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Communications

Characterization of a Silica-Supported Trinuclear Osmium Carbonyl Cluster by Magic-Angle-Spinning Carbon-13 NMR Spectroscopy

Sir:

In recent years, there has been great interest in the use of transition-metal carbonyl clusters to prepare highly dispersed metal particles on oxide supports.[1-4] In addition to providing a route to novel catalysts, these supported clusters may also afford relatively well-defined surface structures. Definitive assignments have proven elusive, however, even within the application of such techniques as extended X-ray absorption fine structure (EXAFS) spectroscopy[5,6] and magic-angle-spinning nuclear magnetic resonance (MAS NMR) spectroscopy.[7] In this communication we show for the first time that it is possible to obtain highly resolved (line widths <2 ppm) ^{13}C NMR spectra of a supported transition-metal carbonyl cluster through the use of high-field operation as well as magic-angle spinning.

Impregnation of silica or alumina with a solution of $Os_3(CO)_{12}$, followed by thermal activation at 100–150 °C, apparently produces a single, strongly bound cluster believed to have one of the structures **1**–**3**.[8] It has not been possible to distinguish unambiguously between these possibilities using IR data in the carbonyl stretch region[8-11] or EXAFS data.[5,6,10,11] Although structure **1** has been most widely accepted, on the basis of gas evolution measurements,[8] both **2**[5] and **3**[12] have also been suggested to be the correct structure. We show below that the three possibilities can be distinguished readily by ^{13}C NMR analysis, which provides incisive spectroscopic evidence in support of structure **1**.

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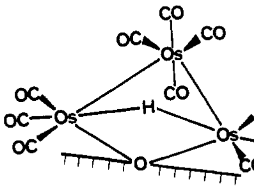

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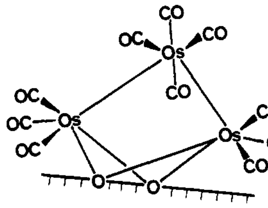

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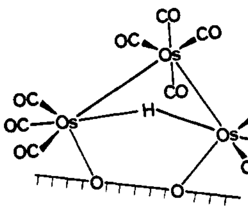

Figure 1 shows the ^{13}C MAS NMR spectrum of an $Os_3(CO)_{12}/SiO_2$ sample (ca. 100 mg, 2.5 wt % Os as prepared), which was generated as previously described,[10] by mixing $Os_3(CO)_{12}$ (ca. 60% ^{13}CO) and fully hydroxylated SiO_2 (Cab-O-Sil, M5, surface area 200 m^2/g, dried 24 h at 120 °C) in boiling *n*-octane under Ar. Although the loading of this sample was higher than that commonly used (ca. 1 wt % Os) for IR or EXAFS studies, we also have obtained spectra at loadings as low as 1.6% and observed no significant differences. These spectra were obtained on a homebuilt spectrometer operating at a frequency of 90.5 MHz for ^{13}C, using high-power proton decoupling. At this high field, magic-angle spinning at the 3-5-kHz speeds attainable for large (7-mm-o.d.) samples is insufficient to completely average the large chemical shift anisotropy (CSA) of the carbonyl ligand,[13] so that we observe an array of spinning sidebands, located at multiples of the spinning frequency on both sides of the isotropic chemical shifts (δ_i).[14] Since the relative intensities of the spinning sidebands are related to the principal components of the chemical shift tensor,[15] the spectrum of Figure 1 yields not only δ_i but also the chemical shift anisotropy for each site. We obtain anisotropy

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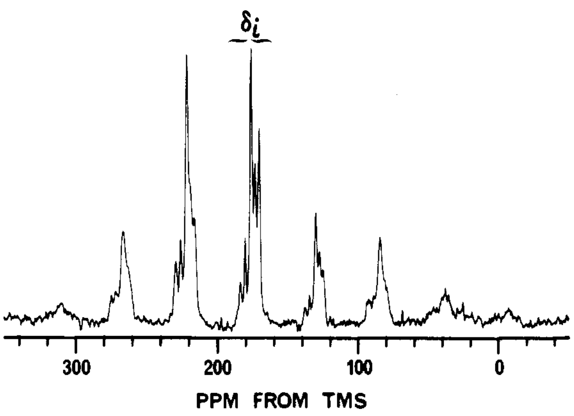


Figure 1. 90.5-MHz ^{13}C MAS NMR spectrum of $Os_3(^{13}CO)_{12}/SiO_2$ obtained with high-power proton decoupling [4.1-kHz spinning speed, 9320 acquisitions with a 5-s recycle time (δ_i indicates the center-band resonances)].

