Structural characterization of [HxRe3(CO)12]x-3 (x = 2, 3) by extended X-ray absorption fine structure spectroscopy

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The SI unit of conductivity is ampere per volt-meter, $A/(V\ m)$ (i.e., siemens per meter, S/m). If ν is in cm^{-1} units as usual, $\nu\epsilon''(\nu)$ has the unit cm^{-1} and

$$\nu\epsilon''(\nu) = \sigma(\nu)\cdot 0.5996\ [V\ m/A]\cdot cm^{-1}$$

$\nu\epsilon''$ is, thus, the conductivity of the medium at wavenumber ν, apart from a constant, dimensioned, factor.

It is worth noting that this relation is much simpler in the older Gaussian units if σ and the current density, $\mathbf{j}$, are chosen in esu.[43] Then σ has the units s^{-1} and

$$\sigma = f\epsilon''/2 = (c/2)\nu\epsilon''$$

Under the classical damped harmonic oscillator treatment of a liquid (ref 1 and citations therein)

$$\int \nu\epsilon''(\nu)\ d\nu = (N/6c^2)g_j|\partial\mu/\partial Q_j|_{eff}^2$$

$$= (N/6c^2)g_j|\partial\mu/\partial Q_j|^2[(n^2 + 2)/3]^2$$

The integral is over the band due to vibration j of degeneracy g_j, $|\partial\mu/\partial Q_j|_{eff}$ is the effective dipole moment change, and $|\partial\mu/\partial Q_j|$ is the actual dipole moment change during vibration j in the liquid, and $[(n^2 + 2)/3]^2$ is the Lorentz local field. $\mathbf{n}$ is often taken to be the refractive index at very high infrared wavenumber but is more correctly[20] the refractive index that would exist at the wavenumber of the absorption band if the band were absent.

N is the number of molecules per unit volume, i.e., Avogadro's number divided by the molar volume, N_a/V_m. Thus the area under a band in the molar conductivity spectrum, $V_m\nu\epsilon''(\nu)$ vs ν, is given by

$$V_m \int \nu\epsilon''(\nu)\ d\nu = (N_a/6c^2)g_j|\partial\mu/\partial Q_j|_{eff}^2$$

If V_m is in cm^3, the area has the units 10^5 cm/mol, i.e., km/mol, and when multiplied by 0.1487 or 9.96 × 10^{-14} it yields $|\partial\mu/\partial Q_j|_{eff}^2$ in the units (D Å^{-1} amu$^{-1/2}$)^2 or the SI units C^2/kg.

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Structural Characterization of [H$_x$Re$_3$(CO)$_{12}$]$^{x-3}$ (x = 2, 3) by Extended X-ray Absorption Fine Structure Spectroscopy

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Extended X-ray absorption fine structure (EXAFS) measurements on the Re L$_{III}$ edge have been used to elucidate the structures of H$_3$Re$_3$(CO)$_{12}$ and [H$_2$Re$_3$(CO)$_{12}$]$^-$. The data analysis is based on empirically determined EXAFS functions, including that of Os$_3$(CO)$_{12}$, to account for the multiple scattering effects characteristic of metal carbonyls. The results confirm the presence of a triangular Re$_3$ skeleton in each cluster, with the Re–Re bonds in the neutral cluster being of equal length (3.285 Å). The disorder in the Re–Re shell characterizing the anionic cluster indicates that not all the Re–Re bonds are of equal length, which implies the presence of bridging hydride ligands associated with the longer Re–Re bonds. Comparison of the EXAFS data with published X-ray diffraction data characterizing [HRe$_3$(CO)$_{12}$]$^{2-}$ shows a trend of decreasing Re–C distances and increasing C–O distances with increasing negative charge on the cluster, which is explained by π-back-bonding.

Introduction

Extended X-ray absorption fine structure (EXAFS) spectroscopy is a powerful technique for the determination of the structure of solids, but application to metal carbonyls and other compounds incorporating linear arrays of atoms is restricted by the difficulty of accounting for the multiple scattering effects. Here, we demonstrate the use of EXAFS for structural characterization of metal carbonyls, taking advantage of experimental reference compounds to account for the multiple scattering effects.

The crystal structure of H$_3$Re$_3$(CO)$_{12}$ has not been reported; attempts to grow crystals suitable for structural analysis by X-ray diffraction (XRD) have been unsuccessful.[1] A full structural analysis of [H$_2$Re$_3$(CO)$_{12}$]$^-$ is also lacking; only the Re–Re distances are known.[2] We have characterized these clusters structurally by EXAFS spectroscopy.

