**Table II.** Force Constant Values Associated with the Stretching of Ru–C Bonds in the $Ru_5C$ Polyhedron

| desig | bonds[a] | FC,[b] $N\ m^{-1}$ |
|---|---|---|
| $k_{RuC}$ | Ru(2)–C, Ru(3)–C | 230 (1)[c] |
| $k'_{RuC}$ | Ru(1)–C, Ru(4)–C, Ru(5)–C | 254 (1) |
| $f_{RuC}$ | Ru(1)–C, Ru(4)–C | −86 (1) |

[a] See Figure 5. [b] FC = force constant. [c] The estimated error is given in parentheses.

symmetric, in-plane ($a_1$) modes occur with nearly equal frequency near 830 $cm^{-1}$.

An approximate normal-coordinate analysis was performed, using the structural model of Figure 5, for the $Ru_5C$ polyhedron in order to test the reasonableness of the assignments suggested above. The results of this analysis are described briefly in the Appendix. It must be concluded that despite the approximations necessary in this treatment these assignments are feasible, although the values of the individual force constants must be treated with some caution.

We thus conclude, based on the assignment of vibrational modes associated with ruthenium–carbido and ruthenium–halogen stretching, the cluster complexes $HRu_5C(CO)_{15}X$, X = Cl and Br, are likely to be closely related in structure to the $[Os_5C(CO)_{15}I]^-$ anion. Consideration of the ruthenium–hydrido stretching frequencies in these complexes suggests that the hydrogen ligand occupies a μ-bridging position across the shortest Ru–Ru bond in each cluster molecule.

## Appendix

**Approximate Normal-Coordinate Analysis of the $Ru_5C$ Polyhedron.** The geometry of the $Ru_5C$ polyhedron was taken to be that of the analogous arrangement in the $[Os_5C(CO)_{15}I]^-$ anion[4] (Figure 5). Internal coordinates were taken to coincide with the five Ru–C bonds and a total of nine Ru–Ru vectors, including the two nonbonded vectors Ru(1)–Ru(5) and Ru(4)–Ru(5).

The metal–metal bond stretching force constants were assigned reasonable values, depending upon the Ru–Ru distances, and were not refined in the calculation. The values chosen ranged from 80 $N\ m^{-1}$ (Ru(1)–Ru(4)) to 10 $N\ m^{-1}$ for the nonbonded "equatorial" vectors. The ruthenium–carbido bonds are of three types (see Discussion), and initially attempts were made to reproduce the three observed Ru–C stretching frequencies by refinement of three independent force constants. This procedure, however, was found to lead to an unsatisfactory estimate of the antisymmetric, in-plane ($b_1$) stretching frequency, and an alternative approach was made in which the "equatorial" Ru–C force constants were constrained to be equal. This permitted the inclusion in the force field of an interaction constant between the stretching of Ru(1)–C and Ru(4)–C. Refinement of these force constants[20] resulted in exact reproduction of the three Ru–C stretching frequencies, as assigned above, with the values of the force constants as given in Table II. Although it would be expected on bond length grounds that $k_{RuC} > k'_{RuC}$, the presence of the interaction constant precludes a direct comparison.

**Registry No.** $HRu_5C(CO)_{15}Cl$, 78891-40-4; $HRu_5C(CO)_{15}Br$, 78919-48-9; $Ru_5C(CO)_{15}$, 51205-07-3.

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(20) J. H. Schachtschneider, Technical Reports No. 231-64 and No. 57-65, Shell Development Co., Emeryville, CA, 1965.

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# Synthesis, Structure, and Ligand Dynamics of the Organometallic Anion $[Ru_3(CO)_9C_2\text{-}t\text{-}Bu]^-$

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*Received April 7, 1981*

The organometal cluster $HRu_3(CO)_9C_2\text{-}t\text{-}Bu$ (I) can be readily deprotonated by $OH^-$ in carbon monoxide atmosphere to yield the corresponding anion, isolated as $[AsPh_4]^+[Ru_3(CO)_9C_2\text{-}t\text{-}Bu]^-$ (II). The variable-temperature $^{13}C$ NMR spectrum of II in the carbonyl region reveals that the barrier to axial-radial exchange at the metal atoms formerly bridged by the hydrogen is lowered by 5 kcal/mol compared with the same process in I. The barrier to intermetallic scrambling is also lower. Crystals of II are monoclinic, space group $P2_1/a$ with $Z = 4$ in a unit cell of dimensions $a = 21.384$ (15) Å, $b = 18.775$ (12) Å, $c = 10.010$ (8) Å, and $\beta = 96.77$ (7)°. The structure has been solved from diffractometer data by Patterson and direct methods and refined by full-matrix least-squares to $R = 0.066$ for 2741 observed reflections. The basic features of the triangular cluster and the organic ligand in II are maintained virtually unchanged from I, but the metal–metal bond formerly bridged by hydrogen is 0.127 Å shorter that in I. In addition, the three carbonyl groups on these metal atoms have undergone a rotation around the metal–metal bond which corresponds to relief of the steric hindrance caused by the hydride ligand.

The structural and stereochemical consequences of bridging ligands in metal cluster complexes are fundamental to our understanding of this class of molecules. In the case of the μ-hydride ligand, it has been suggested that the three-center–two-electron bond can be considered as a protonated metal–metal bond. This model nicely explains the longer metal–metal bond lengths and the larger metal–carbonyl bond angles in μ-hydride-bridged metal–metal bonds. In the case of doubly bridged metal–metal bonds where the other bridging atom(s) is not hydrogen, a shortening of the metal–metal bond is observed.[1] Recently, Adams and Selegue have observed that in the doubly bridged species $(\mu\text{-}H)(\mu\text{-}S_2CH)Os_3(CO)_{10}$ a shortening of the bridged metal–metal bond of about 0.12 Å results when phosphine substitution on the nonbridged osmium atom causes migration of the hydride ligand to give a

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(1) M. R. Churchill in "Transition Metal Hydrides", R. Bau, Ed., American Chemical Society, Washington, D.C., 1975, p 36.

