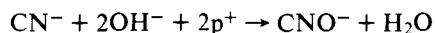


Figure 1. Amount of cyanide reacted following illumination with a 2.5-kW mercury-xenon lamp in 0.1 M KOH in the presence of doped anatase and oxygen. Solution volume was 10 ml. The illumination time and cyanide concentration are shown.

dependent of the CN^- concentration. A spot test for cyanate⁹ showed the presence of CNO^- in solution after irradiation. The studies of different forms of TiO_2 with irradiation for 30 min with the 450-W Xe lamp (Table I) demonstrated that the undoped anatase was the most active form. From the known quantum efficiency and current characteristics of a rutile electrode with this lamp,¹⁰ a quantum efficiency for CN^- oxidation of at least 0.06 is calculated assuming a two-electron reaction and absorption of only radiation beyond 3.0 eV (the TiO_2 band gap). Previous studies¹¹ have shown that the lamp output in this region is three to five times that of mid-day sunlight. When quartz sample tubes containing oxygen-saturated solutions of 1 mM CN^- were placed where they were exposed to sunlight and left for 2 days, essentially complete oxidation of CN^- was found with the tubes that contained TiO_2 and no reaction was found in tubes where TiO_2 was absent.

A mechanism for the process can be proposed based on the known operation of TiO_2 electrodes. Irradiation of a TiO_2 particle with light of energy greater than the band gap causes excitation of an electron to the conduction band leaving a hole in the valence band. Apparently these electrons and holes can be trapped in surface levels with recombination being sufficiently slow that the electron transfer processes can occur. The conduction band electrons reduce oxygen while the valence band holes cause the oxidation of CN^- :



Further oxidation of CNO^- is possible, as is the intermediacy of H_2O_2 from the reduction of oxygen, but we have no evidence for these processes. Since the extent of band bending that exists at a TiO_2 photoanode in the usual electrochemical cell and which assists in the separation of the photogenerated electrons and holes is probably larger than at the surface of a single TiO_2 particle, recombination effects, and hence lower quantum efficiencies, are expected with particles. Indeed the efficiencies found here are lower than those found for photoassisted electrolysis at a polycrystalline TiO_2 electrode coupled to a Pt cathode but are still respectable. The higher efficiency of undoped anatase can perhaps be attributed to a lower recombi-

nation rate in it compared to the doped or rutile forms.

Although this process uses only a small fraction of the available sunlight, it does show promise as a catalytic method for removal of cyanide from waste streams. Cyanide is a rather frequent pollutant, for example in rinse waters following steel surface hardening treatments, and is currently removed at considerable expense by chemical or electrolytic means.¹² Heterogeneous photocatalytic processes employing other semiconducting materials and for the oxidation or reduction of other solution species also appear promising and are currently under investigation in this laboratory.¹³

References and Notes

- (1) A. Fujishima and K. Honda, *Nature (London)*, **238**, 37 (1972).
- (2) S. N. Frank and A. J. Bard, *J. Am. Chem. Soc.*, **97**, 7427 (1975).
- (3) M. S. Wrighton, D. S. Ginley, P. T. Wolczanski, A. B. Ellis, D. L. Morse, and A. Linz, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 1518 (1975).
- (4) A. Fujishima and K. Honda, *J. Chem. Soc. Jpn.*, **74**, 355 (1971).
- (5) S. N. Frank and A. J. Bard, Electrochemical Society, National Meeting, Washington, D.C., May 2-7, 1976, Abstract 294 (Manuscript in preparation).
- (6) T. H. Wolkenstein in *Adv. Catal.*, **23**, 157 (1973).
- (7) T. Freund and W. P. Gomes, *Catal. Rev.*, **3**, 1 (1969).
- (8) H. A. Laitinen, *Chemical Analysis*, McGraw-Hill, New York, N.Y., 1960, p 225.
- (9) F. Feigl and V. Anger, *Spot Tests in Inorganic Analysis*, Elsevier, Amsterdam, 1972, p 358.
- (10) K. L. Hardee and A. J. Bard, *J. Electrochem. Soc.*, submitted for publication.
- (11) D. Laser and A. J. Bard, *Electrochem. Soc.*, **123**, 1027 (1976).
- (12) Q. D. Mehrkam, *Met. Prog.*, **108**, 103 (1975).
- (13) The support of this research by the Robert A. Welch Foundation and the National Science Foundation (MPS 74-23210) is gratefully acknowledged.

