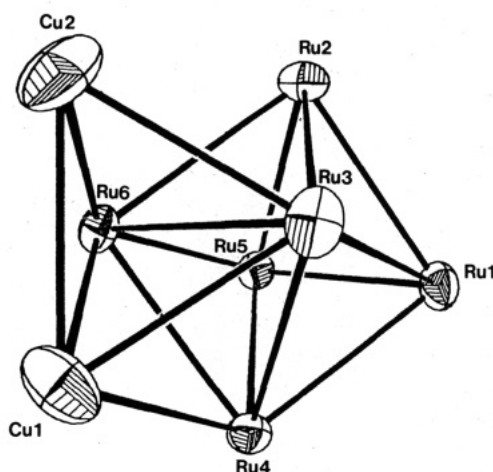
The carbide atom, C(O), is located centrally in the Ru_6 cage, with a mean Ru–C(O) distance of 2.05 ± 0.02 Å. This

Table II. Atomic Coordinates for $(MeCN)_2Cu_2Ru_6C(CO)_{16}$

| | <i>x</i> | <i>y</i> | <i>z</i> | | <i>x</i> | <i>y</i> | <i>z</i> |
|-------|--------------|-------------|--------------|-------|------------|------------|-------------|
| Ru(1) | 0.66591 (4) | 0.74370 (3) | 0.36070 (5) | C(17) | 1.3596 (8) | 0.5031 (5) | 0.2337 (8) |
| Ru(2) | 0.75503 (5) | 0.86284 (3) | 0.21479 (5) | C(18) | 1.4730 (9) | 0.4315 (6) | 0.2232 (11) |
| Ru(3) | 0.86372 (5) | 0.69047 (3) | 0.16676 (5) | C(19) | 1.2300 (8) | 0.7972 (5) | -0.1082 (7) |
| Ru(4) | 0.93619 (5) | 0.68099 (3) | 0.46410 (5) | C(20) | 1.3302 (8) | 0.8186 (6) | -0.1848 (9) |
| Ru(5) | 0.81784 (4) | 0.85759 (3) | 0.51511 (4) | C(21) | 0.8467 (5) | 0.7751 (3) | 0.3415 (5) |
| Ru(6) | 1.03002 (4) | 0.80781 (3) | 0.34530 (5) | O(1) | 0.5420 (5) | 0.8347 (4) | 0.6166 (5) |
| Cu(1) | 1.11856 (9) | 0.64639 (6) | 0.26963 (10) | O(2) | 0.4040 (6) | 0.7874 (5) | 0.1828 (6) |
| Cu(2) | 1.04783 (10) | 0.76068 (7) | 0.08770 (9) | O(3) | 0.5797 (6) | 0.5896 (4) | 0.4351 (7) |
| C(1) | 0.6154 (6) | 0.8161 (4) | 0.5322 (7) | O(4) | 0.4747 (7) | 0.9698 (5) | 0.1832 (10) |
| C(2) | 0.5007 (7) | 0.7735 (5) | 0.2530 (7) | O(5) | 0.6718 (6) | 0.7751 (4) | -0.0598 (5) |
| C(3) | 0.6111 (7) | 0.6498 (5) | 0.4072 (8) | O(6) | 0.6745 (6) | 0.5709 (4) | 0.0885 (7) |
| C(4) | 0.5806 (8) | 0.9285 (5) | 0.1953 (9) | O(7) | 0.9440 (8) | 0.5021 (3) | 0.3393 (6) |
| C(5) | 0.7337 (7) | 0.7803 (4) | 0.0450 (6) | O(8) | 0.7982 (6) | 0.6528 (4) | 0.7047 (6) |
| C(6) | 0.7422 (8) | 0.6176 (5) | 0.1250 (7) | O(9) | 0.8565 (7) | 0.8663 (4) | 0.8250 (5) |
| C(7) | 0.9430 (9) | 0.5701 (5) | 0.3715 (8) | O(10) | 0.6640 (6) | 1.0375 (3) | 0.5215 (7) |
| C(8) | 0.8490 (7) | 0.6651 (4) | 0.6154 (7) | O(11) | 1.0714 (5) | 0.9307 (3) | 0.5983 (5) |
| C(9) | 0.8385 (7) | 0.8633 (4) | 0.7091 (7) | O(12) | 0.8408 (7) | 0.9954 (3) | 0.0769 (6) |
| C(10) | 0.7223 (7) | 0.9707 (4) | 0.5156 (7) | O(13) | 1.1272 (6) | 0.9403 (3) | 0.2140 (6) |
| C(11) | 1.0061 (6) | 0.8906 (4) | 0.5269 (6) | O(14) | 1.3181 (5) | 0.7500 (4) | 0.4621 (6) |
| C(12) | 0.8110 (9) | 0.9440 (4) | 0.1290 (7) | O(15) | 1.2045 (6) | 0.6461 (5) | 0.6372 (7) |
| C(13) | 1.0882 (7) | 0.8894 (4) | 0.2581 (7) | O(16) | 1.0221 (7) | 0.5846 (4) | -0.0600 (6) |
| C(14) | 1.2098 (6) | 0.7688 (4) | 0.4106 (7) | N(1) | 1.2736 (7) | 0.5587 (4) | 0.2452 (7) |
| C(15) | 1.1061 (7) | 0.6597 (4) | 0.5677 (8) | N(2) | 1.1546 (7) | 0.7796 (5) | -0.0480 (6) |
| C(16) | 0.9672 (8) | 0.6272 (5) | 0.0251 (7) | | | | |