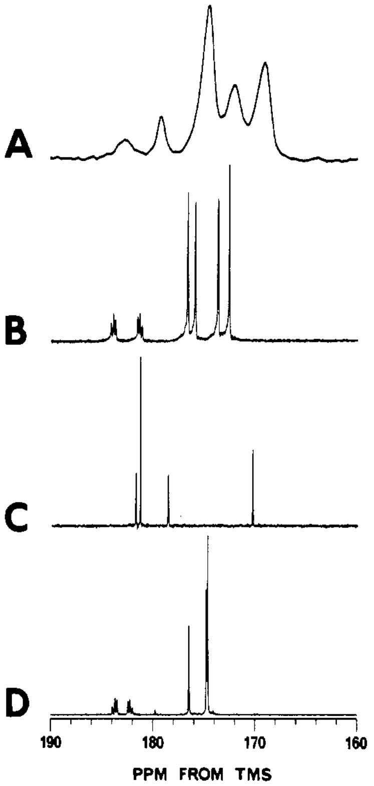


Figure 2. (A) Expanded view of center-band resonances from Figure 1. (B) 75-MHz ^{13}C NMR spectrum (proton decoupled) of $HOs_3(^{13}CO)_{10}[OSi(C_2H_5)_3]$. (C) Spectrum of $Os_3(^{13}CO)_{10}(OCH_3)_2$ in CD_2Cl_2. (D) Spectrum of $HOs_3(^{13}CO)_{10}(O_2CH)$ in CD_2Cl_2.

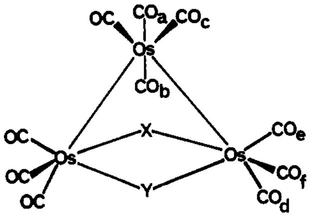
parameters that range from 150 to 250 ppm for the individual resonances. These are smaller by about a factor of 2 than the value of 350 ppm measured for polycrystalline $Os_3(CO)_{12}$,[13] which is rigid on the NMR time scale. This indicates that the chemisorbed cluster is undergoing restricted motion on the silica surface, resulting in partial reduction of the CSA.[16] The nature of this motion is currently under investigation.

The center band of Figure 1 shows considerable fine structure, as shown in an expanded view in Figure 2A, although the breadth of the resonances (ca. 175-Hz full width at half-height) produces some spectral overlap. These large line widths, which are approximately 1 order of magnitude greater than those found for pure polycrystalline metal carbonyl complexes, are likely due to heterogeneity in the microenvironment of the chemisorbed cluster. In Figure 2B–D we show for comparison 75-MHz solution ^{13}C NMR spectra (proton-decoupled) of ca. 50% ^{13}CO-enriched $HOs_3(CO)_{10}(OSiEt_3)$ (**4**), $Os_3(CO)_{10}(OCH_3)_2$ (**5**), and $HOs_3(CO)_{10}(O_2CH)$ (**6**), which are models for surface structures **1**, **2**, and **3**, respectively. In all cases the NMR spectra are consistent with the known structures of these compounds,[17-19] although only partial peak assignments can be made. The two high-frequency peaks observed for **4** and **6**, both of which have C_s symmetry, can be assigned to sites a and b on the basis of their relative intensities[20] and the large $^2J_{CC}$ coupling characteristic of carbonyls that are trans across a metal atom.[21] The other resonance that can be assigned is that due to site d, which, being trans to the hydride ligand, exhibits a large $^2J_{CH}$ coupling in the absence of proton decoupling.[22] Because no J coupling is observed for **5**, which has C_{2v} symmetry, the only assignment that can be made is that the resonance of intensity 4 must be attributed to sites d and e, which are equivalent in this case. It is clear that the spectrum observed for $Os_3(CO)_{12}/SiO_2$ is most similar to that of **4**, and is distinctly different from that of the other two derivatives. Although the chemical shifts of the supported cluster differ by an average of 1.4 ppm from those of **4**, this appears to be well within the normal range of variation observed among $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OX})$ derivatives.[20] Thus these ^{13}C NMR results fully support the as-

