and H_2 pressure. In cases where the anion is sufficiently nucleophilic, methyl transfer occurs. The highly nucleophilic anion $HFe(CO)_4^-$ appears to react as in eq 8–12. It is necessary to

$$CH_3B^+ + HFe(CO)_4^- \rightarrow CH_3HFe(CO)_4 + B \qquad (8)$$

$$CH_3HFe(CO)_4 + CO \rightarrow CH_3C(O)HFe(CO)_4 \qquad (9)$$

$$CH_3HFe(CO)_4 + CO \rightarrow CH_4 + Fe(CO)_5 \qquad (10)$$

$$CH_3C(O)HFe(CO)_4 + CO \rightarrow CH_3C(O)H + Fe(CO)_5 \qquad (11)$$

$$CH_3C(O)H + H_2 \xrightarrow{HFe(CO)_4^-} CH_3CH_2OH \qquad (12)$$

note, at this point, that eq 2–4, 7–9, 11, and 12 add up to give the measured overall stoichiometry, eq 1. As mentioned earlier, formation rates of the ions, $N(CH_3)_4^+$ and $HFe(CO)_4^-$, are high, and reactions 3 and 4 are at or near equilibrium. The methyl-transfer step in reaction 8 is apparently rate limiting.[16] Consistent with this interpretation, the second-order rate constant thus calculated for reaction 8 is comparable to that obtained in the stoichiometric reaction between $N(CH_3)_4^+$ and $HFe(CO)_4^-$ in 1-methyl-2-pyrrolidinone solutions.[17,18] Similar agreement between the results of catalytic and of stoichiometric reactions has also been established for the Mn-catalyst systems. Although kinetic measurements do not give information on the course of the reaction after rate-limiting methyl transfer, step 8, the following arguments for steps 9–12 are valid. Cooke[19] has shown that protonation of the ions $RFe(CO)_4^-$ and $RC(O)Fe(CO)_4^-$ (R = nonyl, amyl), in the presence of CO, yields RH and RC(O)H, respectively, consistent with steps 9–11. Acetaldehyde, postulated as an intermediate in steps 11 and 12, was detected when the solution of $[N(CH_3)_4][HFe(CO)_4]$ in 1-methyl-2-pyrrolidinone solvent was heated under CO and H_2. Consistent with earlier reports,[20] we have shown that reaction 12 is rapid under our reaction conditions. In a recent study, Dombek[21] has shown that $CH_3Mn(CO)_5$ is readily reduced to CH_3CHO and C_2H_5OH under CO/H_2.

Although $Mn(CO)_5^-$ reacts significantly faster than $HFe(CO)_4^-$ with $N(CH_3)_4^+$ (by a factor of 5),[17] this is not reflected in the rates of the catalytic reaction in Table I; experiments 1 and 4 show that $Mn_2(CO)_{10}$ is less reactive than $Fe(CO)_5$. Under the reaction conditions, the manganese system is quickly driven to a lower pH than observed in the iron system. At the lower pH, formation of methyl formate and methylammonium ion is inhibited, and the catalytic reaction is slower. The lower pH in the manganese system suggests that the system is less effective for formic acid decomposition in reaction 7. Consistent with this view, addition of $Fe(CO)_5$, a known catalyst for reaction 7,[22] to the $Mn_2(CO)_{10}$ system (experiment 5) accelerates catalysis of the methanol homologation reaction. In the mixed system, essentially all of the iron is in the form of nonnucleophilic $Fe(CO)_5$, and the products, therefore, retain the high selectivity toward ethanol formation characteristic of the manganese system.