Table III. Bond Lengths (Å) (Esd's in Parentheses)

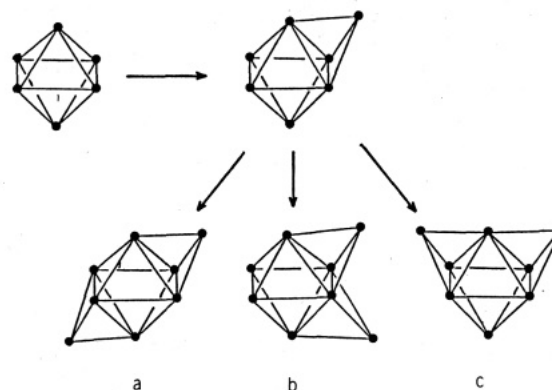
| A. Metal-Metal Bonds | | | |
|--------------------------------------|-----------|---------------|-----------|
| Ru(1)-Ru(2) | 2.906 (1) | Ru(4)-Ru(6) | 2.879 (1) |
| Ru(1)-Ru(3) | 2.856 (1) | Ru(5)-Ru(6) | 2.798 (1) |
| Ru(1)-Ru(4) | 2.834 (1) | | |
| Ru(1)-Ru(5) | 2.846 (1) | Cu(1)-Cu(2) | 2.691 (1) |
| Ru(2)-Ru(3) | 2.805 (1) | Cu(1)-Ru(3) | 2.648 (1) |
| Ru(2)-Ru(5) | 2.969 (1) | Cu(1)-Ru(4) | 2.741 (1) |
| Ru(2)-Ru(6) | 2.940 (1) | Cu(1)-Ru(6) | 2.645 (1) |
| Ru(3)-Ru(4) | 2.959 (1) | Cu(2)-Ru(3) | 2.620 (1) |
| Ru(3)-Ru(6) | 3.072 (1) | Cu(2)-Ru(6) | 2.577 (1) |
| Ru(4)-Ru(5) | 2.890 (1) | Cu(2)···Ru(2) | 3.376 (1) |
| B. Ruthenium-Carbon Bonds | | | |
| Ru(1)-C(1) | 1.991 (4) | Ru(4)-C(7) | 1.917 (5) |
| Ru(1)-C(2) | 1.884 (5) | Ru(4)-C(8) | 1.891 (5) |
| Ru(1)-C(3) | 1.864 (5) | Ru(4)-C(15) | 1.887 (5) |
| Ru(2)-C(4) | 1.867 (6) | Ru(5)-C(1) | 2.320 (4) |
| Ru(2)-C(12) | 1.875 (5) | Ru(5)-C(11) | 2.074 (4) |
| Ru(2)-C(5) | 2.035 (4) | Ru(5)-C(9) | 1.896 (4) |
| Ru(3)-C(5) | 2.148 (5) | Ru(5)-C(10) | 1.899 (5) |
| Ru(3)-C(6) | 1.866 (5) | Ru(6)-C(11) | 2.109 (4) |
| Ru(3)-C(16) | 1.907 (5) | Ru(6)-C(13) | 1.900 (5) |
| Ru(3)···C(7) | 2.932 (5) | Ru(6)-C(14) | 1.867 (4) |
| C. Ruthenium-Carbide Bonds | | | |
| Ru(1)-C(0) | 2.037 (4) | Ru(4)-C(0) | 2.073 (4) |
| Ru(2)-C(0) | 2.031 (4) | Ru(5)-C(0) | 2.050 (3) |
| Ru(3)-C(0) | 2.069 (4) | Ru(6)-C(0) | 2.031 (4) |
| D. Carbon-Oxygen Bonds | | | |
| C(1)-O(1) | 1.149 (5) | C(9)-O(9) | 1.135 (5) |
| C(2)-O(2) | 1.132 (6) | C(10)-O(10) | 1.127 (6) |
| C(3)-O(3) | 1.170 (6) | C(11)-O(11) | 1.150 (5) |
| C(4)-O(4) | 1.143 (7) | C(12)-O(12) | 1.147 (6) |
| C(5)-O(5) | 1.150 (5) | C(13)-O(13) | 1.145 (5) |
| C(6)-O(6) | 1.129 (6) | C(14)-O(14) | 1.151 (5) |
| C(7)-O(7) | 1.115 (6) | C(15)-O(15) | 1.141 (6) |
| C(8)-O(8) | 1.129 (6) | C(16)-O(16) | 1.138 (6) |
| E. Nonbonding Copper-Carbon Contacts | | | |
| Cu(1)-C(7) | 2.719 (5) | Cu(2)-C(13) | 2.594 (5) |
| Cu(1)-C(14) | 2.563 (5) | Cu(2)-C(16) | 2.471 (5) |
| Cu(1)-C(16) | 2.727 (5) | | |
| F. Copper-Acetonitrile Bonds | | | |
| Cu(1)-N(1) | 1.906 (4) | Cu(2)-N(2) | 1.907 (5) |
| N(1)-C(17) | 1.123 (6) | N(2)-C(19) | 1.122 (6) |
| C(17)-C(18) | 1.461 (7) | C(19)-C(20) | 1.454 (7) |

