displacement mechanism was not discussed in detail, this mechanism seems to be similar to mechanism iv.

Furthermore, Delpuech et al.[30] studied two kinds of exchange reactions in $[UO_2(nipa)_2EtOH]^{2+}$ (nipa = nonamethylimidodiphosphoramide, EtOH = ethanol), i.e. the intermolecular exchange between the coordinated ethanol and free ethanol and the intramolecular exchange between the nonequivalent phosphorus atoms of the coordinated nipa. They found that the intermolecular exchange occurs more rapidly than the intramolecular exchange and the activation entropies for both reactions have negative values. These results are consistent with our results. They suggested that the intermolecular exchange proceeds through the I mechanism and the intramolecular exchange proceeds through the mechanism in which the rate-determining step is the dissociation of the coordinated ethanol or the ring opening of one of the two coordinated nipa. The former and the latter mechanisms for the intramolecular exchange correspond to mechanisms iv and ii, respectively. These facts lend support to the conclusion that mechanism iv is the most reasonable mechanism for the present exchange reactions.

Acknowledgment. The authors express their thanks to Professor Gilbert Gordon of Miami University and Professor Thomas W. Swaddle of the University of Calgary for helpful discussions.

Registry No. $UO_2(acac)_2Me_2SO$, 71357-22-7; $UO_2(acac)_2DMF$, 89145-11-9; $UO_2(acac)_2DEF$, 89145-12-0; Hacac, 123-54-6.

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Photolysis of the Tantalum Cluster $Ta_6Br_{12}^{2+}$ in Aqueous Acidic Solution

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Irradiation of $[Ta_6Br_{12}]^{2+}$ in deaerated hydrochloric acid solution led to the photooxidation of the cluster ion and the formation of hydrogen according to $[Ta_6Br_{12}]^{2+} + H^+ \rightarrow [Ta_6Br_{12}]^{3+} + {}^1/_2H_2$. Quantum yields increased with increasing acidity of the solution and with decreasing wavelength of excitation, varying from 3×10^{-4} at 640 nm to 10^{-2} at 254 nm in 1 M HCl. Evidence is presented that the evolution of hydrogen does not involve the intermediate formation of hydrogen atoms. It is assumed that the key step involves a two-electron transfer from $[Ta_6Br_{12}]^{2+}$ to a water molecule in the solvent cage, yielding $[Ta_6Br_{12}]^{4+}$ and H^-, which is scavenged by H^+, generating H_2.

Introduction

In contrast to the case for mononuclear[1-3] and binuclear[3,4] metal complexes not much is known about the photochemistry of polynuclear compounds.[3] In particular, extended metal cluster complexes deserve attention with regard to excited-state properties. In analogy to the situation for large aromatic molecules, the excited states are not likely to be much distorted. While small clusters such as $Fe_3(CO)_{12}$[5] may undergo a photocleavage of metal-metal bonds, the structure of larger clusters such as $[Mo_6Cl_{14}]^{2-}$[6] is not affected photochemically. In contrast, larger clusters may easily undergo bimolecular photoredox reactions accepting or donating electrons. Since clusters frequently have available several oxidation states at small differences of redox potentials, they may participate in multielectron-transfer processes. In addition, redox reactions of larger clusters are generally not associated with the decomposition of these compounds due to the delocalization of the redox orbitals over the whole cluster structure. These considerations suggest that clusters are attractive candidates for reversible multielectron photoredox reactions, which are interesting with regard to processes such as the light-induced splitting of water.[7] We started to explore cluster complexes and report our observations on the photochemistry of $[Ta_6Br_{12}]^{2+}$. The present study is also of interest with regard to the photochemistry of the early transition metals in general. The investigation of light-induced reactions of these metals has been largely restricted to organometallic compounds.[3]

Experimental Section

The compound $[Ta_6Br_{12}]Br_2{\cdot}8H_2O$ was prepared by a published procedure.[8] Its electronic absorption spectrum agreed well with that reported previously.[9]

The light sources were an Osram HBO 100 W/2, an Osram XBO 450 W/4, and a Hanovia Xe/Hg 977 B-1 (1000-W) lamp. The Schott interference filters PIL 254 and 366 were used for the selection of the mercury lines at 254 and 366 nm. Irradiations at 640 nm were achieved with a Schoeffel GM 250-1 monochromator. Solutions of the complex were deaerated by argon and photolyzed in 1-cm spectrophotometer cells at room temperature. For quantum-yield determinations the complex concentrations were such as to have essentially complete light absorption. The total amount of photolysis was limited to less than 5% to avoid light absorption by the photoproduct. Absorbed light intensities were determined by a Polytec pyroelectric radiometer, which was calibrated and equipped with an RkP-345 detector.