Although the reactive species in the RhI_3- and $Ru_3(CO)_{12}$-catalyzed reactions (experiments 2 and 3) have not been conclusively identified, spectroscopic observation of the anions $HRu_3(CO)_{11}^-$ and $Rh(CO)_2I_2^-$ in the reaction mixtures is consistent with the reactivity pattern discussed for the Mn and Fe systems. Significantly, $Rh(CO)_2I_2^-$ also is the reactive nucleophile used in the Monsanto acetic acid process.[23]

The ethanol production rates reported here are comparable to the best current homologation technologies (all based on promoted or unpromoted cobalt carbonyls).[24] The mole percent conversion[25] of methanol to ethanol per hour for the mixed $Mn_2(CO)_{10}/Fe(CO)_5$ system (experiment 6) is 10.4% per hour. Maximum values calculated from the data given in each report by workers at Union Carbide (18.8%/h),[26] Exxon (12.0%/h),[27] Gulf (11.7%/h),[28] British Petroleum (9.7%/h), and Celanese (7.5%/h)[30] are similar. In this connection it is noteworthy that the mechanism identified in the new systems uses component reactions that are widespread for metal carbonyls. In contrast, the cobalt systems all appear to require a feature unique to $HCo(CO)_4$, namely, its unusually high acidity.

Acknowledgment. This research was supported by the Office of Chemical Science, Division of Basic Energy Sciences, U. S. Department of Energy. We thank D. McCullough for assistance in the experimental work and Professor J. Halpern and S. Roth for helpful discussions.

Registry No. CH_3OH, 67-56-1; CH_3CH_2OH, 64-17-5; $Fe(CO)_5$, 13463-40-6; RhI_3, 15492-38-3; $Ru_3(CO)_{12}$, 15243-33-1; $Mn_2(CO)_{10}$, 10170-69-1; 1-methylpiperidine, 626-67-5; trimethylamine, 75-50-3; 1,3-bis(1-methyl-4-piperidyl)propane, 64168-11-2.

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[16] (a) We have found other conditions under which methyl transfer is not rate limiting. There are also indications that in the catalytic reactions ion pairing plays a significant role. (b) $CH_3HFe(CO)_4$ and $CH_3C(O)HFe(CO)_4$ and their conjugate bases are in equilibrium. These equilibria do not affect the rate of the reaction and are omitted for clarity.

[17] Roth, S. A. Ph.D. Thesis, to be submitted for publication.

[18] In the stoichiometric reactions, EtOH and CH_4 are also the products, and the rate is first order in anion and cation. The kinetic orders indicate that reaction 8 is rate limiting for the reaction between $N(CH_3)_4^+$ and $HFe(CO)_4^-$. This reaction can not be studied in methanol because $HFe(CO)_4^-$ is not stable in the absence of free amines.

[19] Cooke, M. P., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 6080.

[20] (a) Sternberg, H. W.; Markby, R.; Wender, I. *J. Am. Chem. Soc.* **1957**, *79*, 6116. (b) Kang, H. C.; Mauldin, C. H.; Cole, T.; Slegeir, W.; Cann, K.; Pettit, R. *J. Am. Chem. Soc.* **1977**, *99*, 8323.

[21] Dombek, B. D. *J. Am. Chem. Soc.* **1979**, *101*, 6466.

[22] The surface of the autoclave has also been observed to have slight catalytic activity for formic acid decomposition.

[23] Forster, D. *J. Am. Chem. Soc.* **1976**, *98*, 846.

[24] In addition to the products shown in Table I, liquid side products were also observed in experiments 1 and 2. However, in experiments 3–6 ethanol and methane (easily separated as a gas) account for more than 99% of the organic product. To compare the multitude of liquid products that can be obtained with cobalt catalysts, see ref 30.

[25] (a) Defined as: (EtOH produced, mmol/MeoH initially, mmol) × 100%. (b) The metal carbonyl catalysts used in these studies are intrinsically more thermally stable than the cobalt carbonyl catalysts, and higher concentrations can be used to partially compensate for their lower specific activity (turnover frequency).

[26] Walker, W. E. U. S. Patent 4277634, 1981.