Figure 2. The Cu_2Ru_6 core.

position is very similar to that observed in other Ru_6C clusters— $2.04 \pm 0.1 \text{ \AA}$ for **1**¹⁰ and 2.05 \AA for $\text{Ru}_6\text{C}(\text{CO})_{17}$.¹²

(9) (a) Data acquired from Molecular Structure Corp., College, Station, TX. Structure solution and refinement were performed by us.

(10) All calculations were performed by using the Enraf-Nonius SDP program package, an integrated set of computer programs for PDP 11 series computers.

Scheme I. 110-Electron Eight-Vortex Polyhedra¹⁴

The eight metal atom core $\text{Cu}_2\text{Ru}_6\text{C}$ (Figure 2) is unusual in that two copper atoms are adjacent to one another ($\text{Cu}(1)-\text{Cu}(2) = 2.693 (1) \text{ \AA}$). $\text{Cu}(1)$ caps the triangular $\text{Ru}(3)(4)(6)$ face of the Ru_6 octahedron, and $\text{Cu}(2)$ caps the newly available $\text{Cu}(1)\text{Ru}(3)(6)$ face. The Cu-Ru distances range from $2.580 (1)$ to $2.741 (1) \text{ \AA}$.

The carbonyl ligands in **2** are arranged in a manner remarkably similar to that found in the parent dianion **1**. Detailed comparison between the two clusters in this respect is precluded by the fact that two sets of structural parameters have been reported for salts of **1**, as either the tetramethylammonium salt² or the tetraphenylammonium salt.¹³ The principal difference between the two salts is that there are three asymmetrically bridging carbonyls in the former and four in the latter. However, in the Me_4N^+ salt a fourth carbonyl is highly disordered and tends toward a semibridging position, and we agree with Johnson et al.¹³ that a more precise determination of the position of this ligand would probably reveal a more recognizably bridging position. The structures of the two salts of **1** may be considered as equivalent with 12 terminal and four bridging carbonyls with varying degrees of asymmetry.