EXAFS measurements were performed on the Re L$_{III}$ edge, providing information about the coordination environment of the Re atoms in the clusters. EXAFS analysis of compounds such as metal carbonyls, in which the metal is in an almost linear array with the C and O atoms of the carbonyl ligands, presents difficulties because the multiple scattering effect is prominent.[3] The analysis calls for a reference (theoretical or experimental) taking account of the multiple scattering, and the methods are illustrated

by the use of experimental references to analyze the EXAFS spectra characterizing alumina-supported crystallites of Rh with chemisorbed CO[4,5] and alumina-supported triosmium carbonyl clusters.[6] The Os–CO contribution from Os$_3$(CO)$_{12}$[7] in a physical mixture serves very well as a reference, being preferable to theoretical references because the values of the coordination parameters determined with the Os–CO reference are physically more realistic.[8,9] In the present research, we have used the Os–C and Os–O* (O* refers to the carbonyl oxygen) shells from Os$_3$(CO)$_{12}$ as a reference for the Re–C and Re–O* contributions, since no structurally well-defined Re carbonyl compound was available having approximately the same geometry as the com-

(1) Huggins, D. K.; Fellmann, W.; Smith, J. M.; Kaesz, H. D. *J. Am. Chem. Soc.* **1964,** *86,* 4841.
(2) Churchill, M. R.; Bird, P. H.; Kaesz, H. D.; Bau, R.; Fontal, B. *J. Am. Chem. Soc.* **1968,** *90,* 7135.
(3) Teo, B. K. *J. Am. Chem. Soc.* **1981,** *103,* 3990.
(4) Van't Blik, H. F. J.; Van Zon, J. B. A. D.; Koningsberger, D. C.; Prins, R. *J. Mol. Catal.* **1984,** *25,* 379.
(5) Van't Blik, H. F. J.; Van Zon, J. B. A. D.; Huizinga, T.; Vis, J. C.; Koningsberger, D. C.; Prins, R. *J. Am. Chem. Soc.* **1985,** *107,* 3139.
(6) Duivenvoorden, F. B. M.; Koningsberger, D. C.; Uh, Y. S.; Gates, B. C. *J. Am. Chem. Soc.* **1986,** *108,* 6254.
(7) Corey, E. R.; Dahl, L. F. *Inorg. Chem.* **1962,** *1,* 521.
(8) Cook, S. L.; Evans, J.; Greaves, G. N. *J. Chem. Soc., Chem. Commun.* **1983,** 1287.
(9) Binsted, N.; Cook, S. L.; Evans, J.; Greaves, G. N.; Price, R. J. *J. Am. Chem. Soc.* **1987,** *109,* 3669.

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[‡] University of Delaware.

TABLE I: Structural Data for Re Powder,[14] ReO$_3$,[15] and Os$_3$(CO)$_{12}$[7] and Data Ranges Used To Extract Experimental References

sample	shell	N	R, Å	Δk, Å^{-1}	Δr, Å
Re powder	1st Re–Re	12	2.751	3.11–18.33	1.66–3.40
ReO$_3$	1st Re–O	6	1.867	2.54–11.04	0.66–2.08
Os$_3$(CO)$_{12}$^{a}	Os–Os	2	2.88		
	Os–C^b	4	1.95	2.90–12.44	0.88–1.98
	Os–O*^{,b}	4	3.09	2.90–12.44	1.98–3.30

^{a}∠ Os–C–O = 169°. ^{b}After subtraction of the Os–Os contribution: coordination number N = 2, interatomic distance R = 2.88 Å, Debye–Waller factor $\Delta\sigma^2$ = –0.001 Å^2, inner potential correction V_0 = –3.3 eV; and an inner potential correction of V_0 = –4.4 eV on the difference file.

plexes to be analyzed. The use of an Os reference for the analysis of Re data has been justified both theoretically and experimentally.[6,10,11]

The detailed structural characterization with EXAFS affords a comparison of the structures of H$_3$Re$_3$(CO)$_{12}$ and [H$_2$Re$_3$(CO)$_{12}$]$^-$ with that of [HRe$_3$(CO)$_{12}$]$^{2-}$, for which an XRD structure has been determined.[12] The results demonstrate the trends associated with the changing negative charge in the series of clusters.

Experimental Section

H$_3$Re$_3$(CO)$_{12}$ was prepared from Re$_2$(CO)$_{10}$ (Strem) by the method of Huggins et al.[13] [(C$_6$H$_5$)$_4$As][H$_2$Re$_3$(CO)$_{12}$] was prepared by the method of Churchill et al.;[2] the synthesis procedure was slightly modified by the addition of a 50% excess of KOH; the anion was recrystallized from a dry solution of CH$_2$Cl$_2$, ethanol, and pentane.[13] The infrared spectrum of H$_3$Re$_3$(CO)$_{12}$ in cyclohexane and that of [(C$_6$H$_5$)$_4$As][H$_2$Re$_3$(CO)$_{12}$] in acetone agree well with the reported spectra.[1,2]

EXAFS measurements were performed to characterize solid H$_3$Re$_3$(CO)$_{12}$ and [(C$_6$H$_5$)$_4$As][H$_2$Re$_3$(CO)$_{12}$]. Each sample was mixed with inert BN and pressed into a thin self-supporting wafer having optimal X-ray absorbance. Each sample was mounted in a controlled-atmosphere EXAFS cell and characterized in helium at liquid-nitrogen temperature at the Re L$_{III}$ edge (10 535 eV). The measurements were performed on X-ray beam line X-11 (equipped with a Si(111) monochromator, estimated resolution 3 eV) at the Brookhaven National Synchrotron Light Source with a ring energy of 2.48 GeV and a ring current between 40 and 120 mA. The monochromator was detuned to 20% of the primary intensity, in order to reduce the higher harmonics content of the incoming X-ray beam.