0020-1669/81/1320-4306$01.25/0

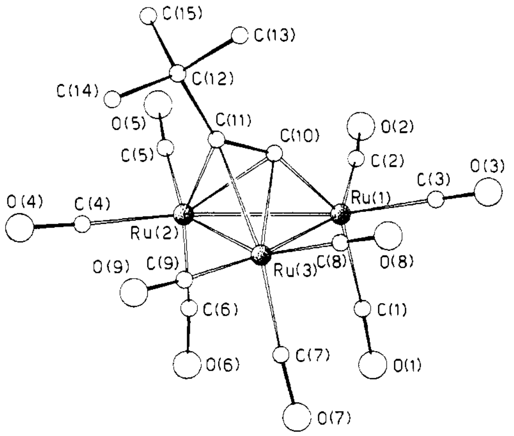
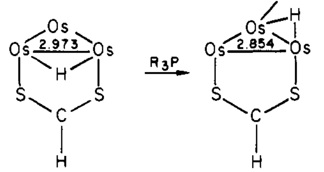


**Figure 1.** Structure of the $[Ru_3(CO)_9C_2\text{-}t\text{-}Bu]^-$ anion with the atomic numbering scheme.

species which has two singly bridged metal–metal bonds (eq 1).[2]



(1)

There have been no reports to date on the effect of removing a bridging hydride from a doubly bridged metal–metal bond in which the other bridging ligand is an organic molecule. Indeed, to our knowledge, there are no reports in the literature of organometal anions of trinuclear clusters.[3] We report here the synthesis, structure, and variable-temperature $^{13}C$ NMR spectra of the anion $[(\mu_3\text{-}C_2\text{-}C(CH_3)_3)Ru_3(CO)_9]^-$ $[(C_6H_5)_4As]^+$, and a discussion of the effects of removal of the bridging hydride on the structure and ligand dynamics of the organometal cluster.

## Results and Discussion

**Synthesis.** $(\mu\text{-}H)Ru_3(CO)_9(\mu_3\text{-}C_2C(CH_3)_3)$[4] (I) can be readily deprotonated at room temperature in THF by addition of a slight excess of ethanolic KOH. The reaction must be performed in carbon monoxide atmosphere or extensive decomposition occurs. This is in contrast to the preparation of $H_3Ru_4CO_{12}^-$ from $H_4Ru_4(CO)_{12}$ which can be performed in a nitrogen atmosphere.[5] Even under carbon monoxide atmosphere, rapid addition of the base gives a red brown solution, indicating extensive decomposition and precipitation of $(As(C_6H_5)_4)_2CO_3$ is observed when $As(C_6H_5)_4Cl$ is added to the reaction solution. Slow addition of the base followed by addition of 1 equiv of $As(C_6H_5)_4Cl$ leads to an orange yellow solution which can be evaporated to dryness and taken up in absolute ethanol to afford 75–80% yields of $[As(C_6H_5)_4]^+$-$[Ru_3(CO)_9(\mu_3\text{-}C_2C(CH_3)_3]^-$ (II) as orange-yellow crystals. These results suggest that I is more susceptible to nucleophilic attack on the carbon monoxide ligands by hydroxide ion than other hydride–metal clusters of ruthenium.

II can be reprotonated quantitatively with trifluoroacetic acid in methylene chloride to give I. II is quite unreactive toward electrophiles such as $CF_3SO_3CH_3$ and $FSO_3CH_3$ at room temperature and is thus a much poorer nucleophile than $HM_3(CO)_{11}^-$ (M = Fe, Os)[6] which is methylated at oxygen under these conditions.

**Table I.** Selected Bond Distances (Å) and Angles (Deg) with Their Estimated Standard Deviations

(a) In the Coordination Sphere of the Metal Atoms

| | | | |
|---|---|---|---|
| Ru(1)-Ru(2) | 2.800 (3) | Ru(2)-C(6) | 1.89 (2) |
| Ru(1)-Ru(3) | 2.790 (3) | Ru(2)-C(10) | 2.18 (2) |
| Ru(2)-Ru(3) | 2.665 (3) | Ru(2)-C(11) | 2.24 (2) |
| Ru(1)-C(1) | 1.90 (2) | Ru(3)-C(7) | 1.85 (3) |
| Ru(1)-C(2) | 1.92 (2) | Ru(3)-C(8) | 1.92 (2) |
| Ru(1)-C(3) | 1.90 (3) | Ru(3)-C(9) | 1.88 (3) |
| Ru(1)-C(10) | 1.95 (2) | Ru(3)-C(10) | 2.16 (2) |
| Ru(2)-C(4) | 1.88 (3) | Ru(3)-C(11) | 2.24 (2) |
| Ru(2)-C(5) | 1.88 (2) | | |

| | | | |
|---|---|---|---|
| Ru(2)-Ru(1)-Ru(3) | 56.9 (1) | C(5)-Ru(2)-C(11) | 105 (1) |
| Ru(3)-Ru(2)-Ru(1) | 61.3 (1) | C(5)-Ru(2)-Ru (1) | 98 (1) |
| Ru(2)-Ru(3)-Ru(2) | 61.7 (1) | C(6)-Ru(2)-C(10) | 128 (1) |
| Ru(2)-Ru(1)-C(1) | 103 (1) | C(6)-Ru(2)-C(11) | 151 (1) |
| Ru(2)-Ru(1)-C(2) | 100 (1) | C(6)-Ru(2)-Ru(1) | 86 (1) |
| Ru(2)-Ru(1)-C(3) | 151 (1) | C(10)-Ru(2)-C(11) | 33 (1) |
| Ru(2)-Ru(1)-C(10) | 51 (1) | C(10)-Ru(2)-Ru(1) | 44 (1) |
| Ru(3)-Ru(1)-C(1) | 103 (1) | C(11)-Ru(2)-Ru(1) | 77 (1) |
| Ru(3)-Ru(1)-C(2) | 154 (1) | C(7)-Ru(3)-C(8) | 97 (1) |
| Ru(3)-Ru(1)-C(3) | 98 (1) | C(7)-Ru(3)-C(9) | 94 (1) |
| Ru(3)-Ru(1)-C(10) | 50 (1) | C(7)-Ru(3)-C(10) | 130 (9) |
| C(1)-Ru(1)-C(2) | 93 (1) | C(7)-Ru(3)-C(11) | 153 (1) |
| C(1)-Ru(1)-C(3) | 97 (1) | C(7)-Ru(3)-Ru(1) | 87 (1) |
| C(1)-Ru(1)-C(10) | 149 (1) | C(7)-Ru(3)-Ru(2) | 99 (1) |
| C(2)-Ru(1)-C(3) | 100 (1) | C(8)-Ru(3)-C(9) | 98 (1) |
| C(2)-Ru(1)-C(10) | 107 (1) | C(8)-Ru(3)-C(10) | 101 (1) |
| C(3)-Ru(1)-C(10) | 103 (1) | C(8)-Ru(3)-C(11) | 107 (1) |
| Ru(3)-Ru(2)-C(4) | 104 (1) | C(8)-Ru(3)-Ru(1) | 98 (1) |
| Ru(3)-Ru(2)-C(5) | 151 (1) | C(8)-Ru(3)-Ru(2) | 153 (1) |
| Ru(3)-Ru(2)-C(6) | 98 (1) | C(9)-Ru(3)-C(10) | 129 (1) |
| Ru(3)-Ru(2)-C(10) | 52 (1) | C(9)-Ru(3)-C(11) | 95 (1) |
| Ru(3)-Ru(2)-C(11) | 53 (1) | C(9)-Ru(3)-Ru(1) | 164 (1) |
| C(4)-Ru(2)-C(5) | 96 (1) | C(9)-Ru(3)-Ru(2) | 102 (1) |
| C(4)-Ru(2)-C(6) | 96 (1) | C(10)-Ru(3)-C(11) | 33 (1) |
| C(4)-Ru(2)-C(10) | 129 (1) | C(10)-Ru(3)-Ru(1) | 44 (1) |
| C(4)-Ru(2)-C(11) | 96 (1) | C(10)-Ru(3)-Ru(2) | 52 (1) |
| C(4)-Ru(2)-Ru(1) | 166 (1) | C(11)-Ru(3)-Ru(1) | 77 (1) |
| C(5)-Ru(2)-C(6) | 101 (1) | C(11)-Ru(3)-Ru(2) | 53 (1) |
| C(5)-Ru(2)-C(10) | 99 (1) | | |