The geometry of the $\text{Ru}_6\text{C}(\text{CO})_{16}$ fragment is not radically altered in forming the dicopper adduct. The m symmetry of the dianion is destroyed thus distinguishing, for example, the hitherto equal $\text{Ru}(1)-\text{C}(1)$ bonds ($1.944 (15) \text{ \AA}$ in **1**) as $\text{Ru}(1)-\text{C}(1)$ and $\text{Ru}(6)-\text{C}(11)$ ($2.001 (4)$ and $2.101 (4) \text{ \AA}$, respectively). The highly asymmetric bridging $\text{CO}(7)$ in **1** is distorted even further ($\text{Ru}(3)-\text{C}(7) = 2.939 (5) \text{ \AA}$, $\text{Ru}(4)-\text{C}(7) = 1.927 (5) \text{ \AA}$). Other distortions are discernible in the geometry of the carbonyl ligands, but inspection of molecular models of **1** and **2** makes it apparent that many of these are caused by a repulsive interaction between the copper atoms and the carbonyls in their vicinity. This observation clearly reduces the significance which might be attached to the relatively short nonbonding contacts between $\text{Cu}(1)$ and $\text{C}(7)$, $\text{C}(14)$, $\text{C}(16)$, and $\text{Cu}(2)$ and $\text{C}(13)$, $\text{C}(16)$, (see Table II).

The geometries of the two acetonitrile ligands are unremarkable, being approximately linear with normal C-C and C-N distances.

The juxtaposition of the two copper atoms in this cluster, without the benefit of bridging ligands, is curious. The recent synthesis and structural characterization of $(\text{CH}_3\text{CN})_2\text{Cu}_2\text{Rh}_6\text{C}(\text{CO})_{15}$ ⁶ by Chini and co-workers established the ability of an LCu unit to cap triangular faces

(11) Ansell, G. B.; Bradley, J. S. *Acta Crystallogr., Sect. B* 1980, B36, 726.

(12) Sirigu, A.; Bianchi, M.; Benedetti, E. *J. Chem. Soc., Chem. Commun.* 1969, 596.

(13) Johnson, B. F. G.; Lewis, J.; Sankey, S. W.; Wong, K.; McPartlin, M.; Nelson, W. J. *J. Organomet. Chem.* 1980, 191, C3.

Table IV. Bond Angles (Deg) (Esd's in Parentheses)