Progress of the photooxidation was monitored by UV-visible spectral measurements with a Varian-Techtron Super Scan 3 recording spectrophotometer and a Zeiss PMQ II spectrometer for measurements at selected wavelengths. The product of the photooxidation $[Ta_6B_{12}]^{3+}$ was identified by its absorption spectrum.[9] The change of absorbance at 640 nm was used to calculate the amount of photooxidation. At 640 nm the molar extinction coefficients are $\epsilon = 6600$ for $[Ta_6Br_{12}]^{2+}$ and $\epsilon = 600$ for $[Ta_6Br_{12}]^{3+}$.

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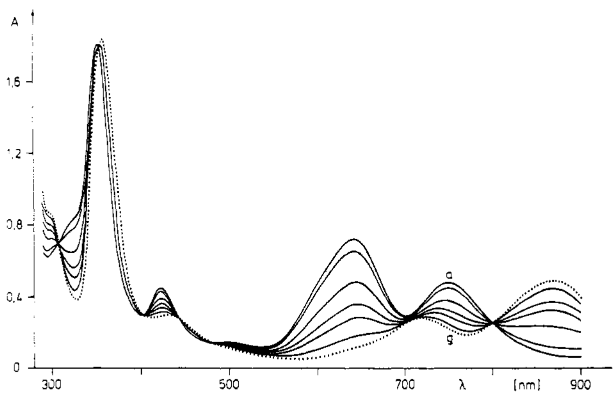

Figure 1. Spectral changes during the photooxidation of 1.12×10^{-4} M $[Ta_6Br_{12}]Br_2$ in 1 M HCl at (a) 0 and (g) 35 min irradiation time, with $\lambda_{irr} > 300$ nm and a 1-cm cell.

The photooxidation of $[Ta_6Br_{12}]^{2+}$ was accompanied by the production of molecular hydrogen, which was identified by its reaction with aqueous $PdCl_2$.[10] For the determination of the volume of H_2 the photolysis was carried out in a 10-mL cell connected to a constant-pressure gas buret.

Results

The absorption spectrum of aqueous $[Ta_6Br_{12}]^{2+}$ (Figure 1) does not depend significantly on the acidity of the solution varying from 0.05 to 5.0 M HCl. Upon irradiation of $[Ta_6Br_{12}]^{2+}$ dissolved in deaerated hydrochloric acid solution the complex underwent oxidation to the ion $[Ta_6Br_{12}]^{3+}$ as shown by the spectral changes accompanying the photolysis (Figure 1). At the isosbestic points the extinction coefficients of the starting complex are equal to those of the photooxidation product $[Ta_6Br_{12}]^{3+}$. After long irradiation times a quantitative formation of $[Ta_6Br_{12}]^{3+}$ took place. Spectrum g of Figure 1 corresponds to 95% conversion. The efficiency of the photooxidation increased with increasing acidity of the solution ($\lambda_{irr} = 366$ nm): $\phi = 8.0 \times 10^{-3}$ at 5.0 M HCl; 6.1×10^{-3} at 2.5 M; 5.4×10^{-3} at 2.0 M; 4.0×10^{-3} at 1.0 M; 2.3×10^{-3} at 0.3 M; 1.4×10^{-3} at 0.05 M. In addition, the quantum yield of photooxidation was strongly dependent on the wavelength of irradiation (1.0 M HCl): $\phi = 1 \times 10^{-2}$ at $\lambda = 254$ nm, $\phi = 4 \times 10^{-3}$ at $\lambda = 366$ nm, and $\phi = 3 \times 10^{-4}$ at $\lambda = 640$ nm. The experimental error of these measurements was ±5%. The quantum yield was hardly affected by changes of the ionic strength. An increase of the ionic strength of a 0.5 M HCl solution by NaCl addition led to a slight increase of the relative photooxidation efficiency ($\lambda_{irr} = 366$ nm): $\phi_{rel} = 1$ at $\mu = 0.5$ M; $\phi_{rel} = 1.11$ at $\mu = 2.0$ M; $\phi_{rel} = 1.16$ at $\mu = 3.0$ M. These small changes may reflect slight changes in the activity coefficients.