As experimental references for the EXAFS data analysis, Os$_3$(CO)$_{12}$[7] (Strem; in a physical mixture with SiO$_2$) and Re metal powder[14] (Aesar; 99.999% pure) were chosen for the Re–CO and Re–Re contributions, respectively. Also ReO$_3$ data[15] (Morton Thiokol) were used in the data analysis procedure. The data characterizing the Re powder and the Re carbonyl clusters were collected on X-ray beam line X-11 at Brookhaven. The data characterizing Os$_3$(CO)$_{12}$ (L$_{III}$ edge: 10 871 eV) and ReO$_3$ were measured on beam line I-5 (equipped with a Si(220) monochromator, estimated resolution 3 eV) at the Stanford Synchrotron Radiation Laboratory with a ring energy of 3 GeV and a ring current between 40 and 80 mA. The gas fillings of the ionization chambers were chosen in such a way that they were made transparent for the higher harmonics in the incoming X-ray beam.

Since different experimental conditions were used for the carbonyl clusters and Re powder, and Os$_3$(CO)$_{12}$ and ReO$_3$, it was possible that a different higher harmonics content for the two sets of measurements might influence the accuracy of the data
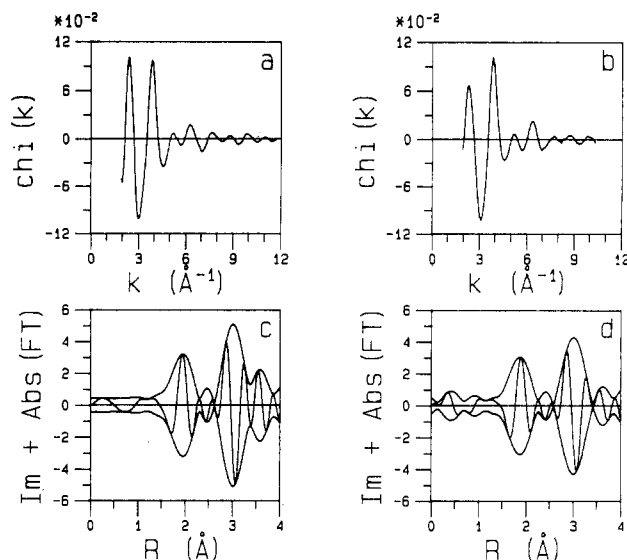

Figure 1. Raw EXAFS data characterizing (a) H$_3$Re$_3$(CO)$_{12}$ and (b) [H$_2$Re$_3$(CO)$_{12}$]$^-$; k^3-weighted Fourier transform (Re–O phase corrected) for (c) the H$_3$Re$_3$(CO)$_{12}$ data (Δk = 3.51–11.14 Å^{-1}) and (d) the [H$_2$-Re$_3$(CO)$_{12}$]$^-$ data (Δk = 3.49–10.23 Å^{-1}).

analysis results. Afterward, we checked this for an Os$_3$(CO)$_{12}$ sample measured both in Brookhaven and in Stanford. No serious differences were observed between the two spectra. Small differences (less than 10% in amplitude) were present, but these could be entirely attributed to a small difference in sample temperature during the measurement (the sample was cooled with liquid nitrogen in different types of dewars). The structural data for Re metal, ReO$_3$, and Os$_3$(CO)$_{12}$ are given in Table I.

Data Analysis and Results

1. Data Reduction. The EXAFS data were obtained from the X-ray absorption spectrum by a cubic spline background subtraction,[16] followed by division by the edge height.[17]

The H$_3$Re$_3$(CO)$_{12}$ data are of very good quality; but the [(C$_6$H$_5$)$_4$As][H$_2$Re$_3$(CO)$_{12}$] data contain an artifact at k > 10.3 Å^{-1}, and the data in this range were not used. The raw data characterizing the two samples are shown in Figure 1, together with their k^3-weighted Fourier transforms.

The data characterizing the reference compounds are all of excellent quality; the raw EXAFS data are shown elsewhere.[6,18]

2. Reference Compounds. In the data analysis procedure, only experimentally determined phases and backscattering amplitudes were used. To obtain these, each particular contribution of interest in the EXAFS data characterizing a reference compound (with accurately known coordination number and coordination distance) had to be isolated from the other contributions; this was done by taking a k^3-weighted Fourier transform (in which the peaks due to the different contributions are separated as well as possible) and then taking an inverse Fourier transform isolating the peak of interest. This straightforward procedure was used to determine a Re–Re reference from the first Re–Re shell in Re powder.[14]

Care was taken to select a good reference for the Re–CO contributions. Structural similarity between the compounds to be analyzed and the reference was a primary criterion. And since the multiple scattering effect in the Re–O* shell is crucial,[6] it was deemed essential to fit with a Re–O reference that exhibits multiple scattering. Os$_3$(CO)$_{12}$ was found to be a good choice: its structure is accurately known,[7] and although no hydrogen is incorporated in the cluster, its structure is otherwise very similar to that proposed for [HRe$_3$(CO)$_{12}$]$^{2-}$;[12] each has a triangular metal skeleton, the same number of CO ligands per metal atom, and the same ratio

(10) Teo, B. K.; Lee, P. A. *J. Am. Chem. Soc.* **1979**, *101*, 2815.