[27] Doyle, G. *J. Mol. Catal.* **1981**, *13*, 237.

[28] Pretzer, W. R.; Koblinski, T.; Bozik, J. E. U. S. Patent 4133966 1979.

[29] Barlow, M. T. European Patent 29723, 1981.

[30] Koermer, G. S.; Slinkard, W. E. *Ind. Eng. Chem. Prod. Res. Dev.* **1978**, *17*, 231. In this case, the steady-state concentration of methanol is used in calculating the conversion rate.

Synthesis, Characterization, and Crystal Structure of the $[Ru_{10}C_2(CO)_{24}]$ Dianion. An Edge-Fused Bioctahedral Dicarbide Cluster

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The formation, structures, and properties of metal clusters incorporating carbon atoms (carbides) relate importantly to the problem of activating carbon monoxide.[1] Recently, it was observed[2] that pyrolysis of $Ru_6(CO)_{18}^{2-}$ (refluxing diglyme, 162 °C)

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[1] Tachikawa, M.; Muetterties, E. L. *Prog. Inorg. Chem.* **1981**, *28*, 203–238.

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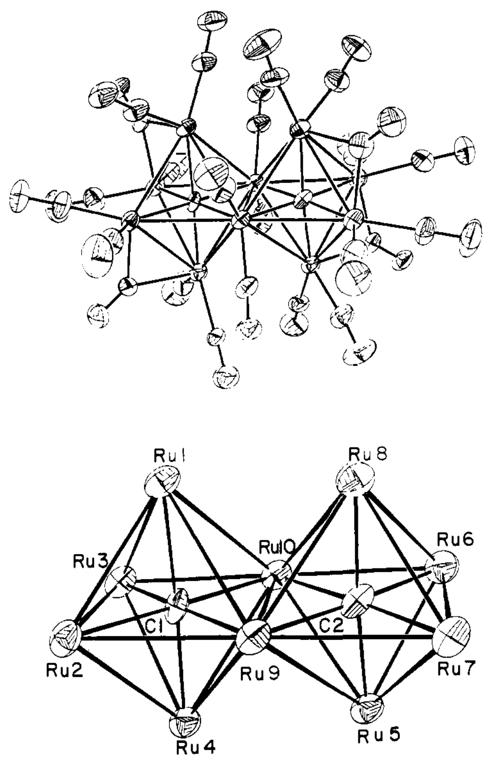

Figure 1. (Top) Entire $[Ru_{10}(\mu_6\text{-}C)_2(CO)_{20}(\mu\text{-}CO)_4{}^{2-}]$ metal cluster anion. Note the D_2 symmetry of this entity. (Bottom) Metal atom framework, with numbering.

cleanly provides $Ru_6C(CO)_{16}{}^{2-}$ (and CO_2). Pyrolysis of $Os_6(CO)_{18}{}^{2-}$ (tetraglyme, 230 °C) gives $Os_{10}C(CO)_{24}{}^{2-}$ instead of the expected $Os_6C(CO)_{16}{}^{2-}$, but indirect evidence for the formation of the latter was acquired. We now report that extended pyrolysis of $Ru_6C(CO)_{16}{}^{2-}$ also provides a decanuclear cluster, but one which has *two* carbide ligands. Besides being the only known cluster with more than six ruthenium atoms, the structure of $Ru_{10}C_2(CO)_{24}{}^{2-}$ shows a unique ten-atom framework consisting of partially fused identical subunits.[3]