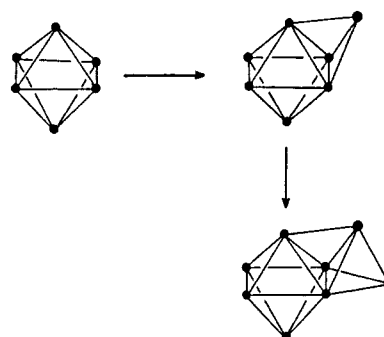
| A. Ru ₆ Octahedron | | | |
|--------------------------------|-----------|-----------------------|-----------|
| Ru(2)-Ru(1)-Ru(4) | 91.23 (1) | Ru(1)-Ru(4)-Ru(6) | 90.63 (1) |
| Ru(3)-Ru(1)-Ru(5) | 92.45 (1) | Ru(3)-Ru(4)-Ru(5) | 89.47 (1) |
| Ru(1)-Ru(2)-Ru(6) | 88.02 (1) | Ru(1)-Ru(5)-Ru(6) | 92.04 (1) |
| Ru(3)-Ru(2)-Ru(5) | 90.93 (1) | Ru(2)-Ru(5)-Ru(4) | 88.86 (1) |
| Ru(1)-Ru(3)-Ru(6) | 86.42 (1) | Ru(2)-Ru(6)-Ru(4) | 89.65 (1) |
| Ru(2)-Ru(3)-Ru(4) | 90.71 (1) | Ru(3)-Ru(6)-Ru(5) | 88.95 (1) |
| B. Copper-Ruthenium Tetrahedra | | | |
| (i) Cu(1)Ru(3)(4)(6) | | (ii) Cu(1)(2)Ru(3)(6) | |
| Ru(3)-Cu(1)-Ru(4) | 66.59 (2) | Cu(2)-Cu(1)-Ru(3) | 58.77 (2) |
| Ru(3)-Cu(1)-Ru(6) | 70.79 (2) | Cu(2)-Cu(1)-Ru(6) | 57.76 (2) |
| Ru(4)-Cu(1)-Ru(6) | 64.61 (2) | Ru(3)-Cu(1)-Ru(6) | 70.79 (2) |
| Cu(1)-Ru(3)-Ru(4) | 58.20 (2) | Cu(1)-Cu(2)-Ru(3) | 59.80 (2) |
| Cu(1)-Ru(3)-Ru(6) | 54.46 (2) | Cu(1)-Cu(2)-Ru(6) | 60.22 (2) |
| Ru(4)-Ru(3)-Ru(6) | 56.99 (1) | Ru(3)-Cu(2)-Ru(6) | 72.47 (2) |
| Cu(1)-Ru(4)-Ru(3) | 55.21 (2) | Cu(1)-Ru(3)-Cu(2) | 61.43 (3) |
| Cu(1)-Ru(4)-Ru(6) | 56.08 (2) | Cu(2)-Ru(3)-Ru(6) | 53.12 (2) |
| Ru(3)-Ru(4)-Ru(6) | 63.48 (1) | Cu(1)-Ru(6)-Cu(2) | 62.02 (2) |
| Cu(1)-Ru(6)-Ru(3) | 54.57 (2) | Cu(2)-Ru(6)-Ru(3) | 54.41 (2) |
| Cu(1)-Ru(6)-Ru(4) | 59.31 (2) | | |
| Ru(3)-Ru(6)-Ru(4) | 59.53 (1) | | |
| C. Angles at Carbon | | | |
| Ru(1)-C(1)-O(1) | 147.7 (4) | Ru(4)-C(7)-O(7) | 167.9 (5) |
| Ru(1)-C(2)-O(2) | 175.8 (6) | Ru(4)-C(8)-O(8) | 177.6 (5) |
| Ru(1)-C(3)-O(3) | 178.2 (5) | Ru(4)-C(15)-O(15) | 175.6 (5) |
| Ru(2)-C(4)-O(4) | 178.9 (6) | Ru(5)-C(1)-O(1) | 129.9 (4) |
| Ru(2)-C(12)-O(12) | 177.6 (5) | Ru(5)-C(11)-O(11) | 139.5 (3) |
| Ru(2)-C(5)-O(5) | 141.2 (4) | Ru(5)-C(9)-O(9) | 177.1 (5) |
| Ru(3)-C(5)-O(5) | 133.9 (4) | Ru(5)-C(10)-O(10) | 176.9 (5) |
| Ru(3)-C(6)-O(6) | 173.4 (5) | Ru(6)-C(11)-O(11) | 136.5 (3) |
| Ru(3)-C(16)-O(16) | 174.2 (5) | Ru(6)-C(13)-O(13) | 175.4 (4) |
| Ru(3)···C(7)-O(7) | | Ru(6)-C(14)-O(14) | 173.4 (4) |
| Ru(1)-C(0)-Ru(6) | 173.7 (2) | | |
| Ru(2)-C(0)-Ru(4) | 177.1 (2) | | |
| Ru(3)-C(0)-Ru(5) | 176.4 (2) | | |
| D. Copper-Acetonitrile Angles | | | |
| Cu(1)-N(1)-C(17) | 174.9 (5) | Cu(2)-N(2)-C(19) | 167.6 (5) |
| N(1)-C(17)-C(18) | 178.2 (6) | N(2)-C(19)-C(19) | 178.7 (6) |

of the trigonal-prismatic Rh_6C core. It was our expectation that the two copper atoms would occupy threefold faces of the octahedral Ru_6C core, forming one of the three possible isomers of the bicapped octahedron (Scheme I). This is the geometry predicted for an eight-atom 110-electron cluster by the extended Hückel molecular orbital treatment applied by Lauher¹⁴ to metal atom polyhedra.

However, after Cu(1) has capped the Ru(3)(4)(6) face, the second copper atom adds not to a remaining Ru_3 face, but to the Cu(1)Ru(3)(6), in an apparent preference for Cu-Cu bonding over Cu-Ru.