(b) In the Carbonyl Groups

| | | | |
|---|---|---|---|
| O(1)-C(1) | 1.13 (3) | O(6)-C(6) | 1.15 (3) |
| O(2)-C(2) | 1.11 (3) | O(7)-C(7) | 1.16 (3) |
| O(3)-C(3) | 1.11 (3) | O(8)-C(8) | 1.12 (3) |
| O(4)-C(4) | 1.16 (4) | O(9)-C(9) | 1.16 (4) |
| O(5)-C(5) | 1.15 (3) | | |

| | | | |
|---|---|---|---|
| Ru(1)-C(1)-O(1) | 177 (2) | Ru(2)-C(6)-O(6) | 175 (2) |
| Ru(1)-C(2)-O(2) | 176 (2) | Ru(3)-C(7)-O(7) | 175 (2) |
| Ru(1)-C(3)-O(3) | 174 (2) | Ru(3)-C(8)-O(8) | 178 (2) |
| Ru(2)-C(4)-O(4) | 178 (2) | Ru(3)-C(9)-O(9) | 176 (2) |
| Ru(2)-C(5)-O(5) | 175 (2) | | |

(c) In the Organic Ligand

| | | | |
|---|---|---|---|
| C(10)-C(11) | 1.27 (3) | C(12)-C(14) | 1.53 (3) |
| C(11)-C(12) | 1.54 (3) | C(12)-C(15) | 1.52 (3) |
| C(12)-C(13) | 1.58 (3) | | |

| | | | |
|---|---|---|---|
| C(11)-C(10)-Ru(1) | 156 (1) | Ru(2)-C(11)-Ru(3) | 73 (1) |
| C(11)-C(10)-Ru(2) | 76 (1) | Ru(2)-C(11)-C(10) | 71 (1) |
| C(11)-C(10)-Ru(3) | 77 (1) | Ru(3)-C(11)-C(10) | 70 (1) |
| Ru(1)-C(10)-Ru(2) | 85 (1) | C(13)-C(12)-C(14) | 109 (2) |
| Ru(1)-C(10)-Ru(3) | 85 (1) | C(13)-C(12)-C(15) | 111 (2) |
| Ru(2)-C(10)-Ru(3) | 76 (1) | C(13)-C(12)-C(11) | 106 (2) |
| C(12)-C(11)-Ru(2) | 134 (1) | C(14)-C(12)-C(15) | 109 (2) |
| C(12)-C(11)-Ru(3) | 138 (1) | C(14)-C(12)-C(11) | 113 (2) |
| C(12)-C(11)-C(10) | 141 (2) | C(15)-C(12)-C(11) | 109 (2) |

**Crystal Structure.** The structure of II consists of $[Ru_3(CO)_9C_2\text{-}t\text{-}Bu]^-$ anions and $[AsPh_4]^+$ cations. A view of the

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(2) R. D. Adams and J. P. Selegue, Abstracts of American Crystallographic Association, August 1980, p 28.

(3) H. D. Kaesz has reported $Fe_3(CO)_9(CH_3C{\equiv}N)^-$ synthesized from $HFe_3(CO)_9(CH_3C{\equiv}N)$ but here the nitrogen bridges the same edge as the hydride: H. D. Kaesz and M. A. Andrews, *J. Am. Chem. Soc.*, **99**, 6763 (1977).

(4) E. Sappa, O. Gambino, L. Milone, and G. Cetini, *J. Organomet. Chem.* **39**, 169 (1972).

(5) H. D. Kaesz, J. W. Koepke, J. R. Johnson, and S. A. R. Knox, *J. Am. Chem. Soc.* **97**, 3947.

(6) D. F. Shiver, D. Lehman, and D. Strope, *J. Am. Chem. Soc.*, **97**, 1594 (1975).

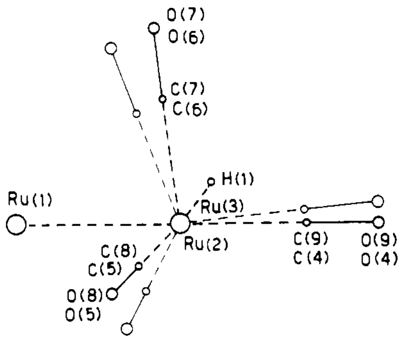

**Figure 2.** Projection along the Ru(2)-Ru(3) bond showing the rotation the carbonyls in II (labeled) have undergone with respect to those of I (unlabeled) with the loss of the hydrogen.

anion, with the atomic numbering scheme, is given in Figure 1; selected bond distances and angles in it are given in Table I. This anion contains an isosceles triangular cluster of three ruthenium atoms with three terminal carbonyls bonded to each metal atom; a *tert*-butylacetylide ligand interacts with all the Ru atoms via one $\sigma$ bond between Ru(1) and C(10) and two $\pi$ bonds between Ru(2), Ru(3), and the acetylenic C(10)-C(11) bond.