(11) Lengeler, B. *J. Phys. (Les Ulis, Fr.)* **1986**, *47*, 75.

(12) Ciani, G.; D'Alfonso, G.; Freni, M.; Romiti, P.; Sironi, A. *J. Organomet. Chem.* **1978**, *157*, 193.

(13) Kirlin, P. S.; DeThomas, F. A.; Bailey, J. W.; Gold, H. S.; Dybowski, C.; Gates, B. C. *J. Phys. Chem.* **1986**, *90*, 4882.

(14) Wyckoff, R. W. G. *Crystal Structures*; Wiley: New York, 1963; Vol 1, p 11.

(15) Wyckoff, R. W. G. *Crystal Structures*; Wiley: New York, 1964; Vol 2, p 52.

(16) Cook, J. W.; Sayers, D. E. *J. Appl. Phys.* **1981**, *52*, 5024.

(17) Van Zon, J. B. A. D.; Koningsberger, D. C.; Van't Blik, H. F. J.; Sayers, D. E. *J. Chem. Phys.* **1985**, *82*, 5742.

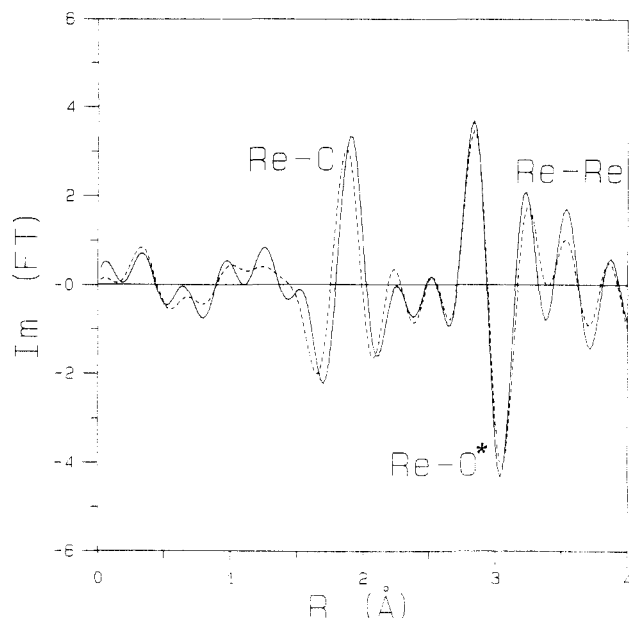(18) Kirlin, P. S.; Van Zon, F. B. M.; Koningsberger, D. C.; Gates, B. C., to be submitted for publication.

Figure 2. Comparison of the imaginary parts of a Re–O phase-corrected k^3-weighted Fourier transform for $H_3Re_3(CO)_{12}$ ($\Delta k = 3.51–10.26$ Å^{-1}) (—) and for $[H_2Re_3(CO)_{12}]^-$ ($\Delta k = 3.49–10.23$ Å^{-1}) (- -).

of axial to equatorial carbonyl ligands. The metal–carbon distances in the two compounds are similar, as are the carbon–oxygen distances. Os is adjacent to Re in the periodic table of the elements, and thus Os components can be used for the analysis of Re spectra, if small changes in V_0 are allowed in the EXAFS data analysis procedure.[6,10,11] In this case, however, a straightforward isolation of the Os–C and Os–O* contributions was not possible because the Os–O* contribution shows overlap with the Os–Os contribution in r space. This Os–Os contribution was first subtracted from the experimental results (as shown elsewhere[6,18]), leaving a spectrum in which the phase of the imaginary part of the Os–O* peak is shifted approximately 180° with respect to the Os–C peak as a consequence of the multiple scattering effect.[3] As shown elsewhere,[6,18] the Os–C and Os–O* peaks seem well separated after a k^3-weighted Fourier transform, and therefore an inverse transform was applied to each in order to determine references for the Re–C and Re–O* contributions.

The first Re–O shell in ReO$_3$[15] was used as a Re–O reference. This reference was not used for fitting of the Re carbonyl spectra, but only to determine Re–O phase-corrected Fourier transforms.

Data ranges used in the extraction of the references and important structural parameters characterizing the reference compounds are given in Table I.

3. Analysis of Data Characterizing $H_3Re_3(CO)_{12}$ and $[H_2$-$Re_3(CO)_{12}]^-$. The data analysis was performed with phase-corrected Fourier transforms. The use of such transforms aids in the attribution of the peaks in r space to shells of the proper neighbors.[6,17] For example, with a Re–Re phase correction, the imaginary part of the Re–Re contribution peaks positively, and with a Re–O phase correction, the imaginary part of the Re–C contribution peaks positively, whereas that of the Re–O* contribution peaks negatively (as a consequence of the multiple scattering effect in the M–O* shell of metal carbonyls[6]).