Steven N. Frank, Allen J. Bard*

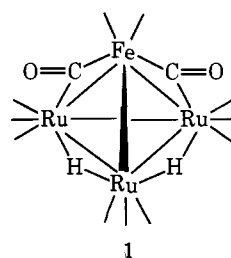
Department of Chemistry, The University of Texas at Austin
Austin, Texas 78712

Received August 6, 1976

The Designed Synthesis of $\text{H}_2\text{FeRu}_2\text{Os}(\text{CO})_{13}$ and $\text{H}_2\text{FeRuOs}_2(\text{CO})_{13}$. The First Examples of Clusters Comprised of Three Different Transition Metals

Sir:

The current interest in transition metal cluster chemistry has illustrated the need for the development of general synthetic methods for the designed synthesis of mixed-metal clusters. Carbonylmetalates have been widely used as synthetic reagents in cluster chemistry and a number of interesting compounds have been prepared.¹⁻⁸ Several of the reported reactions appear to be adaptable to design, especially those of Knight and Mays⁷ who prepared a series of group 7-group 8 tetrameric mixed-metal clusters through the addition of a carbonylmetalate to a closed $\text{M}_3(\text{CO})_{12}$ trimer. Employing a similar reaction, we have synthesized the known cluster $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$, whose structure **1** has been determined by x-ray crystallography,⁹ by the reaction of $\text{Ru}_3(\text{CO})_{12}$ with $\text{Na}_2[\text{Fe}(\text{CO})_4]$. Our synthetic yield of 49% represents a five-fold improvement over the previously reported^{10,11} pyrolysis procedures. As a test of the potential for designed synthesis using this carbonylmetalate approach, we set out to prepare



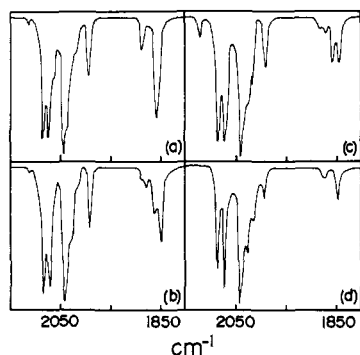


Figure 1. Carbonyl region infrared spectra of (a) $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$, (b) $\text{H}_2\text{FeRu}_2\text{Os}(\text{CO})_{13}$, (c) $\text{H}_2\text{FeRuOs}_2(\text{CO})_{13}$, and (d) $\text{H}_2\text{FeOs}_3(\text{CO})_{13}$, measured in cyclohexane solution.

the first examples of clusters which have three different transition metals in the cluster framework. We now report the preparation and characterization of $\text{H}_2\text{FeRu}_2\text{Os}(\text{CO})_{13}$ and $\text{H}_2\text{FeRuOs}_2(\text{CO})_{13}$.