The photooxidation of the complex was accompanied by a simultaneous evolution of hydrogen. It was established that the photolysis proceeds according to the stoichiometry

$$[Ta_6Br_{12}]^{2+} + H^+ \rightarrow [Ta_6Br_{12}]^{3+} + {}^1/_2H_2$$

In a typical experiment the irradiation of 10 mL of 5×10^{-3} M $[Ta_6Br_{12}]^{2+}$ in 0.1 M HCl resulted in the evolution of 0.117 mL of H_2, corrected for standard temperature and pressure. Simultaneously 19.6% of the complex was photooxidized. This corresponds to a stoichiometric ratio of $[Ta_6Br_{12}]^{3+}/H_2 = 2.04 \pm 5\%$.

Several attempts were made to detect hydrogen atoms as intermediates in the formation of H_2. The photooxidation of transition-metal ions such as Fe^{2+}[11] and Eu^{2+}[12] in acidic solution is also accompanied by the generation of H_2. In these cases convincing evidence was obtained that the evolution of molecular hydrogen is preceded by the intermediate formation of hydrogen atoms. They can be easily detected by ESR spectroscopy if they are formed in a glass of 5 M H_2SO_4 at 77 K.[13] In this medium the photolysis ($\lambda_{irr} = 254$ nm) of $[Ta_6Br_{12}]^{2+}$ was not accompanied by the production of H atoms. For comparison $FeSO_4$ was irradiated under the same experimental conditions. In this case H atoms were generated as indicated by the appearance of a strong ESR signal (doublet with a splitting of 500 G).[13]

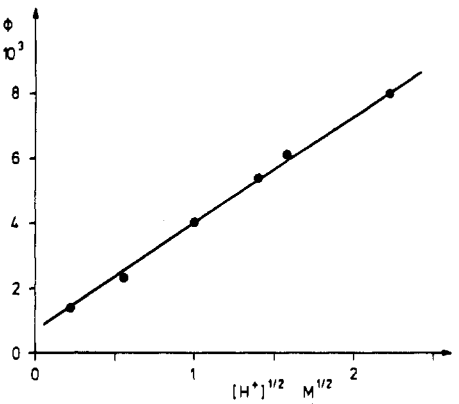

Figure 2. Half-order dependence of the quantum yield of photooxidation on hydrochloric acid concentration.

For the photooxidation of Eu^{2+} in acidic solutions 2-propanol was used as a scavenger of H atoms.[12] The addition of the alcohol leads to a considerable increase of the yield of H_2, indicating the formation of hydrogen atoms. Again, no evidence for H atom formation was obtained when the photolysis of $[Ta_6Br_{12}]^{2+}$ was carried out in the presence of 2-propanol. The irradiations of solutions containing 5×10^{-3} M $[Ta_6Br_{12}]^{2+}$, 5×10^{-3} M 2-propanol, and 0.1 M HCl did not increase the yield of H_2 compared to that for the photolysis of the same solution without the alcohol.

Discussion

The cluster ion $[Ta_6Br_{12}]^{2+}$ and related complexes are well characterized.[14] The cluster is formed by an octahedron of metal atoms. The 12 halide ions are bridging ligands. The cluster can further accommodate six solvent molecules or halide anions as terminal ligands at the six metal atoms. The interaction of the d orbitals of all six metal centers leads to a large number of highly delocalized bonding and antibonding MO's,[15] which give rise to many electronic transitions[9,16] involving essentially only d electrons.[16,17] It is generally accepted that all absorption bands extending from about 250 nm to the near-infrared region are associated with d–d transitions of the cluster. Only below 250 nm do bands appear that are believed to belong to ligand-to-metal charge-transfer transitions.[16,17]

Upon irradiation the complex cation $[Ta_6Br_{12}]^{2+}$ dissolved in deaerated solutions of hydrochloric acid underwent an oxidation to $[Ta_6Br_{12}]^{3+}$ with simultaneous evolution of hydrogen.

The photooxidation of transition-metal cations such as Fe^{2+}[11] and Eu^{2+}[12] in acidic solution is also accompanied by the generation of hydrogen, which takes place via the inter-