Re–O phase-corrected Fourier transforms of the data characterizing $H_3Re_3(CO)_{12}$ and $[(C_6H_5)_4As][H_2Re_3(CO)_{12}]$ are shown in Figure 2. It is immediately clear that the two clusters are very much alike in structure, but some differences are apparent: in $[H_2Re_3(CO)_{12}]^-$ the Re–C distance is less and the Re–O* distance is slightly greater than in $H_3Re_3(CO)_{12}$. Both peaks are somewhat smaller in the $[H_2Re_3(CO)_{12}]^-$ spectrum, and the small peak on the right-hand side of the Re–O* peak (partly due to the Re–Re contribution) is much smaller in the spectrum characterizing this cluster.

In further analysis of the EXAFS data, the difference file technique was used.[6,17] First, a Re–C contribution was calculated that agreed as well as possible with the Re–C peak of the data
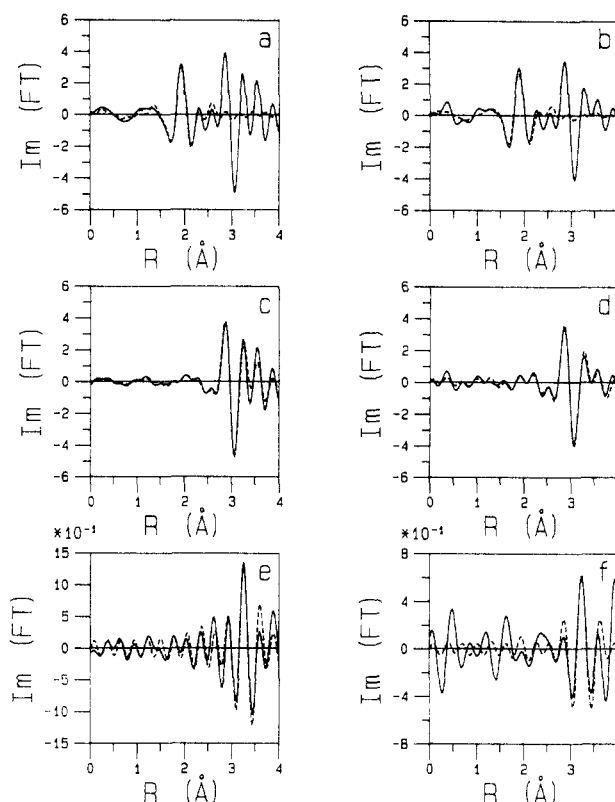

Figure 3. Illustration of subsequent steps in the difference file technique for EXAFS data analysis. Experimental results (—) and best Re–C contribution (- -) for (a) $H_3Re_3(CO)_{12}$ and (b) $[H_2Re_3(CO)_{12}]^-$. Experimental results minus Re–C contribution (—) and best Re–O* contribution (- -) for (c) $H_3Re_3(CO)_{12}$ and (d) $[H_2Re_3(CO)_{12}]^-$. Experimental results minus Re–C and Re–O* contributions (—) and best Re–Re contribution (- -) for (e) $H_3Re_3(CO)_{12}$ and (f) $[H_2Re_3(CO)_{12}]^-$. k^3-Weighted Fourier transforms taken with $\Delta k = 3.51–11.14$ Å^{-1} for (a), (c) (Re–O phase corrected), and (e) (Re–Re phase corrected); k^3-weighted Fourier transforms taken with $\Delta k = 3.49–10.23$ Å^{-1} for (b), (d) (Re–O phase corrected), and (f) (Re–Re phase corrected).

in a Re–O phase-corrected k^3-weighted Fourier transform, with the Re–C coordination number held constant and equal to 4. This contribution was then subtracted from the data, and fitting was done to find coordination parameters for the combined Re–O* + Re–Re peak. As a first guess, a Re–O* contribution was calculated with coordination number (N), disorder ($\Delta\sigma^2$), and inner potential correction (V_0) equal to the values in the Re–C contribution and with a coordination distance that resulted in the best agreement with the imaginary part of the experimental peak in r space. Since as a first approximation no important differences are expected between the CO ligands in the Re and Os carbonyls, N, $\Delta\sigma^2$, and V_0 should be almost equal for the Re–C and Re–O* contributions. After subtraction of this first-guess Re–O* contribution, the best Re–Re parameters were determined. For the Re–Re contribution, the coordination number was held constant and equal to 2. Subsequently, all three contributions were added and compared with the data in k space and in r space after a k^3-weighted Fourier transform.