Pyrolysis of $\text{Ru}_3(\text{CO})_{12}$ with $\text{Os}_3(\text{CO})_{12}$ has been reported¹² to yield the mixed-metal trimers $\text{Ru}_2\text{Os}(\text{CO})_{12}$ and $\text{RuOs}_2(\text{CO})_{12}$. In our hands this pyrolysis gave a 1:2:2:1 mixture¹³ of the four trimers, Ru_3 -, Ru_2Os -, RuOs_2 -, and $\text{Os}_3(\text{CO})_{12}$, respectively, which could not be easily separated by conventional chromatography. In a typical cluster synthesis, a dried and deoxygenated THF solution of this trimer mixture which contained 30 mg of $\text{Ru}_2\text{Os}(\text{CO})_{12}$ and 30 mg of $\text{RuOs}_2(\text{CO})_{12}$ was added to a THF solution of 80 mg of $\text{Na}_2[\text{Fe}(\text{CO})_4]$ and refluxed for 75 min. Evaporation of solvent under vacuum, followed by addition of hexane and then 20% H_3PO_4 , gave a brown hexane layer which was dried over MgSO_4 and chromatographed on silica gel. Elution with hexane afforded two principal fractions. The first consisted of unreacted trimers, a trace of $\text{H}_4\text{Ru}_4(\text{CO})_{12}$, and $\text{Fe}_3(\text{CO})_{12}$ formed from unreacted $[\text{Fe}(\text{CO})_4]^{2-}$. The second fraction contained the tetrameric mixed-metal clusters from which orange-red $\text{H}_2\text{FeRu}_2\text{Os}(\text{CO})_{13}$ and orange $\text{H}_2\text{FeRuOs}_2(\text{CO})_{13}$ were eluted in that order in yields of 30 and 40%, respectively, based on the initial quantity of mixed-metal trimers. Confirmation of our hypothesis that the new clusters were formed by addition of $[\text{Fe}(\text{CO})_4]^{2-}$ to $\text{Ru}_2\text{Os}(\text{CO})_{12}$ and $\text{RuOs}_2(\text{CO})_{12}$, rather than from random scrambling, comes from the observation that treatment of a 1:1 mixture of $\text{Ru}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$ with $[\text{Fe}(\text{CO})_4]^{2-}$ under similar reaction conditions did not give either of the new species.

The new clusters have been characterized by their infrared, NMR, electronic absorption, and mass spectra. The mass spectra of $\text{H}_2\text{FeRu}_2\text{Os}(\text{CO})_{13}$ and $\text{H}_2\text{FeRuOs}_2(\text{CO})_{13}$ afforded parent ions of 818 and 908 mass units, respectively, with the observed isotopic distribution correlating well with the calculated distribution.¹⁴ For each cluster the parent ion was followed by mass peaks representing successive loss of the 13 carbonyl ligands with the most intense peak in the spectra occurring after loss of six carbonyls.

The carbonyl region infrared spectra of $\text{H}_2\text{FeRu}_2\text{Os}(\text{CO})_{13}$ and $\text{H}_2\text{FeRuOs}_2(\text{CO})_{13}$ are shown in Figure 1 along with the spectra of $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ and $\text{H}_2\text{FeOs}_3(\text{CO})_{13}$ ¹⁵ for comparison. All the spectra are virtually identical, with the new clusters differing from the bimetallic clusters only by a splitting of the two bands in the bridging carbonyl region. This spectral similarity strongly suggests that $\text{H}_2\text{FeRu}_2\text{Os}(\text{CO})_{13}$ and $\text{H}_2\text{FeRuOs}_2(\text{CO})_{13}$ have structures **2** and **3** analogous to the structure established⁹ for $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ but with osmium replacing one and two rutheniums, respectively. The four band bridging carbonyl pattern shown by each of the new clusters suggests the existence of two structural isomers in which carbonyl ligands bridge different metal-metal bonds. For exam-

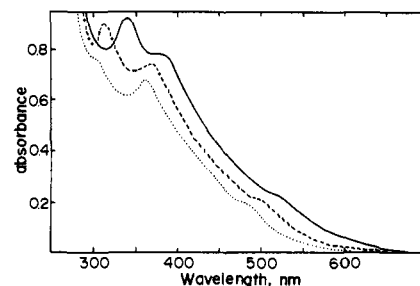
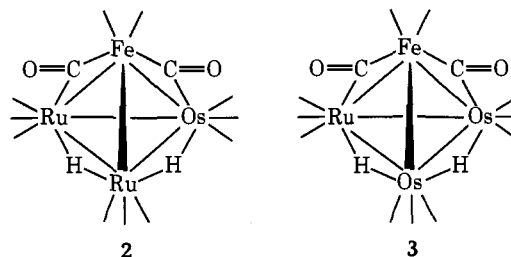


