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PHOTOINDUCED SYNTHESIS OF THE MIXED METAL "MANGANESE RHENIUM CUBANE" $[Mn_3Re(CO)_{12}(SC_6H_5)_4]$

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Summary

The photoinduced synthesis and spectroscopic properties of the new mixed metal compound $[Mn_3Re(CO)_{12}(SC_6H_5)_4]$ by UV irradiation of a mixture of $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$ with $S_2(C_6H_5)_2$ is described. No mixed sulphur/selenium compounds $[M_4(CO)_{12}S_nSe_{4-n}(C_6H_5)_4]$ (M = Mn or Re, n = 1—3) could be obtained by analogous photoreactions.

Introduction

Recent work on photoinduced reactions of $Mn_2(CO)_{10}$ with S_2R_2 or Se_2R_2 ($R = C_6H_5$) showed formation of the tetrameric species $[Mn(CO)_3SR]_4$ or $[Mn(CO)_3SeR]_4$ [1]. Some interest in this type of "pseudo cubane" compounds resides in their value as structural analogues of the bacterial ferredoxines [2]. We now wish to report the results of our efforts to synthesize new mixed metal "cubanes".

Results and discussion

In a further development of syntheses involving photoinduced reactions [1] we prepared the mixed metal organosulphur cluster $[Mn_3Re(CO)_{12}(SR)_4]$. Combination of the photogenerated thiyl radicals with the reactive radicals $Mn(CO)_5$ and $Re(CO)_5$ by loss of CO affords the known dimeric $[M(CO)_4SR]_2$ (M = Mn, Re), the tetrameric $[Mn(CO)_3SR]_4$ and the new $[Mn_3Re(CO)_{12}(SR)_4]$. The attempted preparation of a mixed manganese cluster containing sulphur and selenium by photolysis of $Mn_2(CO)_{10}$ with S_2R_2 and Se_2R_2 proved to be unsuccessful. Steric requirements for such a distorted "cubane" presumably do not allow two different chalcogens to appear in the radical recombination product.

The mixed tetranuclear cluster $[Mn_3Re(CO)_{12}(SR)_4]$ has been characterized

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by elemental analysis and by infrared and mass spectra. The infrared spectrum of this dodecacarbonyl exhibits only two active carbonyl stretching modes, both with a shoulder indicating high symmetry (2030vs, 2021m, 1958m, 1951m cm^{-1} (n-pentane)) and confirming the presence of a $Re(CO)_3$ group.

Despite the high molecular weight a weak molecular ion peak is observed at $M = 1124$ (calcd. 1123.2). Fragmentation of the molecular ion occurs first by successive loss of the 12 carbonyls and then loss of the phenyl groups. The isotopic distribution patterns are as expected (4 sulphur and 1 rhenium atom).

The degraded ions $M^+ - 3CO$, $M^+ - 9CO$ and $M^+ - 10CO$ show the highest intensity of the CO fragmentation pattern. The peak of the metal chalcogen cage $Mn_3ReS_4{}^+$ ion is only moderate intense, indicating a lower stability compared with the very stable $Mn_4Se_4{}^+$ [1]. In accord with the spectroscopic data and the known structure of $[Re(CO)_3SC_6H_5]_4$ [3] we suggest for $[Mn_3Re(CO)_{12}(SR)_4]$ a distorted pseudo cubane structure.

Photoreactions with other metal carbonyls are under investigations.

Experimental

All manipulations were carried out under dry nitrogen. Solvents were distilled from sodium wire under N_2. The C, H, and O analyses were determined with a Heraeus EA 415 analyzer. Infrared spectra were recorded on Perkin—Elmer 180 and mass spectra on Varian Mat CH 7 (70 eV) apparatus. Ultraviolett irradiations were performed with a high pressure mercury lamp (Hanau 150 W) in a Schlenk tube equipped with a pressure valve.

Photoinduced reactions

(a) Of a mixed metal compound. A solution of 0.5 mmol (195 mg) $Mn_2(CO)_{10}$, 0.5 mmol $Re_2(CO)_{10}$ (326 mg) and 0.5 mmol S_2R_2 (109 mg) in n-pentane (15 ml) was irradiated for 12 h at room temperature. During photoreaction the initial yellow solution turned dark and a brown precipitate appeared. Vacuum sublimation (100°C, 10^{-2} mmHg, 2 h) gave first unreacted white high volatile $Re_2(CO)_{10}$ then at 130°C (10^{-2} mmHg, 4 h) from dimeric $[M(CO)_4SR]_2$ (M = Mn, Re) and tetrameric $[Mn(CO)_3SR]_4$ $[Mn_3Re(CO)_{12}(SR)_4]$ (<20%) was yielded. Analysis: Found: C, 38.0; H, 2.3; O, 16.8. $C_{36}H_{20}Mn_3O_{12}ReS_4$ calcd.: C, 38.4; H, 1.70; O, 17.10%.

(b) Of a mixed chalcogen compound. 0.5 mmol $Mn_2(CO)_{10}$ (195 mg), 0.5 mmol S_2R_2 (109 mg) and 0.5 mmol Se_2R_2 (156 mg) were dissolved in 15 ml n-pentane and irradiated for 14 h at room temperature to give a red brown solution and a precipitate. Spectroscopic examination (infrared + mass spectra) of the reaction mixture showed only homochalcogenic products such as $[Mn(CO)_4SR]_2$, $[Mn(CO)_3SR]_4$, $[Mn(CO)_4SeR]_2$ and traces of $[Mn(CO)_3SeR]_4$. Photoreaction of $Re_2(CO)_{10}$ produced analogous, homochalcogenic, dimeric and tetrameric species.

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