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mediate formation of H atoms. This is contrary to the findings in the present work. The photooxidation of $[Ta_6Br_{12}]^{2+}$ is apparently not accompanied by the transient formation of H atoms. The efficiency of the photooxidation of the cluster increased with increasing acidity of the solution. There are essentially two different mechanisms that may be responsible for this dependence. If the key step is a bimolecular reaction of the electronically excited cluster with H^+, a Stern–Volmer relationship would apply. However, a plot of the reciprocal quantum yield vs. the reciprocal hydrogen ion concentration does not yield a straight line. We found that our results fit the equation

$$\phi = \phi_0 + k[H^+]^{1/2}$$

This half-order dependence (Figure 2) is based on the Noyes model involving competition between geminate recombination and scavenging of a geminate pair.[18] On the basis of this model we suggest that the photolysis proceeds according to the mechanism (an asterisk denotes an electronically excited state and braces a solvent cage)

$$\{Ta_6Br_{12}{}^{2+},H_2O\} \xrightarrow{h\nu} \{Ta_6Br_{12}{}^{2+*},H_2O\} \tag{1}$$

$$\{Ta_6Br_{12}{}^{2+*},H_2O\} \rightarrow \{Ta_6Br_{12}{}^{2+},H_2O\} \tag{2}$$

$$\{Ta_6Br_{12}{}^{2+*},H_2O\} \rightarrow \{Ta_6Br_{12}{}^{4+},OH^-,H^-\} \tag{3}$$

$$\{Ta_6Br_{12}{}^{4+},OH^-,H^-\} \rightarrow \{Ta_6Br_{12}{}^{2+},H_2O\} \tag{4}$$

$$\{Ta_6Br_{12}{}^{4+},OH^-,H^-\} + H^+ \rightarrow \{Ta_6Br_{12}{}^{4+},OH^-\} + H_2 \tag{5}$$

$$\{Ta_6Br_{12}{}^{4+},OH^-,H^-\} + H_2O \rightarrow \{Ta_6Br_{12}{}^{4+},OH^-\} + H_2 + OH^- \tag{6}$$

$$\{Ta_6Br_{12}{}^{4+},OH^-\} + H^+ \rightarrow \{Ta_6Br_{12}{}^{4+},H_2O\} \tag{7}$$

$$\{Ta_6Br_{12}{}^{4+}\} + \{Ta_6Br_{12}{}^{2+}\} \rightarrow 2\{Ta_6Br_{12}{}^{3+}\} \tag{8}$$

The excitation (eq 1) may be followed by deactivation (eq 2) competing with the transfer of two electrons. This results in a geminate pair formation (eq 3). The transfer of two electrons from $[Ta_6Br_{12}]^{2+}$ to a water molecule in the solvent cage producing a hydride ion can be rationalized on the basis of the following considerations. The ions Fe^{2+} or Eu^{2+} can undergo only one-electron oxidations. Consequently, the reduction of a water molecule leads to the formation of a H atom. In contrast, $[Ta_6Br_{12}]^{2+}$ can be oxidized not only to $[Ta_6Br_{12}]^{3+}$ but also to $[Ta_6Br_{12}]^{4+}$ in a two-electron transfer.[19] Reaction 3 may thus involve the formation of a hydride ion. This would explain the absence of H atoms as intermediate products. The two-electron transfer does not occur necessarily in a single step but may take place also by two consecutive one-electron-transfer processes.[20] After the first electron transfer the radical pair $[Ta_6Br_{12}]^{3+}$/hydrogen atom could undergo a rapid second electron transfer to form $[Ta_6Br_{12}]^{4+}/H^-$. Hydrogen atoms are well-known to be strong oxidizing agents.[22] The hydride ion finally formed may be stabilized by association with the cluster. In a limiting description H^- could be coordinated to the cluster. Geminate recombination (eq 4) competes then with the reaction of H^- in the solvent cage with H^+ from the bulk (eq 5). In support of this assumption there are many recent observations which suggest that intermediate hydride formation occurs during the photochemical water reduction by transition-metal complexes.[22,23] The H_2-forming step (eq 5) introduces also the acid dependence of the photooxidation according to the Noyes model. The non-zero intercept of the plot (Figure 2) may reflect a small acid-independent contribution of the side reaction (6). Such a half-order dependence applies also to the photooxidation of Fe^{2+} [11] and Eu^{2+} [12] in acidic solution with the distinction that in these cases H atoms are formed instead of H^- ions.