Heating $(NEt_4)_2[Ru_6C(CO)_{16}]$ (450 mg, 0.34 mmol) in dry tetraglyme (50 mL) at 210–230 °C for 80 h afforded a deep purple solution and a ruthenium mirror. The solution was filtered into aqueous $(NEt_4)Cl$[4] (1 g in 150 mL), and the resulting precipitate was crystallized from acetone/ether to yield $(NEt_4)_2[Ru_{10}C_2(CO)_{24}]$ (134 mg, 0.068 mmol, 35%). Formulation of the $Ru_{10}C_2(CO)_{24}{}^{2-}$ dianion was established by negative ion fast atom bombardment (FAB) mass spectroscopy (m/z 1716 (^{102}Ru)), elemental analysis, and other spectroscopic data.[5] The formation of $Ru_{10}C_2(CO)_{24}{}^{2-}$ is not affected by added $Ru_3(CO)_{12}$. An active role for the counterion, however, is suggested by observations that whereas pyrolysis of $NEt_4{}^+$, $NEt_3CH_2Ph^+$, and $NBu_4{}^+$ salts are comparably successful, the use of Na^+, $NMe_3CH_2Ph^+$, or $N(PPh_3)_2{}^+$ salts results only in decomposition.

A single-crystal X-ray diffraction analysis of the $Ph_3PCH_2CH_2PPh_3{}^{2+}$ salt[6] shows the cluster dianion to have the formulation $[Ru_{10}(\mu_6\text{-}C)_2(CO)_{20}(\mu\text{-}CO)_4{}^{2-}]$; see Figure 1. The metal complex has approximate D_2 symmetry; the central carbido-metallic framework is based upon two octahedral $Ru_6(\mu_6\text{-}C)$ moieties fused at a common equatorial edge, Ru9–Ru10. (Alternatively, the cluster core can be viewed as two square-pyramidal Ru_5C units attached off axis at their square bases.) The ten ruthenium atoms define a portion of a body-centered-cubic array. Each ruthenium atom is bonded to two terminal carbonyl ligands; all but the two "hinge" ruthenium atoms (Ru9 and Ru10) are linked pairwise by single, symmetrically bridging carbonyl groups, which span apical–equatorial metal–metal vectors. The two carbide ligands lie in the principal equatorial plane of the framework; the Ru–C distances[7] show only slight variations and average to 2.070 Å, which is consistent with related octahedral $Ru_6(\mu_6\text{-}C)$ structures.[3b,8-10]

The Ru–Ru distances[7] show some systematic variations with the result that the octahedra surrounding C1 and C2 are not perfectly regular; rather, the "front" and "rear" triangular faces (relative to Figure 1b), are, cyclically, large and small. Thus, around C1, the upper rear triangle (Ru3–Ru1–Ru10) and the lower front triangle (Ru2–Ru4–Ru9) are smaller than the lower rear triangle (Ru3–Ru4–Ru10) and the upper front triangle (Ru2–Ru1–Ru9). Around C2 the situation is reversed, with the lower rear and upper front triangular faces now being smaller, etc. The net result is that the two octahedra are twisted relative to one another, and the Ru1–C1–Ru4 vector is staggered slightly relative to the Ru8–C2–Ru5 vector. Although the specific triangular pattern may be an extended result of the relatively short carbonyl-bridged Ru–Ru bonds, we propose that the overall twist is a result of nonbonded repulsion between the apical $Ru(CO)_2$ groups. The apical Ru–Ru distances, Ru1–Ru8 = 3.138 (2) Å and Ru4–Ru5 = 3.122 (2) Å, are only slightly longer than any of the four long Ru(apical)–Ru(hinge) distances (average 3.088 Å), but we have elected not to draw these as bonds in our figures for reasons discussed below.

The limiting low-temperature ^{13}C NMR spectrum[11] of $Ru_{10}C_2(CO)_{24}{}^{2-}$ (from ca. 50% ^{13}CO-enriched $Ru_3(CO)_{12}$) shows six equally intense singlet carbonyl resonances, one at δ 242 (bridging) and five in the range of δ 194–205 (terminal). This pattern is fully consistent with the solid-state structure. Between −60 and 20 °C exchange between the bridging carbonyls and *one* set of terminal carbonyls is observed. Details of this process are still being probed, but it very likely involves interchange of the sets of bridged and nonbridged apical–equatorial Ru–Ru edges, which would racemize the cluster. The signal for the carbide

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[2] Hayward, C. T.; Shapley, J. R. *Inorg. Chem.* **1982**, *21*, 3816–3820.