Figure 2. Electronic absorption spectra of $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ (—), $\text{H}_2\text{FeRu}_2\text{Os}(\text{CO})_{13}$ (---), and $\text{H}_2\text{FeRuOs}_2(\text{CO})_{13}$ (···) measured in hexane solution.

ple, one isomer of $\text{H}_2\text{FeRu}_2\text{Os}(\text{CO})_{13}$ would possess two bridged Fe-Ru bonds and the other isomer would have one bridged Fe-Ru and one bridged Fe-Os bond.



The ^1H NMR spectra of $\text{H}_2\text{FeRu}_2\text{Os}(\text{CO})_{13}$ and $\text{H}_2\text{FeRuOs}_2(\text{CO})_{13}$ in CDCl_3 solution at 26 °C exhibit poorly resolved multiplets centered at τ 29.0 and 29.7, respectively, providing further support for the structural similarity of the new clusters to $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ which shows¹¹ a sharp singlet at τ 28.4. The spectra show the expected trend in increased upfield shift with increased Os content of the cluster. Preliminary temperature dependent studies show that the multiplets of each of the new clusters coalesce to sharp singlets by 90 °C suggesting that the structural isomers rapidly interconvert at elevated temperature. The similarity of the electronic absorption spectra of the complexes shown in Figure 2 further supports the structural assignments. The spectra follow the trend established for $\text{Fe}_3(\text{CO})_{12}$, $\text{Ru}_3(\text{CO})_{12}$, and $\text{Os}_3(\text{CO})_{12}$ ¹⁶ and for the mixed-metal iron-ruthenium trimers¹¹ in showing a spectral blue shift as the second- or third-row metal content increases. Detailed NMR and x-ray crystallographic studies currently in progress for these new clusters should further elucidate their structural and fluxional characteristics.

Acknowledgments. We thank M. A. Andrews and H. D. Kaesz for a copy of their mass spectral correlation program MASPAN, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grant MPS 7505909) for support of this research.

References and Notes

- (1) R. B. King, *Prog. Inorg. Chem.*, **65**, 235 (1972).
- (2) P. Chini, *Inorg. Chim. Acta Rev.*, **2**, 31 (1968).
- (3) U. Anders and W. A. G. Graham, *J. Am. Chem. Soc.*, **89**, 539 (1967).
- (4) U. Anders and W. A. G. Graham, *Chem. Commun.*, 291 (1966).
- (5) J. K. Ruff, *Inorg. Chem.*, **7**, 1818 (1968).
- (6) J. K. Ruff, P. White, Jr., and F. Dahl, *J. Am. Chem. Soc.*, **93**, 2159 (1971).
- (7) J. Knight and M. J. Mays, *J. Chem. Soc., Dalton Trans.*, 1022 (1972).
- (8) S. Martinengo and P. Chini, *Gazz. Chim. Ital.*, **102**, 344 (1972).
- (9) C. J. Gilmore and P. Woodward, *Chem. Commun.*, 1463 (1970).
- (10) J. Knight and M. J. Mays, *Chem. Ind., London*, 1159 (1968).
- (11) D. B. W. Yawney and F. G. A. Stone, *J. Chem. Soc. A*, 502 (1969).
- (12) B. F. G. Johnson, R. D. Johnston, J. Lewis, I. G. Williams, and P. A. Kilty, *Chem. Commun.*, 861 (1968).
- (13) The composition of this mixture was evidenced by chemical ionization mass spectrometry by comparison of the relative peak intensities of the parent ions.
- (14) $\text{H}_2\text{FeRu}_2\text{Os}(\text{CO})_{13}$: m/e (observed relative intensity); 824 (18), 823 (12),