This anion remains virtually unchanged when compared with the neutral I.[7] Thus the metal orbitals involved with the organic ligand are unaffected by the additional electron density on the cluster resulting from deprotonation. Only the Ru(2)-Ru(3) bond length, corresponding to the side of the metal triangle formerly bridged by the hydride, is 0.127 Å shorter than in I [Ru(2)-Ru(3) = 2.665 (3) and 2.792 (3), Ru(1)-Ru(2) = 2.800 (3) and 2.795 (3), Ru(1)-Ru(3) = 2.790 (3) and 2.799 (3) Å in II and in I, respectively]. The same degree of shortening was observed by Adams[2] on removal of the bridging hydride from a doubly bridged osmium cluster. Thus in II, metal-metal bonding is increased by removal of the hydride, entirely consistent with the protonated metal-metal bond model suggested for other clusters.

The hydride in I has been accurately located by a neutron diffraction study,[7] and this allows us to discuss the effect of removing the hydride on the stereochemistry of the carbonyl groups on the bridged metal atoms Ru(2) and Ru(3). Figure 2, a projection along the Ru(2)-Ru(3) bond, shows the rotation the carbonyls CO(4), CO(5), CO(6), Co(7), CO(8), and CO(9) in II (labeled) have undergone with respect to those of I (unlabeled) with the loss of the hydrogen atom. The C(4)-Ru(2)-Ru(3) and C(9)-Ru(3)-Ru(2) angles, corresponding to the equatorial carbonyls, remain almost unchanged [104.4 and 103.4° in I, 104 and 102° in II], whereas the C(6)-Ru(2)-Ru(3) and C(7)-Ru(3)-Ru(2) angles decrease on going from I to II [112.8 and 113.6° in I, 98 and 99° in II]. All these changes are consistent with a relief of steric hindrance considering the location of the bridging hydride in I.

The almost linear arrangement of the hydride with CO(5) and CO(8) [C(5)-Ru(2)-H(1) = 175.8°, C(8)-Ru(3)-H(1) = 176.9°] has been invoked as evidence that the Ru-H-Ru bond is an "open" three-center-two-electron bond in I.[7] Comparing the Ru(3)-Ru(2)-C(5) and Ru(2)-Ru(3)-C(8) angles in I [145.2 and 144.1°] and in II [151 and 153°], we observe an increase which is in accord with a shift of the bond axis of the coordination site formerly occupied by the hydride on Ru(2) and Ru(3) toward the metal-metal bond axis and supports the picture of Ru(2)-H-Ru(3) as an "open" three-center bond in I.

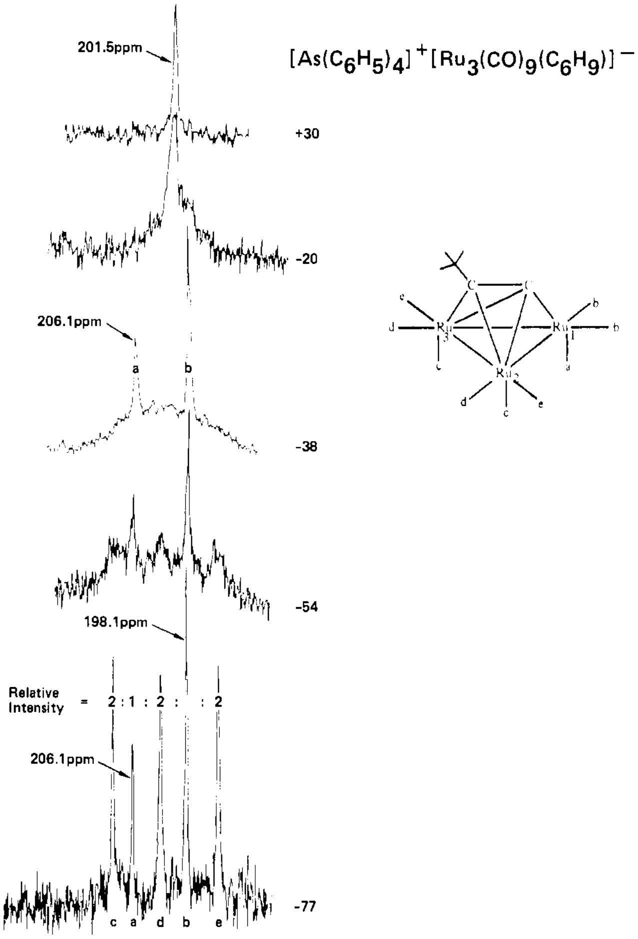

**Figure 3.** Variable-temperature $^{13}$C NMR spectra of II in the carbonyl region in $CD_2Cl_2$ at 22.63 MHz.

The bonding of the acetylenic ligand toward the metal cluster is very similar to that found in I as shown by the comparison of the more significant bond distances (Å) and angles (degrees): Ru(1)-C(10) = 1.947 (3) in I and 1.95(2) in II, Ru(2)-C(10) = 2.207 (3) and 2.18 (2), Ru(2)-C(11) = 2.268 (3) and 2.24 (2), Ru(3)-C(10) = 2.214 (3) and 2.16 (2), Ru(3)-C(11) = 2.71 (3) and 2.23 (2), C(10)-C(11) = 1.315 (3) and 1.27 (3), Ru(1)-C(10)-C(11) = 153.7 (2) and 156 (2), C(10)-C(11)-C(12) = 141.0 (2) and 141 (2).

**Variable-Temperature $^{13}$C NMR Spectroscopy.** We have previously reported the variable-temperature $^{13}$C NMR spectra of I.[8] A three-stage exchange process for the carbonyl ligands is observed. The first stage of the exchange involves axial-radial exchange of the CO groups on the unique ruthenium at Ru(1) ($\Delta G^{\ddagger}$ = 13.2 ± 0.5 kcal/mol[9]). The second stage of the exchange involves axial-radial exchange at Ru(2) and Ru(3) ($\Delta G^{\ddagger}$ = 15.6 kcal/mol). The third stage of the exchange brings about intermetallic scrambling of the CO groups, probably by a Cotton-type mechanism ($\Delta G^{\ddagger} > 18$ kcal/mol), and one CO resonance is observed in the high-temperature limit.

