genides is readily extended to Q = Te and A = alkaline earths.

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**Supplementary Material Available:** A table of atomic and thermal parameters (1 page). Ordering information is given on any current masthead page.

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# A Diffuse Reflectance FTIR Spectroscopic (DRIFTS) Investigation of Carbon-Supported Metal Carbonyl Clusters

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For the first time, as far as we can determine, an infrared (IR) spectroscopic technique has been successfully applied to characterize metal carbonyl clusters and CO chemisorbed on metal particles that are dispersed on carbon. Amorphous carbons that have been subjected to medium-to-high temperatures are routinely opaque to IR radiation thereby preventing the use of conventional IR techniques,[1-4] although high-frequency bands of physisorbed toluene on carbon black have recently been reported.[5] Using Diffuse Reflectance IR Fourier Transform Spectroscopy (DRIFTS) incorporating a modified controlled environment cell,[6] we have obtained IR spectra for $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, and $Os_3(CO)_{12}$ impregnated on a 1400 $m^2/g$ carbon black, we have quantitatively followed the decomposition of these clusters at different temperatures by DRIFTS, and we have recorded spectra of CO adsorbed on the small reduced metal crystallites that remain after decomposition.[7] We would like to report here two sets of IR spectra illustrating the agreement of these results with previously reported spectra and demonstrating the applicability of DRIFTS to study carbons and carbon-supported catalysts.

The catalysts were prepared anaerobically with use of standard Schlenk techniques and an incipient wetness impregnation of Black Pearls 2000 (Cabot Corp.) with $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$ in dried, degassed THF and $Os_3(CO)_{12}$ in $CH_2Cl_2$.[7] This carbon black was treated in $H_2$ at 1223 K for 12 h to remove sulfur and oxygen from the surface. The optimal diluent was found to be $CaF_2$, and a carbon:$CaF_2$ dilution weight ratio of 1:200 was used.[7]

Spectra were collected on a Mattson Instruments Sirius 100 FTIR spectrometer with use of a substantially modified version of an HVC-DRP (Harrick) closed environment DRIFTS cell in conjunction with a praying mantis assembly (Harrick DRA-2CS). The assembly was modified to allow height adjustment of the powder sample from outside the spectrometer cavity so that the energy throughput could readily be maximized.[6] The fully decarbonylated samples obtained after reduction in $H_2$ at 673 K for 16 h and He flushing were used to obtain background spectra. The background interferograms for both the supported carbonyls and adsorbed CO spectra were obtained by averaging 10000 scans while the sample inteferograms were obtained by averaging 1000 scans for the supported carbonyls and 10000 scans for the adsorbed CO spectra. The FTIR parameters were set for a resolution of 4 $cm^{-1}$. Data manipulation consisted of base line correcting the absorbance spectra and then transforming the base line corrected absorbance spectra into diffuse reflectance spectra (Kubelka-Munk units), thereby eliminating the possibility of spectral inversion due to the mathematical form of the Kubelka-Munk function. Agreement between absorbance and diffuse reflectance spectra was excellent.

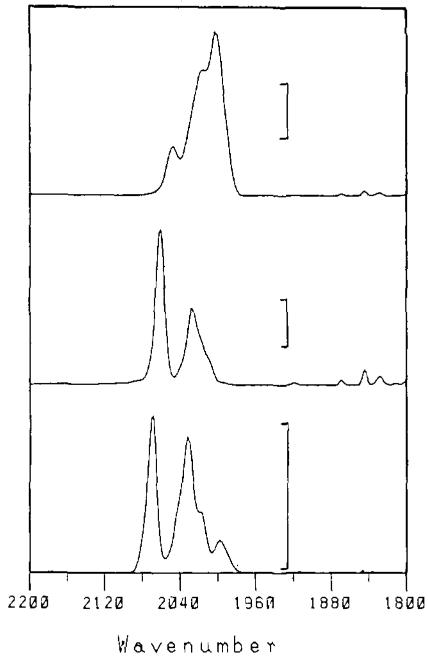

**Figure 1.** DRIFTS spectra of carbon-supported carbonyls under flowing He at 300 K: (A, top) $Fe_3(CO)_{12}/C$ (15 wt % Fe) with frequencies at 2047, 2018, 2000, 1990 (s) $cm^{-1}$; (B, middle) $Ru_3(CO)_{12}/C$ (10 wt % Ru) with frequencies at 2060, 2027, and 2010 (s) $cm^{-1}$; (C, bottom) $Os_3(CO)_{12}/C$ (10 wt % Os) with frequencies at 2068, 2031, 2015 (s), and 2002 $cm^{-1}$. (Scale = 0.0002 Kubelka-Munk units.)