Usually, such a first cycle in the difference file technique does not yield the best agreement possible, and therefore the previously calculated Re–O* and Re–Re contributions were subtracted from the data, and better parameters were sought for the Re–C shell. This procedure was repeated for each of the contributions until a good overall agreement had been obtained. At this stage the only constraints were (1) that the coordination numbers of the Re–C, Re–O*, and Re–Re shells were fixed at 4, 4, and 2, respectively, and (2) that the inner potential corrections for the Re–C and Re–O* shells were kept equal. The subsequent steps in the difference file technique are shown in Figure 3 for $H_3Re_3(CO)_{12}$ and $[(C_6H_5)_4As][H_2Re_3(CO)_{12}]$. The Re–C, Re–O*, and Re–Re contributions have been calculated with the best parameters. The
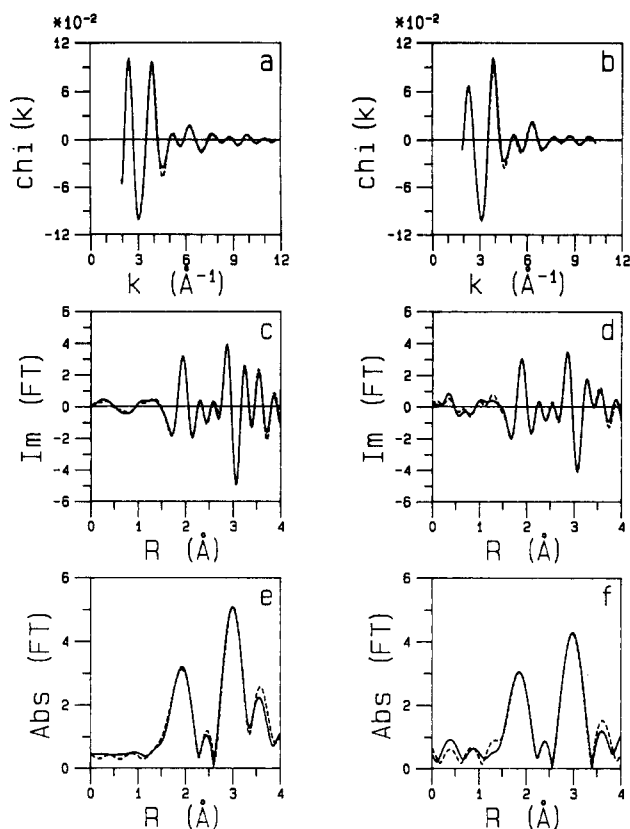
Figure 4. EXAFS analysis results obtained with the best calculated coordination parameters. Experimental results (—) and sum of the calculated Re–C, Re–O*, and Re–Re contributions (--) in k space for (a) H$_3$Re$_3$(CO)$_{12}$ and (b) [H$_2$Re$_3$(CO)$_{12}$]$^-$; imaginary part after k^3-weighted Fourier transform for (c) H$_3$Re$_3$(CO)$_{12}$ and (d) [H$_2$Re$_3$(C-O)$_{12}$]$^-$; magnitude of the k^3-weighted Fourier transform for (e) H$_3$Re$_3$-(CO)$_{12}$ and (f) [H$_2$Re$_3$(CO)$_{12}$]$^-$. Re–O phase-corrected Fourier transforms taken with Δk = 3.51–11.14 Å^{-1} for H$_3$Re$_3$(CO)$_{12}$ and Δk = 3.49–10.23 Å^{-1} for [H$_2$Re$_3$(CO)$_{12}$]$^-$.

TABLE II: Structural Data for H$_3$Re$_3$(CO)$_{12}$ and [(C$_6$H$_5$)$_4$As][H$_2$Re$_3$(CO)$_{12}$] (from EXAFS) and for [Et$_4$N]$_2$[HRe$_3$(CO)$_{12}$] (from XRD[12])

sample	shell[a]	N	R, Å	$\Delta\sigma$, Å^2
H$_3$Re$_3$(CO)$_{12}$	Re–Re	2	3.285	−0.0003
	Re–C	4	1.976	0.0015
	Re–O*	4	3.102	0.0013
[H$_2$Re$_3$(CO)$_{12}$]$^-$	Re–Re	2	3.246	0.0038
	Re–C	4	1.934	0.0024
	Re–O*	4	3.112	0.0018
[HRe$_3$(CO)$_{12}$]$^{2-}$	Re–Re	1.33	3.016	
		0.67	3.125	
	Re–C	4	1.83	
	Re–O*	4	3.07	

[a] For EXAFS results: Re–Re parameters with respect to the first Re–Re shell in Re powder, Re–C parameters with respect to the Os–C shell in Os$_3$(CO)$_{12}$, and Re–O* parameters with respect to the Os–O* shell in Os$_3$(CO)$_{12}$. Accuracies: R ±0.05 Å (Re–Re), ±0.02 Å (Re–C, Re–O*); $\Delta\sigma^2$ ±0.001 Å^2.

final results are shown in Figure 4. The best parameters determined in the analysis are given in Table II.