The copper-copper distance of 2.69 Å is certainly consistent with a bonding interaction between the copper atoms, although this is not a sufficient criterion for metal-metal bonding.¹⁵ This compared with values of 2.76 Å for tetrahedral $Cu_4(SPh)_6^{2-}$,¹⁶ ~2.60 Å for octahedral $H_6Cu_6(PPh_3)_6$,¹⁷ and a mean value of ~2.82 Å for the cubic series $Cu_8(i-MNT)_6^{4-}$,^{18a} $Cu_8(DED)_6^{4-}$,^{18b} and Cu_8-

Scheme II



$(DTS)_6^{4-}$.^{18a} In each of these cases, bridging ligands are present, and metal-metal bonding is invoked. Indeed, in the case of the three cubic clusters the constancy of the Cu-Cu distance in spite of the differing steric properties of the three bidentate bridging ligands has been taken as strong evidence for metal-metal bonding as opposed to a nonbonding, ligand-imposed juxtaposition.

In **2**, the copper atoms are not simply held at a short internuclear distance from each other by virtue of the proximity of the capping positions on adjacent triangular faces of the octahedral Ru_6C core. Such a geometry, similar to isomer b in Scheme I, would be described by equal Cu(1)-Ru(4) and Cu(2)-Ru(2) distances. The fact, these distances differ by 0.65 Å, Cu(2)-Ru(2) being elongated to 3.38 Å in order to accommodate the short Cu(1)-Cu(2) contact. This preference for a short copper-copper dis-

(14) Lauher, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 5305.(15) Mehrotra, P. K.; Hoffmann, R. *Inorg. Chem.* **1978**, *17*, 2187.(16) Coucouvanis, D.; Murphy, C. N.; Kanodia, S. K. *Inorg. Chem.* **1980**, *19*, 2993.(17) Bezman, S. A.; Churchill, M. R.; Osborn, J. A.; Wormald, J.; *J. Am. Chem. Soc.* **1971**, *93*, 2063.(18) (a) McCandlish, L. E.; Bissell, E. C.; Coucouvanis, D.; Fackler, J. P.; Knox, K. *J. Am. Chem. Soc.* **1968**, *90*, 7357. (b) Hollander, F. J.; Coucouvanis, D. *Ibid.* **1977**, *99*, 6268. i-MNT, DED, and DTS are abbreviations for the sulfur ligands $[(CN)_2C=CS_2]^{2-}$, $[(C_2H_5O_2C)_2C=CS_2]^{2-}$, and $[C_4O_2S_2]^{2-}$ (dithio squarate).(19) Bradley J. S.; Ansell, G. B., submitted for publication in *Acta Crystallogr.*

tance at the expense of a copper-ruthenium bond certainly seems consistent with the presence of an attractive copper-copper interaction.

Since there exists no thermodynamic data for copper-ruthenium bond strengths in molecular species, it is difficult to explain convincingly the geometry adopted by the cluster. Indeed any explanation based purely upon comparisons between Cu-Ru and Cu-Cu bond energies will have to accommodate the structure of a related copper-ruthenium cluster, (toluene)₂Cu₂Ru₆(CO)₁₈, in which the two copper atoms cap opposite faces of the Ru₆ octahedral core.¹⁹

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Registry No. 1, 73413-28-2; 2, 80679-05-6; Cu(CH₃CN)₄BF₄, 15418-29-8.

Supplementary Material Available: Tables of general temperature factor expressions and of observed and calculated structure factors (28 pages). Ordering information is given on any current masthead page.

Communications

Synthesis and Characterization of an Exceptionally Air-Stable Organometallic Nickel(II) Complex of the Organolithium Reagent (C₆H₅)₂P(S)CH₂Li. The X-ray Crystal Structure of Chloro(triphenylphosphine)[diphenyl(methylene)phosphoranyldithio-S,C]nickel(II), NiCH₂P(S)Ph₂(PPh₃)Cl

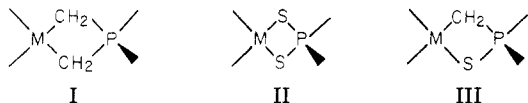
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Summary: The synthesis and single-crystal X-ray structure of an organometallic complex of nickel(II) formed from the lithium reagent LiCH₂P(S)Ph₂, Ni(mtp)(PPh₃)Cl, are described.