The IR spectra of the supported carbonyls at 300 K are shown in Figure 1. The observed frequencies for $Ru_3(CO)_{12}$ (2060, 2027 and 2010 $cm^{-1}$) agree well with reported values of 2059–2064, 2026–2033, and 2012–2018 $cm^{-1}$ for the cluster in solution[8-11] and the cluster supported on dehydroxylated $SiO_2$.[9,12,13] The observed frequencies for $Os_3(CO)_{12}$ (2068, 2031, 2015, and 2002 $cm^{-1}$), agree well with reported values (2065–2068, 2033–2037, 2014–2020, and 2000–2003 $cm^{-1}$) for the cluster in solution[14-17] and on dehydroxylated $SiO_2$.[18-20] This indicates that both $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ remain intact on the carbon following impregnation, as the familiar interaction with hydroxyl groups on oxide supports is avoided,[13,17,18] and it illustrates a major advantage of using carbon as a support for these compounds. The $Fe_3(CO)_{12}/C$ sample shows peaks at 2047, 2018, 2000, and 1990 (s) $cm^{-1}$. The peaks at 2047 and 2018 $cm^{-1}$ are characteristic of $Fe_3(CO)_{12}$ in solution,[21-23] while frequencies for $Fe(CO)_5$ are

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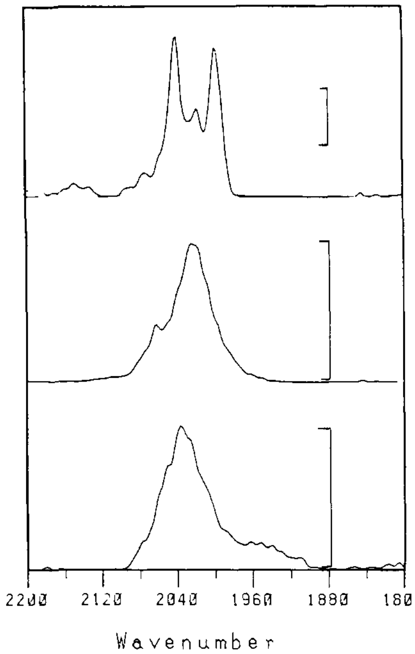

**Figure 2.** DRIFTs spectra of adsorbed CO on reduced carbon-supported metal crystallites under flowing He at 300 K: (A, top) 15% Fe/C with frequencies at 2042 (physisorbed CO on carbon), 2018, and 2000 cm$^{-1}$; (B, middle) 10% Ru/C with frequencies at 2063 and 2024 cm$^{-1}$; (C, bottom) 10% Os/C with frequency at 2035 cm$^{-1}$. (Scale = 0.00001 Kubelka-Munk units.)

known to occur at 2020 and 2000 cm$^{-1}$.[22,24] Although the formation of $HFe_3(CO)_{11}$ from $Fe_3(CO)_{12}$ on $SiO_2$ is well-known,[25] the partial decomposition of $Fe_3(CO)_{12}$ to $Fe(CO)_5$ on dehydroxylated $SiO_2$ has also been reported.[26] The latter reaction is clearly favored on carbon, as verified by Mössbauer spectroscopy.[27]

The IR spectra obtained after exposure of the decomposed, reduced clusters to CO (11 Torr of CO in He) and subsequent flushing in He are shown in Figure 2. The principal band at 2024 cm$^{-1}$ for Ru corresponds well with that reported for CO on Ru on a Ru(001) single crystal[28] (2022 cm$^{-1}$) and on supported zerovalent Ru,[29-32] while the weak shoulder at 2063 cm$^{-1}$ corresponds to the band for CO on partially oxidized Ru.[9,11,33] The observed frequency of 2035 cm$^{-1}$ for adsorbed CO on Os corresponds well with reported values of 2025–2030 cm$^{-1}$ for zerovalent Os.[34,35] Exposure of Fe/C to CO, however, leads to the formation of $Fe(CO)_5$, in agreement with chemisorption measurements[36-39] and Mössbauer spectroscopy.[27]

In conclusion, DRIFTS was successfully used to obtain the infrared spectra of the carbon-supported carbonyls of Fe, Ru, and Os and the adsorbed CO on these reduced metal crystallites. The results obtained are in good agreement with reported literature frequencies and demonstrate that the application of DRIFTS to carbon-supported catalysts is possible; however, substantial modifications must be made to commercial equipment to successfully acquire the data.