Discussion

A triangular metal framework has been proposed for each of the clusters H$_3$Re$_3$(CO)$_{12}$ and [H$_2$Re$_3$(CO)$_{12}$]$^-$.[1,2] In the neutral cluster, each of the Re–Re bonds is bridged with a hydride ligand, and in the anionic cluster, two of the three Re–Re bonds are bridged with hydride ligands. The EXAFS results corroborate these models; a nearly linear Re–Re–Re skeleton can be ruled out because in r space no Re–Re peak is observed at ~6.5 Å (data not shown). Such a peak should be prominent because the intermediate Re atom would cause multiple scattering.[3] Models
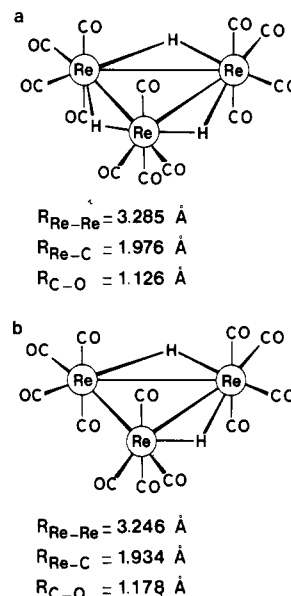

R_{Re-Re} = 3.285 Å
R_{Re-C} = 1.976 Å
R_{C-O} = 1.126 Å

R_{Re-Re} = 3.246 Å
R_{Re-C} = 1.934 Å
R_{C-O} = 1.178 Å

Figure 5. Structural models for (a) H$_3$Re$_3$(CO)$_{12}$ and (b) [H$_2$Re$_3$(C-O)$_{12}$]$^-$. The presence of the bridging H ligands is inferred from chemical arguments only.

TABLE III: Comparison of Re–C and C–O Bond Distances in the [H$_x$Re$_3$(CO)$_{12}$]$^{x-3}$ (x = 1–3) Clusters

sample	Re–C, Å	C–O, Å
H$_3$Re$_3$(CO)$_{12}$	1.976	1.126
[H$_2$Re$_3$(CO)$_{12}$]$^-$	1.934	1.178
[HRe$_3$(CO)$_{12}$]$^{2-}$ [12]	1.83	1.24

for H$_3$Re$_3$(CO)$_{12}$ and [H$_2$Re$_3$(CO)$_{12}$]$^-$ are shown in Figure 5.

The Re–Re distances determined for H$_3$Re$_3$(CO)$_{12}$ and [H$_2$-Re$_3$(CO)$_{12}$]$^-$ are typical of Re–Re bonds.[19] The mean Re–Re distance in H$_3$Re$_3$(CO)$_{12}$ is greater than that in [H$_2$Re$_3$(CO)$_{12}$]$^-$, which is expected because in the neutral cluster all three Re–Re bonds have bridging hydride ligands, and these bridged Re–Re bonds are usually longer than nonbridged Re–Re bonds.[19] Also, the Debye–Waller term (an indication of the disorder in a coordination shell) is larger in the case of the [H$_2$Re$_3$(CO)$_{12}$]$^-$ cluster. This result indicates a range of Re–Re distances rather than a single, well-defined one. However, there is some difference between the mean value for the Re–Re bond in [H$_2$Re$_3$(CO)$_{12}$]$^-$ determined by EXAFS (3.246 ± 0.05 Å) and that determined by XRD (3.13 ± 0.02 Å).[2] Since from the cluster structure no other contributions are expected around R ~ 3.2 Å (the nearest contribution being an interaction between Re and C from the CO ligands on the other Re atoms at R ~ 3.8 Å), this discrepancy cannot be explained by interference with other contributions in the EXAFS spectrum. It must be kept in mind, however, that in calculating the mean bond length from XRD, all Re–Re bonds are weighted equally. (The bridged Re–Re bonds are 3.170 Å and 3.181 Å, and the nonbridged Re–Re bond is 3.035 Å.[2]) In contrast, in determining the mean bond length by EXAFS, the bonds with the smallest $\Delta\sigma^2$ are weighted more heavily. Thus, the larger value of the mean Re–Re bond length determined with EXAFS is consistent with the fact that the hydrogen-bridged Re–Re bonds have a smaller Debye–Waller factor (i.e., are less affected by lattice vibrations) than the nonbridged Re–Re bond.

A comparison of the Re–C and C–O bond distances in the [H$_x$Re$_3$(CO)$_{12}$]$^{x-3}$ (x = 1–3) clusters obtained from EXAFS and XRD (Table III) shows that as the cluster becomes more negatively charged, the Re–C distance decreases and the C–O distance increases. This trend can be explained by increased π-back-bonding in the case of the more negatively charged clusters, because then the Re atoms can donate more electrons to the π^*-orbitals of the CO ligands, thus increasing the Re–C bond

(19) Ciani, G.; Sironi, A.; Albano, V. G. *J. Organomet. Chem.* **1977**, *136*, 339.

strength and decreasing the C–O bond strength.

The high quality of the EXAFS data obtained in this work allows more than a determination of differences in C–O distance with respect to the reference compound; the data also provide information about the differences in the M–C–O angles. As the enhancement of the M–O* contribution is a function of M–C–O angle (the enhancement being stronger when the M–C–O angle approaches 180°[3]), enlargement of the M–C–O angle with respect to the Os–C–O angle in the reference compound $Os_3(CO)_{12}$ is indicated in the EXAFS data analysis by a larger N and/or a smaller $\Delta\sigma^2$ for the M–O* contribution with respect to the M–C contribution. From theoretical calculations[3] it may be concluded that in the case of low-Z scatterers like oxygen, a change in M–C–O angle may well be approximated by a change in $\Delta\sigma^2$ only.