[3] Most large clusters are relatively compact; see: (a) Chini, P. *J. Organomet. Chem.* **1980**, *200*, 37–61. (b) Chini, P.; Longoni, G.; Albano, V. G. *Adv. Organomet. Chem.* **1976**, *14*, 285–344 for structures and discussion. A notable exception is $Rh_{12}(CO)_{30}{}^{2-}$, which shows two apically connected octahedrons.

[4] Filtration into aqueous solutions of other quaternary ammonium or phosphonium salts ($NEt_3CH_2Ph^+$, $N(PPh_3)_2{}^+$, $Ph_3PCH_2CH_2PPh_3{}^{2+}$, etc.) yield metathesized products of these counterions.

[5] $(NEt_4)_2(Ru_{10}C_2(CO)_{24})$: Anal. Calcd for $C_{42}H_{40}N_2O_{24}Ru_{10}$: C, 25.64; H, 2.05; N, 1.42. Found: C, 25.95; H, 2.04; N, 1.39. IR (THF) ν_{CO} 2046 (w), 2003 (vs), 1962 (w, sh), 1922 (w, sh), 1798 (m) cm^{-1}; IR (KBr) 2052 (w), 2013 (m, sh), 1999 (vs), 1964 (m, sh), 1959 (m), 1934 (w), 1928 (w, sh), 1796 (m, sh), 1793 (m, sh), 1787 (m), 1779 (m) cm^{-1}. ^1H NMR (acetone-d_6, 20 and −60 °C) no hydride signal from δ +40 to −50.

[6] (a) The technique used for data collection has been described in detail previously; see: Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265–271. (b) Crystal data: $[Ph_3PCH_2CH_2PPh_3{}^{2+}]$ $[Ru_{10}(CO)_{24}C_2{}^{2-}]\cdot 2(CH_3)_2CO$, M_r 2375.8, triclinic, space group $P\bar{1}$, $a = 12.885$ (3) Å, $b = 15.325$ (3) Å, $c = 20.448$ (4) Å, $\alpha = 104.49$ (1)°, $\beta = 96.59$ (2)°, $\gamma = 94.67$ (1)°, $V = 3858$ (1) Å^3, $Z = 2$. Diffraction data were collected on a Syntex P2$_1$ automated four-circle diffractometer. Data were corrected for absorption (μ(Mo Kα) = 19.7 cm^{-1}). The structure was solved and refined to convergence, resulting in $R_F = 4.6\%$ and $R_{wF} = 5.2\%$ for those 6381 reflections with $|F_o| > 1.0\sigma(|F_o|)$.

[7] A complete list of bond distances is supplied in the supplementary material. For convenience the Ru–Ru distances (Å) are reproduced here: (a) carbonyl-bridged Ru(apical)–Ru(eq), Ru1–Ru3 = 2.816 (1), Ru4–Ru2 = 2.819 (2), Ru5–Ru6 = 2.803 (1), Ru8–Ru7 = 2.814 (2); (b) nonbridged Ru(apical)–Ru(eq), Ru1–Ru2 = 2.986 (1), Ru4–Ru3 = 2.979 (2), Ru5–Ru7 = 2.976 (2), Ru8–Ru6 = 2.990 (2); (c) Ru(apical)–Ru(hinge), Ru1–Ru10 = 2.863 (1), Ru4–Ru9 = 2.849 (1), Ru5–Ru10 = 2.873 (1), Ru8–Ru9 = 2.866 (1), Ru1–Ru9 = 3.089 (1), Ru4–Ru10 = 3.072 (1), Ru5–Ru9 = 3.098 (2), Ru8–Ru10 = 3.094 (2); (d) "hinge" distance, Ru9–Ru10 = 2.872 (1); (e) Ru(eq)–Ru(eq) and Ru(eq)–Ru(hinge), Ru2–Ru3 = 2.931 (2), Ru2–Ru9 = 2.925 (2), Ru3–Ru10 = 2.889 (2), Ru6–Ru7 = 2.950 (2), Ru6–Ru10 = 2.892 (2), Ru7–Ru9 = 2.901 (2) Å; (f) Ru(apical)–Ru(apical), Ru1–Ru8 = 3.138 (2), Ru4–Ru5 = 3.122 (2).