**Acknowledgment.** This research was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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# Total Synthesis of Debromoaplysiatoxin and Aplysiatoxin

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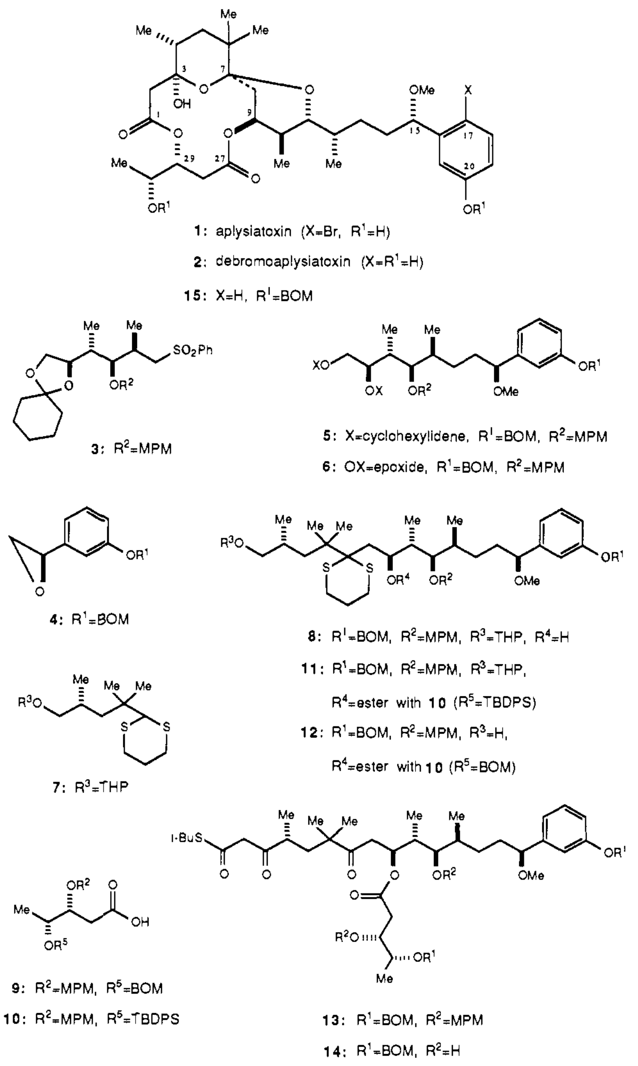
Aplysiatoxin (**1**) and debromoaplysiatoxin (**2**) were first isolated from the digestive gland of the sea hare *Stylocheilus longicauda* by Kato and Scheuer. On the basis of the elegant spectroscopic and chemical degradation studies, they elucidated the gross

**Chart I**



**1**: aplysiatoxin (X=Br, R$^1$=H)

**2**: debromoaplysiatoxin (X=R$^1$=H)

**15**: X=H, R$^1$=BOM

**3**: R$^2$=MPM

**5**: X=cyclohexylidene, R$^1$=BOM, R$^2$=MPM

**6**: OX=epoxide, R$^1$=BOM, R$^2$=MPM

**4**: R$^1$=BOM

**8**: R$^1$=BOM, R$^2$=MPM, R$^3$=THP, R$^4$=H

**11**: R$^1$=BOM, R$^2$=MPM, R$^3$=THP, R$^4$=ester with **10** (R$^5$=TBDPS)

**12**: R$^1$=BOM, R$^2$=MPM, R$^3$=H, R$^4$=ester with **10** (R$^5$=BOM)

**7**: R$^3$=THP

**9**: R$^2$=MPM, R$^5$=BOM

**10**: R$^2$=MPM, R$^5$=TBDPS

**13**: R$^1$=BOM, R$^2$=MPM

**14**: R$^1$=BOM, R$^2$=H

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