Ylides coordinate to metal ions both as monodentate and bidentate ligands.^{1,2} The bidentate coordination of phosphorus ylide anions I is analogous to coordination by



phosphoranyldithioate ligands II. The phosphoranyldithioates are found to have many important properties.³ In view of the nearly identical electronegativities⁴ of carbon and sulfur we were intrigued with the possibility that the anion CH₂P(S)R₂⁻ might function as an organometallic chelate, bonding to metals through both carbon and sulfur. Furthermore, M-S bond lability⁵ suggested that organometallic products of type III might display some interest in new organometallic chemistry.

Seyferth and co-workers^{6,7} have shown that phosphine oxides and sulfides react with methyllithium to yield LiCH₂P(X)(C₆H₅)₂, X = S and O. The lithium methylenethiophosphinate, Li(mtp), reacts readily with metal halide species, and, in the case of (Ph₃P)₂NiCl₂, the reaction product NiCH₂P(S)Ph₂(PPh₃)Cl, Ni(mtp)(PPh₃)Cl, has been characterized by X-ray crystallography. This compound is the first member of an ostensibly, rather large class of new sulfur-containing transition-metal organometallic species. The nickel(II) complex shows exceptional stability to reaction with air.

Preparation. Methyllithium (ca. 1.2 M in diethyl ether) is added dropwise to 1 equiv of triphenylphosphine sulfide in a 1:2 THF-Et₂O solution under nitrogen. The resulting amber solution is stirred for 1 h, and 1 equiv of NiCl₂(PPh₃)₂ is added directly to the reaction mixture. A red precipitate forms immediately, although stirring is continued for 24 h. The yield is 75%. The precipitate initially was removed by filtration under nitrogen but subsequently was found to be stable in air. Repeated recrystallization from CH₂Cl₂ and washing with acetone produces bright red orthorhombic crystals, mp ca. 140 °C dec. Anal. Calcd for NiC₃₁H₂₇P₂SCl: C, 63.35; H, 4.63%. Found: C, 63.24; H, 4.87%.

Results and Discussion. The Ni(mtp)(PPh₃)Cl is soluble in dichloromethane and tetrahydrofuran; however, only the dichloromethane solutions are stable in air for more than a few minutes. The infrared spectrum exhibits weak methylene vibrations at 2920 and 2840 cm⁻¹, in addition to the peaks arising from the phosphine and mtp phenyl groups. The ¹H NMR spectra for the diamagnetic material in CD₂Cl₂ at ambient temperature shows a broad resonance at δ -0.56 which is assigned to the methylene protons. A doublet ²J_{PCH} ≈ 10 Hz is observed at temperatures below -20 °C in CDCl₃. Several peaks are found in the phenyl region (δ 7.3-7.7). The methylene proton resonance shows that the complex is fluxional in solution. Mixed ligand dithiolate complexes of nickel(II) generally are fluxional.⁸ In this case either Ni-S or Ni-C bond rupture (or both) may occur with a low activation energy (less than 40 kJ/mol).

While spectroscopic studies were ambiguous with regard to the structure of Ni(mtp)(PPh₃)Cl, the X-ray crystal structure is not. Standard crystallographic procedures⁹

(1) Schmidbaur, H. *Acc. Chem. Res.* 1975, 8, 62.

(2) Stein, J.; Fackler, J. P., Jr.; Pappas, C.; Chen, H.-W. *J. Am. Chem. Soc.* 1981, 103, 2192-2198.

(3) Wasson, J. R.; Woltermann, G. M.; Stoklosa, H. J. *Fortschr. Chem. Forsch.* 1973, 35, 65-129.

(4) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry"; Wiley: New York, 1980.

(5) Fackler, J. P., Jr.; Thompson, L. D.; Lin, I. J. B.; Stephenson, T. A.; Gould, R. O.; Alison, J. M. C.; Fraser, A. J. F. *Inorg. Chem.*, in press.

(6) Seyferth, D.; Welch, D. E. *J. Organomet. Chem.* 1964, 2, 1-7.

(7) Seyferth, D.; Welch, D. E.; Herren, J. K. *J. Am. Chem. Soc.* 1963, 85, 642-643.

(8) See, for example: Masters, A.; Fackler, J. P., Jr. *Inorg. Chim. Acta* 1980, 39, 111-118.