The low-temperature limiting spectrum of a 15% $^{13}$CO-enriched sample of II in $CD_2Cl_2$ is attained at -77 °C. The CO region consists of five resonances in a 2:1:2:2:2 ratio (Figure 3). The same number of resonances in the same relative intensities is observed for I, indicating that the ori-

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[7] M. Catti, G. Gervasio, and S. A. Mason, *J. Chem. Soc., Dalton Trans.*, 2260 (1977).

[8] E. Rosenberg, L. Milone, and S. Aime, *Inorg. Chim. Acta*, **15**, 53 (1975).

[9] Estimated from coalescence temperatures (using an error of ±10 °C) using the equation $\Delta G_c^{\ddagger} = 4.57(T_c)(9.97 - \log T_c/\delta\nu)$: D. Kost, E. H. Carlson and M. Raban, *J. Chem. Soc. D*, 656 (1971).

**Table II.**[a] $^{13}CO$ NMR Data for $[Ru_3(CO)_9C_2\text{-}t\text{-}Bu]^-$ (II) and $HRu_3(CO)_9C_2\text{-}t\text{-}Bu$ (I)

| CO group | δ(I) | δ(II) | Δδ |
|---|---|---|---|
| axial + radial at<br>Ru(2) and Ru(3) | 194.3<br>186.2<br>185.2 | 208.8<br>202.0<br>193.5 | 14.5<br>14.8<br>8.3 |
| axial at Ru(1) | 196.5 | 206.1 | 9.6 |
| radial at Ru(1) | 190.1 | 198.1 | 8.0 |

[a] All chemical shifts are reported positive dowfield relative to $Me_4Si$ and were referenced to the solvent $CDCl_3$ for I and to $CD_2Cl_2$ for II.

entation of the organic ligand is the same for I and II in solution. The chemical shifts of all the CO resonances are shifted downfield an average of about 10 ppm. (The $^{13}CO$ NMR data for I and II are shown in Table II.) The downfield shift on deprotonation is consistent with a reduction in the CO bond order as a result putting additional charge on metal which increases dative $d_\pi$–$\pi^*$ bonding.[10] This is in good agreement with shift of $\nu(C{\equiv}O)$ to lower frequencies (see Experimental Section). As the temperature is increased to −38 °C, the three CO resonances of relative intensity 2 at 208.8, 202.0, and 193.5 ppm broaden and coalesce while the resonances at 206.1 (relative intensity = 1) and 198.1 ppm (relative intensity = 2) remain relatively unchanged. Therefore in II, axial–radial exchange at Ru(2) and Ru(3) is the lowest energy exchange process. The barrier ($\Delta G^* = 10.5 \pm 0.5$ kcal/mol) is lowered by 5 kcal compared with the same process in I. The barrier to axial–radial exchange at Ru(1), on the other hand, is only about 1 kcal lower in II ($\Delta G^* = 12.2 \pm 0.5$ kcal/mol). The barrier to intermetallic exchange is considerably lower in II than in I, with a single averaged resonance appearing at 201.5 ppm at 30 °C, compared with 150 °C for I. The predicted average chemical shift for the carbonyl resonances associated with Ru(2) and Ru(3) is 201.4 ppm, and the predicted average for the carbonyl resonances at Ru(1) is 202.1 ppm ($\Delta\delta = 0.7$ ppm at 17.5 ± 2.0 Hz). At 30 °C, localized axial–radial exchange should be rapid enough to give two sharp resonances ($w_{1/2} = 2$ Hz) in a 2:1 ratio if intermetallic scrambling is slow on the NMR time scale at this temperature. If, on the other hand, intermetallic scrambling is moderately rapid on the NMR time scale, a single broadened resonance or two broadened resonances should be observed in this region. Since the single resonance observed at 201.5 ppm is relatively sharp at +30 °C ($w_{1/2} = 12$ Hz), it seems likely that intermetallic scrambling is very rapid on the NMR time scale at +30 °C and that the resonance at 201.5 ppm cannot result from accidental overlap of the resonances averaged by localized exchange only unless there are changes in the chemical shifts of the carbonyl resonances with temperature. Since we cannot rigorously exclude small variations in chemical shift with temperature, we are currently undertaking an investigation of the high-temperature $^{13}C$ NMR spectra of the phosphine deriatives of I and II to resolve this point. These results will be reported separately.

**Table III.** Fractional Atomic Coordinates ($\times 10^4$) of the Nonhydrogen Atoms with Estimated Standard Deviations in Parentheses

| | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| Ru(1) | 394 (1) | 2538 (1) | −1881 (2) |
| Ru(2) | 448 (1) | 2203 (1) | 856 (2) |
| Ru(3) | −220 (1) | 3334 (1) | −75 (2) |
| As | 2534 (1) | 5428 (1) | −3698 (2) |
| O(1) | 1619 (8) | 3341 (9) | −1974 (19) |
| O(2) | 925 (8) | 1164 (10) | −2884 (23) |
| O(3) | −340 (9) | 3144 (12) | −4370 (20) |
| O(4) | 301 (10) | 2159 (14) | 3838 (21) |
| O(5) | 783 (8) | 645 (9) | 582 (21) |
| O(6) | 1739 (7) | 2890 (9) | 1244 (18) |
| O(7) | 795 (9) | 4438 (9) | −106 (23) |
| O(8) | −1146 (9) | 4087 (11) | −2136 (21) |
| O(9) | −678 (10) | 3881 (12) | 2493 (22) |
| C(1) | 1155 (10) | 3048 (11) | −1969 (23) |
| C(2) | 730 (9) | 1676 (13) | −2556 (21) |
| C(3) | −49 (12) | 2901 (14) | −3498 (30) |
| C(4) | 364 (10) | 2186 (14) | 2706 (36) |
| C(5) | 672 (10) | 1236 (11) | 738 (27) |
| C(6) | 1250 (12) | 2637 (11) | 1037 (23) |
| C(7) | 424 (12) | 3993 (14) | −64 (27) |
| C(8) | −813 (10) | 3810 (12) | −1360 (26) |
| C(9) | −511 (11) | 3697 (13) | 1490 (30) |
| C(10) | −285 (7) | 2262 (9) | −852 (20) |
| C(11) | −586 (9) | 2232 (10) | 166 (21) |
| C(12) | −1166 (10) | 1867 (13) | 648 (20) |
| C(13) | −1736 (9) | 2011 (13) | −480 (23) |
| C(14) | −1335 (11) | 2166 (16) | 1986 (27) |
| C(15) | −1041 (11) | 1074 (14) | 809 (27) |
| C(16) | 2492 (5) | 5530 (6) | −1847 (9) |
| C(17) | 2660 (5) | 6171 (6) | −1198 (9) |
| C(18) | 2663 (5) | 6226 (6) | 192 (9) |
| C(19) | 2497 (5) | 5641 (6) | 933 (9) |
| C(20) | 2329 (5) | 5000 (6) | 284 (9) |
| C(21) | 2326 (5) | 4944 (6) | −1107 (9) |
| C(22) | 2523 (6) | 6337 (5) | −4466 (13) |
| C(23) | 3080 (6) | 6717 (5) | −4526 (13) |
| C(21) | 3062 (6) | 7389 (5) | −5120 (13) |
| C(25) | 2187 (6) | 7683 (5) | −5654 (13) |
| C(26) | 1930 (6) | 7301 (5) | −5594 (13) |
| C(27) | 1948 (6) | 6631 (5) | −5000 (13) |
| C(28) | 3286 (6) | 4978 (6) | −4011 (13) |
| C(29) | 3587 (5) | 4532 (6) | −3022 (13) |
| C(30) | 4117 (5) | 4144 (6) | −3277 (13) |
| C(31) | 4345 (5) | 4203 (6) | −4522 (13) |
| C(32) | 1044 (5) | 4649 (6) | −5511 (13) |
| C(33) | 3514 (5) | 5036 (6) | −5256 (13) |
| C(34) | 1853 (5) | 4884 (6) | −4495 (14) |
| C(35) | 1287 (5) | 4870 (6) | −3929 (14) |
| C(36) | 771 (5) | 4500 (6) | −4569 (14) |
| C(37) | 820 (5) | 4144 (6) | −5776 (14) |
| C(38) | 1385 (5) | 4158 (6) | −6342 (14) |
| C(39) | 1902 (5) | 4528 (6) | −5702 (14) |

Removal of the hydride ligand thus increases the intramolecular lability of the CO ligands. This could arise from increased charge on the metal atoms which reduces electron donation from CO and lowers the barriers CO scrambling. Alternatively, it could be argued that opening of the $\mu$-hydride bridge is necessary for axial–radial exchange to occur at Ru(2) and Ru(3). Observation of a kinetic deuterium isotope effect on the rate of axial–radial exchange at Ru(2) and Ru(3) in I would resolve this problem, and such a study is currently under way. Our preliminary results show there is an observable kinetic deuterium isotope effect on this process, and the details will be reported separately.[11] This interpretation is also supported by the recent investigation of CO-scrambling processes in $H_3Ru_3(CO)_{12}^-$ and $H_2Ru_3(CO)_2^{2-}$.[12] That intermetallic scrambling in I is much faster than in II is consistent with the idea that localized CO mobility must first be present in order to allow formation of CO-bridged intermediates by which this process takes place.[13]

## Experimental Section

**Materials.** $Ru_3(CO)_{12}$ was synthesized from $RuCl_3 \cdot 3H_2O$ (Mathey-Bishop) by known procedures. I was synthesized from $Ru_3(CO)_{12}$ and *tert*-butylacetylene (Farchan Chemicals) by a previously published procedure.[4] Tetrahydrafuran was purified by distillation from a

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(10) O. A. Gansow, D. A. Schlexnayder, and B. Y. Kimura, *J. Am. Chem. Soc.*, **94**, 3406 (1972).

(11) S. Aime, L. Milone, C. Thorsen, and E. Rosenberg, manuscript in preparation.

(12) S. G. Shore and K. E. Inkrott, *J. Am. Chem. Soc.*, **100**, 3954 (1978), and references therein.

(13) For a review of cluster carbonyl exchange processes, see S. Aime and L. Milone, *Prog. Nucl. Mag. Res. Spectrosc.*, **11**, 149 (1977).

**Table IV.** Thermal Parameters ($\times 10^4$) for the Nonhydrogen Atoms with Estimated Standard Deviations in Parentheses[a]

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Ru(1) | 543 (10) | 648 (11) | 654 (12) | −175 (9) | 113 (8) | −102 (8) |
| Ru(2) | 487 (9) | 638 (11) | 666 (12) | −84 (10) | 28 (8) | 63 (8) |
| Ru(3) | 532 (10) | 572 (10) | 757 (13) | −189 (10) | −11 (9) | 91 (8) |
| As | 598 (11) | 193 (11) | 671 (13) | 2 (10) | −51 (9) | 24 (9) |
| O(1) | 809 (123) | 1030 (133) | 1251 (166) | −129 (119) | 259 (117) | −335 (107) |
| O(2) | 1029 (131) | 1098 (142) | 2068 (220) | −650 (148) | 626 (137) | 73 (108) |
| O(3) | 1041 (159) | 1813 (207) | 908 (146) | 378 (134) | 12 (116) | 291 (138) |
| O(4) | 1316 (169) | 2358 (236) | 838 (145) | 100 (170) | 273 (133) | 30 (148) |
| O(5) | 1166 (139) | 531 (108) | 2253 (211) | 9 (120) | 302 (134) | 98 (96) |
| O(6) | 600 (91) | 1042 (132) | 1334 (156) | −179 (117) | −155 (99) | −150 (91) |
| O(7) | 1110 (154) | 777 (119) | 2260 (224) | −628 (128) | 188 (144) | −201 (104) |
| O(8) | 1037 (138) | 1395 (167) | 1337 (176) | 99 (141) | −247 (123) | 277 (126) |
| O(9) | 1562 (183) | 1854 (211) | 1381 (185) | −896 (164) | 224 (146) | 461 (151) |
| C(1) | 415 (135) | 684 (141) | 898 (171) | −212 (124) | 128 (125) | −233 (114) |
| C(2) | 604 (122) | 1020 (196) | 868 (149) | −497 (144) | 178 (105) | 6 (126) |
| C(3) | 701 (168) | 866 (203) | 1023 (232) | 75 (181) | 227 (157) | −77 (150) |
| C(4) | 514 (137) | 973 (178) | 1552 (320) | 105 (216) | −35 (183) | 37 (120) |
| C(5) | 801 (162) | 448 (122) | 1249 (242) | −188 (138) | −53 (157) | 123 (112) |
| C(6) | 825 (185) | 670 (154) | 820 (171) | −103 (126) | 9 (146) | 130 (138) |
| C(7) | 762 (191) | 749 (175) | 1435 (234) | −411 (172) | 144 (172) | 57 (149) |
| C(8) | 685 (146) | 717 (163) | 915 (197) | −35 (41) | −55 (135) | 36 (124) |
| C(9) | 921 (173) | 813 (172) | 1051 (236) | −392 (167) | −243 (165) | 380 (138) |
| C(10) | 417 (96) | 516 (114) | 624 (137) | −291 (104) | 138 (95) | −30 (81) |
| C(11) | 587 (133) | 448 (123) | 612 (146) | −179 (112) | 80 (116) | −70 (104) |
| C(12) | 578 (149) | 1229 (193) | 589 (133) | −141 (126) | 56 (115) | −103 (132) |
| C(13) | 418 (109) | 1144 (195) | 1025 (170) | −18 (152) | −74 (108) | −222 (116) |
| C(14) | 951 (176) | 1845 (283) | 1022 (224) | −522 (210) | 576 (160) | −175 (178) |
| C(15) | 990 (172) | 814 (185) | 1157 (226) | 79 (165) | 115 (155) | −61 (143) |