- 822 (29), 821 (18), 820 (47), 819 (59), 818 (76), 817 (82), 816 (94), 815 (100), 814 (88), 813 (94), 812 (65), 811 (47), 810 (41), 809 (35), 808 (24), 807 (18), 806 (18), 805 (12). $H_2FeRuOs_2(CO)_{13}$: 911 (13), 910 (28), 909 (20), 908 (65), 907 (53), 906 (93), 905 (98), 904 (100), 903 (88), 902 (93), 901 (58), 900 (55), 899 (38), 898 (25), 897 (20), 896 (13), 895 (8).
- (15) J. R. Moss and W. A. G. Graham, *J. Organomet. Chem.*, **23**, C23 (1970).
 (16) (a) P. Chini, *Pure Appl. Chem.*, **23**, 489 (1970). (b) $Os_3(CO)_{12}$: $\lambda_{max}(\epsilon)$ 327 (9600) W. Gladfelter, unpublished observation).

Gregory L. Geoffroy,* Wayne L. Gladfelter

Department of Chemistry, The Pennsylvania State University
 University Park, Pennsylvania 16802

Received August 16, 1976

Excited-State Reactivity Patterns of Hexakisarylisicyano Complexes of Chromium(0), Molybdenum(0), and Tungsten(0)

Sir:

The photochemical behavior of metal complexes possessing low-lying metal to ligand charge transfer (MLCT) excited states is poorly understood at present, owing to the virtual absence of systematic investigations on such systems.¹ For this reason we have initiated a research program aimed at the elucidation of the photochemistry of low-valent metal complexes containing arylisocyanide ligands. Many of these complexes exhibit intense visible absorption bands attributable to MLCT transitions,² and with third-row d^6 metals such as W(0) and Re(I) there is reason to believe that these transitions are much less energetic than the lowest $d-d$ excitation. Our studies to date have shown that the system comprised of hexakisarylisicyano complexes of Cr(0), Mo(0), and W(0) appears particularly promising from a photochemical standpoint. Accordingly, we communicate here the results of experiments that demonstrate the rich photochemical properties of this system.

Emission data from measurements of ML_6 complexes ($M = Cr(0), Mo(0), W(0)$; $L = CNPh, CNiPh$; $Ph = phenyl, Iph = 2,6$ -diisopropylphenyl) in pyridine at room temperature and in 2-MeTHF at 77 K are set out in Table I. Emission from the Mo(0) and W(0) complexes was also observed in 2-methylpentane, benzene, and 2-MeTHF solutions at room temperature. In each case the emission band is red-shifted and broadened in going from 77 to 298 K. Only extremely weak emission was observed for $Cr(CNiPh)_6$ at 298 K in fluid solutions.

The low temperature emission band of each of the W(0) complexes overlaps an absorption system (at 550 nm in $W(CNPh)_6$) that is found on the low energy tail of the lowest intense feature (Figure 1). Similar behavior was observed for the Mo(0) complexes. The Cr(0) complexes exhibit much weaker and broader emissions than those seen in the Mo(0) and W(0) complexes; in each case this emission overlaps the lowest intense absorption band (Figure 2). The emission lifetimes in 2-methylpentane for the $M(CNiPh)_6$ complexes are

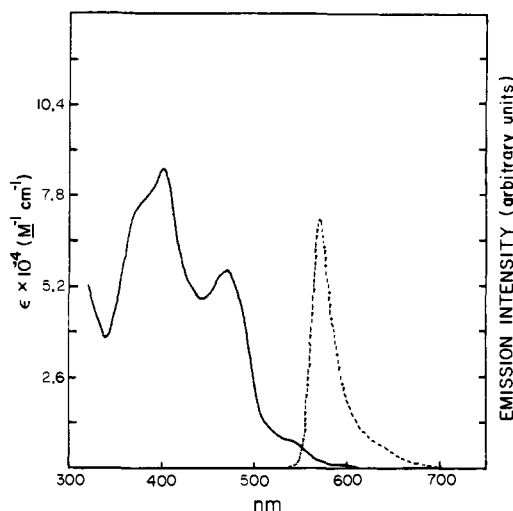
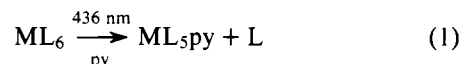