Finally, reaction 7 leads to the stable oxidation product $[Ta_6Br_{12}]^{3+}$. This conproportionation is well-known to occur with a rate constant of $K = 6.9 \times 10^7$ M^{-1} s^{-1} and an equilibrium constant of $K = 9.02 \times 10^4$.[19]

The nature of the reactive excited state requires some comments. Although definite conclusions cannot yet be drawn, some kind of charge transfer to solvent (CTTS) transition seems to initiate the observed photoredox reaction. Many bimolecular excited-state electron-transfer reactions involve molecules such as $[Ru(bpy)_3]^{2+}$ in their lowest energy excited state, which is relatively long-lived.[24] Such a mechanism is certainly not operative here because the quantum yields decrease considerably upon light absorption by longer wavelength bands. On the other hand, a long-lived excited state of $[Ta_6Br_{12}]^{2+}$ is not required when the primary step of the photoredox reaction involves a water molecule in the solvation shell of the complex. Consequently, higher excited states with much shorter lifetimes but larger redox potentials may participate in the electron-transfer process. Such a situation could be equivalent to the CTTS excitation leading also to the photooxidation of a molecule and the reduction of the solvent. In this case CTTS excitation may be achieved by direct light absorption into CTTS bands[3] as was observed for ferrocene in halocarbon solvents.[25] However, a direct CTTS excitation is apparently not necessary. Reactive CTTS states may also be populated from higher energy internal excited states by radiationless transitions. This mechanism seems to apply to a variety of cyano complexes[26] such as $[Ru(CN)_6]^{4-}$. CTTS bands may not be identified at all if they appear in a region where the complex exhibits strong absorptions belonging to internal transitions. Such "nonspectroscopic" CTTS states were suggested to initiate the photooxidation of 1,2-dithiolene complexes of Ni, Pd, and Pt in halocarbon solvents.[27] We propose that the same mechanism applies to the photooxidation of $[Ta_6Br_{12}]^{2+}$ since CTTS bands could not be identified but may be obscured by the strong absorption bands of the cluster. Of course, excited-state electron-transfer processes to a solvent molecule involving higher energy internal excited states and the population of nonspectroscopic CTTS states by deactivation from internal excited states could be identical processes and any distinction may be artificial. A further consideration of this problem is certainly necessary.

A final aspect concerns the origin of the wavelength dependence of the photooxidation efficiency. The decrease of the quantum yield with increasing wavelength of irradiation

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seems to be characteristic of this type of photooxidation.[27] It may reflect the participation of higher vibrational levels of a single excited state. In addition or as an alternative, more than one internal excited state of the cluster may be involved. The electron transfer from higher energy excited states could become more efficient due to an increase of the redox potentials.

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Registry No. $[Ta_6Br_{12}]^{2+}$, 12343-63-4; $[Ta_6Br_{12}]^{3+}$, 12343-64-5; H_2, 1333-74-0; HCl, 7647-01-0; H_2O, 7732-18-5.

Contribution from the Istituto di Chimica Generale dell'Università di Milano, 20133 Milano, Italy,
Centro del CNR per lo studio della sintesi e della struttura dei composti dei metalli di transizione,
20133 Milano, Italy, and Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973

Synthesis of Bimetallic Fe–Ni Carbonyl Clusters: Crystal Structure of $[N(CH_3)_3CH_2Ph][Fe_3Ni(CO)_8(\mu\text{-}CO)_4(\mu_3\text{-}H)]$

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Redox condensation of $[Fe_3(CO)_{11}]^{2-}$ with $Ni(CO)_4$ in tetrahydrofuran affords the tetranuclear dianion $[Fe_3Ni(CO)_{12}]^{2-}$. Subsequent protonation with acids results in formation of the corresponding $[Fe_3Ni(CO)_{12}H]^-$ anion. This monoanionic species has also been obtained by reaction of $[Fe_3(CO)_{11}]^{2-}$ with $NiCl_2 \cdot x EtOH$. Both Fe_3Ni systems have been isolated in the solid state in high yield with a variety of tetrasubstituted ammonium and phosphonium salts. An X-ray diffraction study of the trimethylbenzylammonium salt of $[Fe_3Ni(CO)_{12}H]^-$ reveals a structure with a tetrahedron of metal atoms surrounded by eight terminal and four edge-bridging carbonyl groups. The hydride ligand has been located over the center of an Fe_2Ni face at a distance of 0.60 (3) Å from the trimetal plane. The corresponding $[Fe_3Ni(CO)_{12}]^{2-}$ dianion is suggested to posses an analogous structure on the basis of its IR spectrum. Crystallographic data for $[C_{10}H_{16}N]^+[C_{12}HFe_3NiO_{12}]^-$: fw 713.64, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 7.416$ (1) Å, $b = 13.849$ (2) Å, $c = 14.108$ (2) Å, $\alpha = 103.13$ (2)°, $\beta = 103.15$ (2)°, $\gamma = 99.23$ (2)°, $R(F^2) = 0.030$ for 3860 reflections measured at room temperature.