| | $U$, Å$^2$ | | $U$, Å$^2$ | | $U$, Å$^2$ |
|---|---|---|---|---|---|
| C(16) | 514 (44) | C(24) | 971 (70) | C(32) | 975 (61) |
| C(17) | 705 (54) | C(25) | 915 (66) | C(33) | 938 (62) |
| C(18) | 822 (60) | C(26) | 1067 (72) | C(31) | 700 (54) |
| C(19) | 879 (64) | C(27) | 814 (58) | C(35) | 943 (60) |
| C(20) | 1020 (70) | C(28) | 647 (49) | C(36) | 1195 (71) |
| C(21) | 787 (58) | C(29) | 336 (57) | C(37) | 1262 (73) |
| C(22) | 702 (53) | C(30) | 1086 (65) | C(38) | 1376 (76) |
| C(23) | 793 (57) | C(31) | 991 (69) | C(39) | 961 (63) |

[a] The anisotropic parameters are in the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})]$.

solution of sodium benzophenone ketyl.

**Spectra.** Proton NMR spectra were measured on a Varian EM360 spectrometer. $^{13}C$ NMR spectra were measured on a Bruker HFX-90 spectrometer operating in the Fourier transform mode. $^{13}CO$-enriched II was prepared from 15%-enriched $Ru_3(CO)_{12}$, which was prepared by exchanging $Ru_3(CO)_{12}$ with 0.5 atm of 90%-enriched $^{13}CO$ gas at 40–50 °C for 5 days. $^{13}C$ NMR spectra were run in the presence of 0.05 M chromium tris(acetylacetonate) as a relaxation reagent.

**Synthesis of $[AsPh_4][Ru_3(CO)_9C_2\text{-}t\text{-}Bu]$.** A 636-mg (1.0 mmol) sample of $HRu_3(CO)_9C_2\text{-}t\text{-}Bu$ was dissolved in 40–50 mL of THF under a CO atmosphere, and 60 mg (1.1 mmol) of KOH in 5 mL of absolute ethanol was added dropwise over a period of 20 min with stirring. Then 420 mg (1 mmol) of $[AsPh_4]Cl\cdot 2H_2O$ in 2 mL of absolute ethanol was added, and the reaction was evaporated to dryness under vacuum. The reaction residue was then taken up in 25 mL of absolute ethanol and recrystallized at −20 °C to yield 750–800 mg (75–80%) of yellow-orange crystals of $[AsPh_4][Ru_3(CO)_9C_2\text{-}t\text{-}Bu]$: IR $\nu$(CO) 2040 (m), 1995 (s), 1965 (s), 1945 (s, br) cm$^{-1}$; $^1H$ NMR $\delta$ 1.4 (9, s), 8.0–8.2 (20, multiplet). Anal. Calcd: C, 45.93; H, 2.87. Found: C, 45.75; H, 2.89.

**X-ray Data Collection.** An irregularly shaped yellow-orange crystal, having approximate dimensions ca. 0.15 × 0.22 × 0.27 mm, was used for the structure determination. It was mounted on a glass fiber on a eucentric head. The preliminary cell dimensions and the space group were determined from rotation and Weissenberg photographs. Systematic absences are compatible with the monoclinic space group $P2_1/a$. The crystal was transferred on a Siemens AED single-crystal diffractometer, with the $c$ axis along the $\phi$ axis of the diffractometer. Refined cell parameters were obtained by a least-squares treatment of $\theta$ values of 18 reflections accurately measured, using the Mo K$\alpha$ radiation. The crystal data are as follows: $C_{39}H_{29}AsO_9Ru_3$; mol wt = 1019.78; monoclinic; $a = 21.384$ (15), $b = 18.775$ (12), $c = 10.010$ (8) Å; $\beta = 96.77$ (7)°; $V = 3991$ (5) Å$^3$; $Z = 4$; $\rho$(calcd) = 1.697 g cm$^{-3}$; $\mu$(Mo K$\alpha$) = 19.70 cm$^{-1}$; space group $P2_1/a$.

A complete set of intensity data was collected, at room temperature, with $\theta$ in the range $3 < \theta < 24°$, on the same diffractometer using the niobium-filtered Mo K$\alpha$ radiation ($\lambda = 0.71069$ Å) at a takeoff angle of 4°. The pulse height discriminator was set to accept 90% of the Mo K$\alpha$ peak radiation. The $\theta/2\theta$ scan technique was used with a variable scan rate ranging from 2.5 to 10°/min. Scan range was ±0.5° from peak center. A standard reflection was measured after every 20 reflections as a check on crystal and instrument stability. No significant change in the measured intensities was observed during data collection. For intensities and background, the five-point technique[14] was used. A total of 6284 independent reflections were measured of which 2741 were employed in the analysis having $I > 2\sigma(I)$ $[\sigma^2(I) = \text{total counts} + (0.01(\text{intensity}))^2]$; the remaining 3543 were labeled as unobserved. The structure amplitudes were obtained after the ususal Lorentz and polarization corrections; the absolute scale and the overall temperature factor were established by Wilson's method. No absorption corrections were applied in view of the irregular shape of the crystal and of the low linear absorption coefficient.