Figure 1. Absorption and emission spectra of $W(CNPh)_6$ in 2-MeTHF at 77 K.

as follows: $\tau(Cr) < 10$ ns, $\tau(Mo) 40.2 \pm 0.5$ μs , $\tau(W) 7.6$ μs (77 K); $\tau(Mo) 43 \pm 2$ ns, $\tau(W) 83 \pm 2$ ns (298 K). The much shorter lifetime for the Cr(0) complex suggests that in that case the emission is an allowed (singlet \rightarrow singlet) $L\pi^* \rightarrow d\pi$ process. As the emissions from the Mo(0) and W(0) complexes have longer lifetimes, they probably represent $L\pi^* \rightarrow d\pi$ transitions with triplet \rightarrow singlet character, although the designation of the lowest spin-orbit excited state as a "triplet" is undoubtedly a gross oversimplification.¹ⁱ

Irradiation of ML_6 ($M = Cr, Mo, W$) in pyridine solutions at 436 nm gives photosubstitution (eq 1):³



The quantum yields decrease in an interesting pattern, $[Cr(CNPh)_6] (0.23) \sim [Cr(CNiPh)_6] (0.23) > [Mo(CNPh)_6] (0.055) > [Mo(CNiPh)_6] (0.022) > [W(CNPh)_6] (0.011) \gg [W(CNiPh)_6] (0.0003)$. The lowering of the yield for substitution in going to the heavier metals and increased steric hindrance of the ligand suggests that for the Mo(0) and particularly for the W(0) complexes the mechanism has associative character.⁴ That is, the small quantum yield for $W(CNPh)_6$, which is drastically decreased in $W(CNiPh)_6$, may be accounted for by direct nucleophilic attack on the positively charged metal center in an MLCT state, $[M^+(CNPh)_6^-]^*$. Such attack could not occur without great steric strain in $W(CNiPh)_6$. Our results for the two tungsten arylisocyanides, therefore, provide a convincing case for a bimolecular excited state substitution pathway, and stand in striking contrast to the many dissociative photosubstitution reactions that have been documented for $M(CO)_n$ ($n = 4, 5, 6$) complexes.^{5,6}

Irradiation of $M(CNiPh)_6$ ($M = Cr, Mo, W$) in well-de-

Table I. Emission Data^a for ML_6 Complexes

Complex	77 K		298 K	
	λ_{max} (nm) ^b	$\bar{\nu}_{max}$ (cm ⁻¹) ^c	λ_{max} (nm) ^b	$\bar{\nu}_{max}$ (cm ⁻¹) ^c
$Cr(CNPh)_6$	590 (400)	16 900 (1800)	Not obsd	Not obsd
$Mo(CNPh)_6^d$	559 (450)	17 900 (1100)	613 (420)	16 300 (2700)
$W(CNPh)_6^d$	571 (450)	17 500 (900)	638 (420)	15 700 (3200)
$Cr(CNiPh)_6$	583 (380)	17 200 (2100)	600 (380)	16 700
$Mo(CNiPh)_6$	568 (450)	17 600 (1200)	579 (450)	17 300 (2000)
$W(CNiPh)_6$	578 (400)	17 300 (1150)	578 (420)	17 300 (1800)

^a All spectra were corrected for phototube and monochromator response; 77 K measurements were made in 2-MeTHF glasses; 298 K measurements were made in pyridine solutions. ^b Excitation wavelengths (nm) are given in parentheses. ^c Full widths (cm⁻¹) at half-height are given in parentheses. ^d Quantum yields at 77 K are as follows: Mo, 0.78 ± 0.08 ; W, 0.93 ± 0.07 (excitation at 450 nm; measured relative to $Ru(bpy)_3Cl_2$ yield of 0.376 ± 0.036 , as reported by J. N. Demas and G. A. Crosby, *J. Am. Chem. Soc.*, **93**, 2841 (1971)).