For both the $H_3Re_3(CO)_{12}$ and the $[H_2Re_3(CO)_{12}]^-$ clusters, the Debye–Waller factors characterizing the Re–C and Re–O* shells do not differ beyond the accuracy of ±0.001 Å[2] (Table II). This result implies that the mean Re–C–O angle in these complexes is approximately equal to the Os–C–O angle in $Os_3(CO)_{12}$,

viz. 169°. In the XRD structure determination of $[HRe_3(CO)_{12}]^{2-}$ a mean Re–C–O angle of 169° was found as well.[12] Thus, we infer that there is only very little influence of the overall charge on the cluster (and thus the extent of π-back-bonding) on the Re–C–O angle.

In summary, with the aid of good reference compounds, it is very possible to do a rather complete structure determination of a metal carbonyl with EXAFS. Special attention must be paid to the choice of references for the metal–carbonyl contributions because of the multiple scattering effect.

Ab Initio Computation of Silicon-29 Nuclear Magnetic Resonance Chemical Shifts for a Range of Representative Compounds

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^{29}Si NMR shielding tensors (and the chemical shifts derived therefrom) were calculated for 28 representative silicon compounds, employing optimized molecular structures and a split-valence contracted basis set, both with and without d functions on the silicon, in a gauge-invariant representation. The larger of these two basis sets, 6-31G(*), agreed with experimental chemical-shift data as well or slightly better than did reported computations employing larger basis sets. The following substituent-substitution series of compounds were investigated: SiH_4/SiF_4, $SiH_4/Si(CH_3)_4$, $Si(CH_3)_4/SiF_4$, and part of two series involving the $SiCl_4$ molecule. Since these series of molecules show a wide range of [29]Si chemical shifts, with the shift values plotted for some series exhibiting a pronounced hump rather than a linear form, they represent a good test of the theoretical approach employed. Within these series and within a group of silyl derivatives, the calculated and experimental chemical-shift data agreed quite well. A group of disilicon compounds, $H_3Si-X-SiH_3$ with X = nothing, O, NH, and CH_2, were also studied, as was the SiF_6^{2-} anion and some other structures considered to be exemplifications. The effects on the shielding of rotational isomerization as well as of induced geometrical and electronic changes were investigated for several molecules. The paramagnetic and diamagnetic contributions to the magnetic shielding were analyzed, and an apparent relationship between the [29]Si paramagnetic term and the electron-withdrawing power of the substituents on the silicon was found.

Introduction

Because of a low gyromagnetic ratio, low sensitivity, and meager isotopic abundance, nuclear magnetic resonance (NMR) based on the [29]Si isotope, although available,[1] was not employed by preparative chemists for the characterization and analysis of silicon-containing molecules until after commercialization of the Fourier transform technique for NMR. Now however, ^{29}Si NMR has become a standard tool for use in both inorganic and organic silicon chemistry. Moreover, few preparative chemists today still think of silicon as merely a misbehaving carbon analogue. Hence silicon chemistry is finally beginning to be treated as a field in its own right, so that its typical features, such as (1) the rarity of substituent numbers (i.e., the number of nearest-neighbor bonded atoms) other than four in stable species and (2) the omnipresence of redistribution reactions involving the scission of any bond to silicon other than the Si–C bond, are now being exploited rather than studiously ignored. As a result, silicon chemistry is flourishing, and many new chemical structures of potential practical importance are being found (essentially all with tetracoordinate silicon).

Concomitant with the evolution of experimental silicon chemistry, during the past 15 years there has been a rapid development of practical, nonempirical quantum-chemical techniques for computing molecular properties of interest to experimentalists. These include details of molecular geometry and those physical properties characterizable in terms of the overall electron distribution. Although the parameters that predicate NMR spectra have proven to be a challenge to compute, for both theoretical and computational reasons, advances in these areas now permit these parameters to be obtained to a useful level of accuracy by ab initio methods for several active nuclei.

The work reported here represents the initial application to the [29]Si nucleus of an ab initio self-consistent field (SCF) method using "gauge-invariant" atomic orbitals[2] (the GIAO method). This method,[3,4] which has successfully been applied to a number of

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(1) Holzman, G. R.; Lauterbur, P. C.; Anderson, J. H.; Koth, W. *J. Chem. Phys.* **1956**, *25*, 172. (The first published compilation of [29]Si chemical shifts.)
(2) Jameson, C. J. *Nuclear Magnetic Resonance*, Vol. 12, Royal Society of Chemistry: London, 1983; p 1.
(3) Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789; also described in *J. Chem. Phys.* **1976**, *65*, 3123.
(4) McMichael Rohlfing, C.; Allen, L. C.; Ditchfield, R. *Chem. Phys.* **1981**, *63*, 185.