Introduction

Nickel subgroup metals show significant differences in their homometallic carbonyl cluster chemistry.[2] A first contact point between nickel and platinum has been established with the synthesis of isoelectronic $[M_6(CO)_6(\mu\text{-}CO)_6]^{2-}$ and $[M_9(CO)_9(\mu\text{-}CO)_9]^{2-}$ (M = Ni, Pt) dianions, although the nickel derivatives are not isostructural with the platinum ones.[3-5] The recent characterization of a series of bimetallic Fe–Pd and Fe–Pt carbonyl clusters has suggested that the fact that the corresponding palladium carbonyl clusters do not exist may probably be ascribed to intrinsic weakness of the Pd–CO bond, at least where low-nuclearity clusters are concerned.[6,7] The isolation of isostructural $[Fe_4M(CO)_{16}]^{2-}$ (M = Pd, Pt) species during that work prompted us to investigate the chemistry of the analogous bimetallic Fe–Ni carbonyl compounds.

Experimental Section

All reactions were performed under pure nitrogen or carbon monoxide in freshly distilled and dried solvents. IR spectra were recorded on a Perkin-Elmer 457 grating spectrophotometer using calcium fluoride cells. Analytical data were obtained as described elsewhere.[8] NMR spectra were recorded on a Varian XL-100 instrument. The $[Fe_3(CO)_{11}]^{2-}$ and $NiCl_2 \cdot x EtOH$ starting materials were prepared by following methods previously given in the literature.[8]

Synthesis of $[PPh_3(CH_2Ph)]_2[Fe_3Ni(CO)_{12}]$. $[PPh_3(CH_2Ph)]_2[Fe_3(CO)_{11}]$ (2.23 g) and $Ni(CO)_4$ (1 mL) were dissolved in anhydrous THF (25 mL) in a 100-mL, two-necked, round-bottomed flask equipped with a condenser cooled to about −30 °C. The solution was stirred at room temperature, while the evolving carbon monoxide was continuously removed with a slow stream of nitrogen. After 6 h of stirring, the resulting brown solution was evaporated to dryness. The residue was dissolved in acetone (20 mL), the mixture filtered, and the product precipitated by slow diffusion of 2-propanol (40 mL). After a week, well-shaped crystals of $[PPh_3(CH_2Ph)]_2[Fe_3Ni(CO)_{12}]$ (2.01 g, 84% yield) were isolated by filtration and dried under vacuum. Anal. Calcd: $[PPh_3(CH_2Ph)]^+$, 55.66; Fe, 13.21; Ni, 4.63; CO, 26.49; $[PPh_3(CH_2Ph)]^+$:Fe:Ni:CO = 2:3:1:12. Found: $[PPh_3(CH_2Ph)]^+$, 55.68; Fe, 13.03; Ni, 4.57; CO, 26.11; $[PPh_3(CH_2Ph)]^+$:Fe:Ni:CO = 2.03:2.99:1.00:12.16.

The tetra-*n*-butyl- and trimethylbenzylammonium salts of $[Fe_3Ni(CO)_{12}]^{2-}$ were analogously synthesized from the corresponding $[Fe_3(CO)_{11}]^{2-}$ salts and isolated. All these salts are readily soluble in polar solvents such as THF, acetone, acetonitrile, and dimethyl sulfoxide (Me_2SO), less soluble in alcohols, and insoluble in apolar solvents such as toluene or heptane.

Synthesis of $[PPh_3(CH_2Ph)][Fe_3Ni(CO)_{12}H]$ from $[Fe_3Ni(CO)_{12}]^{2-}$. $[PPh_3(CH_2Ph)]_2[Fe_3Ni(CO)_{12}]$ (1.07 g) was dissolved in THF (25 mL) under nitrogen atmosphere in a 100-mL Schlenk tube. Upon dropwise addition of 48% H_3PO_4 (0.3 mL), the stirred dark brown solution turned rapidly green, and the IR spectrum of the solution showed the complete disappearance of absorptions due to the dianion and the appearance of the absorptions due to the corresponding $[Fe_3Ni(CO)_{12}H]^-$ derivative. The solution was evaporated to dryness under vacuum and the residue suspended in methanol (25 mL). The precipitation of $[PPh_3(CH_2Ph)][Fe_3Ni(CO)_{12}H]$ was completed by addition of an excess of triphenylbenzylphosphonium chloride (0.5 g) and water (20 mL) with stirring. The resulting microcrystalline precipitate was filtered under nitrogen, washed with a mixture of

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† Deceased.

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