[8] Bradley, J. S.; Ansell, G. B.; Hill, E. W. *J. Organomet. Chem.* **1980**, *184*, C33–C35.

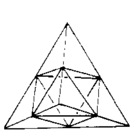
[9] Johnson, B. F. G.; Lewis, J.; Sankey, S. W.; Wong, K.; McPartlin, M.; Nelson, W. J. H. *J. Organomet. Chem.* **1980**, *191*, C3–C7.

[10] Bradley, J. S.; Pruett, R. L.; Hill, E.; Ansell, G. B.; Leonowicz, M. E.; Modrick, M. A. *Organometallics* **1982**, *1*, 748–752.

[11] At −60 °C the ^{13}C NMR spectrum (90 MHz, CD_2Cl_2) of $[N(PPh_3)_2]_2[Ru_{10}C_2(CO)_{24}]$ is δ 457.1 (s, 2 C, μ_6-C), 241.8 (s, 4 C, μ_2-CO), 205.3 (s, 4 C), 203.0 (s, 4 C), 202.3 (s, 4 C), 200.7 (s, 4 C), 193.8 (s, 4 C).

ligands appears at δ 457, a position that appears to be characteristic of Ru_6C cores.[12]

In comparison with the four previously characterized decanuclear clusters, $Ru_{10}C_2(CO)_{24}^{2-}$ is unique in both its structure and its electron count (138 valence electrons). The framework of $Os_{10}C(CO)_{24}^{2-}$[13] is a tetracapped octahedron (see I) and its 134 valence electrons can be explained by Wade–Mingos rules.[14,15] In contrast $Rh_{10}S(CO)_{22}^{2-}$,[16] $Rh_{10}P(CO)_{22}^{3-}$,[17] and $Rh_{10}As(CO)_{22}^{3-}$[18] each displays a bicapped square antiprism of metal atoms (see II) surrounding the non-metal atom and each has the 142 electrons predicted by Lauher.[19] Using a similar treatment, Ciani and Sironi[20] predicted 134 electrons for a ten-atom D_{2h} framework formed by two edge-fused octahedra plus apical–apical bonds (see III). The distorted framework observed for $Ru_{10}C_2(CO)_{24}^{2-}$ suggests that the "extra" four electrons present in the real compound may occupy metal–metal antibonding orbitals largely localized on the apical ruthenium atoms, thereby affecting the apical–apical interactions primarily and other bonds to the apical atoms to a lesser extent.



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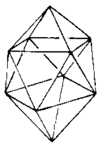

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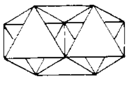
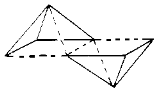


III



IV

The electron count displayed by $Ru_{10}C_2(CO)_{24}^{2-}$ may be rationalized in the following way, which depends on the fact that a 74-electron square pyramid (e.g., $Ru_5C(CO)_{15}$) has 18 electrons per metal atom, if localized M–M bonds are assumed, but an 86-electron octahedron (e.g., $Ru_6C(CO)_{17}$) does not.[15,19] Removing two $Ru(CO)_2$ caps (maintaining inversion symmetry) leaves two square pyramids sharing a basal edge (see IV). This structure may be viewed as two discrete $Ru_4C(CO)_{10}^-$ "butterfly" units connected in a slipped fashion. The connection involves *five* Ru–Ru contacts between the subunits, which satisfies the 5-electron deficiency of each $Ru_4C(CO)_{10}^-$ moiety (cf. $Fe_4C(CO)_{12}^{2-}$).[21] Thus, the $Ru_8C_2(CO)_{20}^{2-}$ framework (114 electrons) is electron precise and adding the two capping $Ru(CO)_2$ units (each 12 electrons and providing no extra framework pairs[15]) gives the observed formulation.[22]