**Solution and Refinement of the Structure.** Approximate positional parameters of the ruthenium atoms were determined by Patterson and direct methods. Successive Fourier maps with phases of these atoms revealed the positions of all other nonhydrogen atoms. Refinement was carried out by full-matrix least squares[15] first isotropically and then anisotropically for all the atoms except the 24 carbon atoms of the four phenyl rings. These were treated as rigid groups with $d$(C–C) = 1.395 Å. The hydrogen atoms could not be precisely localized in a difference Fourier and were placed in their geometrically calculated positions with isotropic thermal parameters (mean values of the thermal parameters of the carbon atoms to which they are attached) in the final structure factor calculation. The function

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(14) Hoppe, W., *Acta Crystallogr., Sect. A*, 1969, **A25**, 67 (1969).

(15) Computer programs were those of the SHELX-76 system (G. M. Sheldrick, University of Cambridge, England).

minimized during the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$; unit weights were chosen in the first cycles, and then the reflections were weighted according to the scheme $w = 1.1995/\sigma^2(F_o) + 0.005F_o^2)$ with $\sigma(F_o)$ based on counting statistics. The final $R$ and $R_w$ values were 6.6 and 7.0%, respectively (observed reflections only). The analytical scattering factors for neutral Ru, As, O, C, and H were used; both the real and imaginary components of anomalous dispersion were included for Ru and As atoms.[16] The final positional and thermal parameters for the nonhydrogen atoms are given in Tables III and IV respectively.

All calculations were performed on the Cyber 7600 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna, with financial support from the University of Parma.

**Acknowledgment.** We gratefully acknowledge the support of the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We also thank Professor Fratielo and R. Perrigan for arranging use of NMR facilities at the California State University, Los Angeles.

**Registry No.** I, 57673-31-1; II, 76741-75-8.

**Supplementary Material Available:** Listings of calculated coordinates of the hydrogen atoms and observed and calculated structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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[16] "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974.

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# Thiocyanation, Selenocyanation, and Halogenation Reactions of Dithiocarbamate Complexes of Gold(I) and Silver(I). Generation of Gold(II) and Silver(II) Complexes[1]

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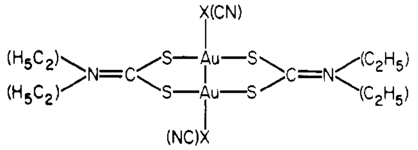
*Received August 26, 1980*

The reaction of (*N,N*-diethyldithiocarbamato)gold(I) (which exists as a dimer with eight-membered rings involving linear S-Au-S bonds) with $Br_2$, $I_2$, $(SCN)_2$, or $(SeCN)_2$ in $CS_2$ at −78 °C has permitted the isolation of what are believed to be dark green gold(II) complexes of the type shown, on the basis of the analytical and physical data obtained:



When allowed to warm to room temperature, the complexes undergo a rearrangement to form yellow salts of the type $[Au(detc)_2][Au(X(CN))_2]$ (detc = *N,N*-diethyldithiocarbamate), which have previously been reported by Beurskens et al. These salts are obtained as the initial reaction products when the reactions are carried out at room temperature in chloroform, with a dimer:(pseudo)halogen ratio of 1:1. If a ratio of 1:2 is employed under the latter conditions, complexes of the type $[Au(detc)(X(CN))_2]$ result, as previously noted by Blaauw et al., except for $I_2$, which continues to give only the $[Au(detc)_2][AuI_2]$ product. The isolation of the green gold(II) complexes casts considerable doubt on the interpretation given to the kinetic data obtained by Kita et al. for reactions of this type. The corresponding gold(II) di-*n*-butyldithiocarbamate thiocyanate derivative was found to be considerably more stable than its diethyl analogue, most probably due to the ponderable effects of the longer *n*-butyl groups. The hexameric Ag(I) homologue, $[Ag(detc)]_6$, proved to be more resistant to oxidation by $(SCN)_2$, yielding only a partially substituted $[Ag_6(detc)_5SCN]$ product at −78 °C. When the reaction was carried out at room temperature, partial oxidation to Ag(II) was observed, $[Ag_6(detc)_6(SCN)_4]$ being isolated. Even at room temperature, $(SeCN)_2$ failed to oxidize the hexamer, $[Ag_6(detc)_5SeCN]$ being formed.

## Introduction

Chemists have long puzzled over the discontinuous common oxidation states exhibited by the group 1B metals. Whereas +2 is the dominant oxidation state for copper, it is virtually nonexistent for gold[2] and is relatively rare for silver. In a vintage example of chemical serendipity, we have discovered a way to generate gold(II) and silver(II) complexes by the oxidative addition of pseudohalogens and halogens to gold(I) and silver(I) dithiocarbamate complexes. We now wish to report the results of our studies in this area.

## Experimental Section

**Preparation of Compounds.** The sodium salt of diethyldithiocarbamic acid, $Na[S_2CN(C_2H_5)_2]\cdot 2.5H_2O$, was purchased from Sigma Chemical Co. and was desiccated below 0 °C. The following compounds were prepared according to methods given in the literature: $(SCN)_2$[3] ($CS_2$ solution at −78 °C, used immediately after preparation), $(SeCN)_2$[4] (diethyl ether solution at −10 °C, used immediately after preparation), $Na[S_2CN(C_4H_9)_2]$,[5] $[Au(S_2CN(C_2H_5)_2)]_2$[6] and $[Au(S_2CN(C_4H_9)_2)]_2$.[6]

**$[Au(S_2CN(C_2H_5)_2)SCN]_2$ and $[Au(S_2CN(C_2H_5)_2)_2][Au(SCN)_2]$.** A 23-mL quantity of a −78 °C $CS_2$ solution containing 1.02 mmol of $(SCN)_2$ was slowly added to a slurry of 0.261 g (0.378 mmol) of $[Au(S_2CN(C_2H_5)_2)]_2$ in 20 mL of $CS_2$ at −78 °C. The addition

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[1] Abstracted, in part, from the M.S. thesis of D.C.C., University of Delaware, June 1978. Presented in parts at the 175th National Meeting of the American Chemical Society, Anaheim, CA, March 12-16, 1978 (Abstract INOR 23) and at the 14th Middle Atlantic Regional Meeting of the American Chemical Society, Valley Forge, PA, April 25, 1980 (Abstract UDGR 4).

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