Dicarbide clusters have been observed previously only for cobalt and rhodium; two general classes have been characterized. In one class, represented by $Co_{13}C_2(CO)_{24}^{4-}$[23] and $Rh_{15}C_2(CO)_{23}^-$,[24] the carbon atoms are well separated and occupy two distinct cavities (trigonal prismatic for Co, octahedral for Rh) within the cluster framework. The second class, consisting of $Co_{11}(C_2)(CO)_{22}^{3-}$[25] and $Rh_{12}(C_2)(CO)_{25}$,[26] populate a single cavity with a C_2 unit. Although $Ru_{10}C_2(CO)_{24}^{2-}$ is a member of the first class, its more condensed structure brings the two carbon atoms in closer proximity. This suggests the possibility of conversion to the second class under appropriate conditions.

Acknowledgment. This research was supported at the University of Illinois by NSF Grant CHE 81-00140 (to J.R.S.) and at SUNY-Buffalo by NSF Grant CHE 80-23448 (to M.R.C.). FAB mass spectra were obtained at the University of Illinois by J. C. Cook, Jr., in part under a grant from the National Institute of General Medical Sciences (GM 27029).

Supplementary Material Available: Listings of atomic coordinates, bond lenghts, and bond angles (13 pages). Ordering information is given on any current masthead page.

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(12) The value observed for $(CH_3CN)_2Cu_2Ru_6C(CO)_{16}$ is δ 458.[10] The shift reported[8] for $Ru_6C(CO)_{16}^{2-}$ has been redetermined as δ 459: Bradley, J. S., personal communication.

(13) Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; McPartlin, M.; Nelson, W. J. H. *J. Chem. Soc., Chem. Commun.* **1980**, 224–226.

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(22) If the Ru_{10} cluster is divided into two $Ru_5C(CO)_{12}^-$ subunits, each subunit is five electrons deficient, but there are seven Ru–Ru contacts. However, an 86-electron octahedral complex has formally only 11 M–M bonds (108 − 86 = 22) even though there are 12 M–M contacts in the octahedral frame.[15] (Note that the equivalent geometry for 86 electrons, a capped square pyramid, clearly has only 11 M–M bonds.[19]) Thus, if in joining the Ru_5C subunits, *one* of the Ru–Ru contacts per octahedron formed is not counted as bonding, the five-electron deficiency per subunit is satisfied by five Ru–Ru bonds.

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Reactions of Nucleophiles with α-Halo Ketones[1]

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Nucleophilic substitutions occurring by electron-transfer radical chain processes ($S_{RN}1$) at the α-C atoms of α-nitro ketones and esters[3] or of α-halomercury ketones[4] are recognized. Since the radical anion of α-bromo-*p*-nitroacetophenone rapidly loses bromide ion,[5] α-halo ketones are also candidates for $S_{RN}1$ processes.

We have examined the reactions of sterically hindered α-haloisobutyrophenones (**1**) with $Me_2C{=}NO_2^-$ and found that with *p*-nitro or *p*-cyano substituents competing ionic and free-radical substitution processes lead to different products. However, since the free radical process is not observed in the reaction of a variety

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(1) Electron transfer processes. Part 32. This work was supported by Grants CHE-7823866 and CHE-8119343 from the National Science Foundation.

(2) Postdoctoral Fellow of the Consejo Superior de Investigaciones Cientificos de Espana, 1979–1981.

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