Table I. ^{13}C NMR Parameters of Surface and Model Species

complex	δ	rel intens	assgnt	coupling const/Hz
$Os_3(CO)_{12}/SiO_2$	182.6	1	*a*, *b*	
	179.2	1	*a*, *b*	
	174.4	4	*c*–*f*	
	172.0	2	*c*–*f*	
	169.0	2	*c*–*f*	
$HOs_3(CO)_{10}(OSiEt_3)^a$	183.3	1	*a*, *b*	33[c]
	180.5	1	*a*, *b*	33[c]
	175.9	2	*c*, *e*, *f*	
	175.2	2	*c*, *e*, *f*	
	173.0	2	*d*	13.6[d]
	172.1	2	*c*, *e*, *f*	
$Os_3(CO)_{10}(OCH_3)_2^b$	181.6	2	*a*, *c*, *f*	
	181.2	4	*d*	
	178.5	2	*a*, *c*, *f*	
	170.2	2	*a*, *c*, *f*	
$HOs_3(CO)_{10}(O_2CH)^b$	183.6	1	*a*, *b*	33[c]
	182.2	1	*a*, *b*	33[c]
	176.4	2	*c*, *e*, *f*	
	174.7	2	*c*, *e*, *f*	3.9[d]
	174.61	2	*c*, *e*, *f*	
	174.58	2	*d*	13.8[d]

[a] In $CDCl_3$. [b] In CD_2Cl_2. [c] $^2J_{CC}$. [d] $^2J_{CH}$.



(**4**) X = H; Y = OSiEt$_3$
(**5**) X = Y = OCH$_3$
(**6**) X = H; Y = O$_2$CH

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signment of the chemisorbed cluster to structure **1**.

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Registry No. $Os_3(CO)_{12}$, 15696-40-9; silica, 7631-86-9.

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Electrochemical Redox Behavior of the Mononuclear Rhenium Heptahydride Complexes $ReH_7(PR_3)_2$: Evidence for the η^2-H_2 Ligand in This Class of Complex

Sir:

The question of the formulation of transition-metal hydrides as molecular hydrogen complexes ($M(\eta^2\text{-}H_2)$) or "classical" hydrides (H–M–H) has generated much interest and many important discoveries[1,2] since the isolation and structural characterization of the first molecular hydrogen complex by Kubas et al.[3] However, in spite of the existence of an extensive array of non-organometallic mixed polyhydride–phosphine complexes of rhenium,[4] which are perhaps of a greater variety than for any other transition metal, the possibility that some of these might be formulated as containing the η^2-H_2 ligand has scarcely been addressed. The one very important exception is the study of $ReH_7(PPh_3)_2$ by Crabtree,[2] in which convincing evidence has been provided (via ^1H NMR spectroscopy) for its formulation as $Re(H_2)H_5(PPh_3)_2$. In contrast, the species $[ReH_8(PPh_3)]^-$ and $ReH_5(PPh_3)_3$ can be regarded as classical polyhydrides.[2] Upon examining the electrochemical properties of several complexes of the type $ReH_7(PR_3)_2$, we find evidence that they can all be formulated as $Re(H_2)H_5(PR_3)_2$. Furthermore, we believe that the electrochemical properties of such polyhydrides can, in certain instances, provide a quick and easy means of pointing to the presence of the η^2–H_2 ligand.

In an earlier report[5] we described the cyclic voltammetric (CV) properties of the complexes $ReH_5(PPh_3)_2L$ (L = PPh_3, PEt_2Ph, pyridine, piperidine, cyclohexylamine). Solutions of these complexes in 0.2 M TBAH–CH_2Cl_2 were found to exhibit an oxidation in the potential range +0.10–0.40 V vs SCE, with a coupled reduction wave ($E_{p,a} - E_{p,c} \simeq 70$–$140$ mV, $i_{p,c}/i_{p,a} < 1$). Bulk electrolysis at a potential of +0.60 V led to decomposition of the complexes. A more recent reinvestigation of such systems in our laboratory has focused on the electrochemical properties of the complexes $ReH_5(PPh_3)_3$, $ReH_5(PMe_2Ph)_3$, $ReH_5(PMePh_2)_3$, and $ReH_5(PCyPh_2)_3$ (Cy = cyclohexyl).[6-9] A single-scan CV of $ReH_5(PPh_3)_3$ in 0.1 M TBAH–CH_2Cl_2 is shown in Figure 1a[10,11] and reveals that there are two oxidation processes ($E_{p,a}$ = +0.35 and +1.0 V vs Ag/AgCl), the first of which possesses a coupled reduction wave at $E_{p,c}$ = +0.22 V vs Ag/AgCl. The process at

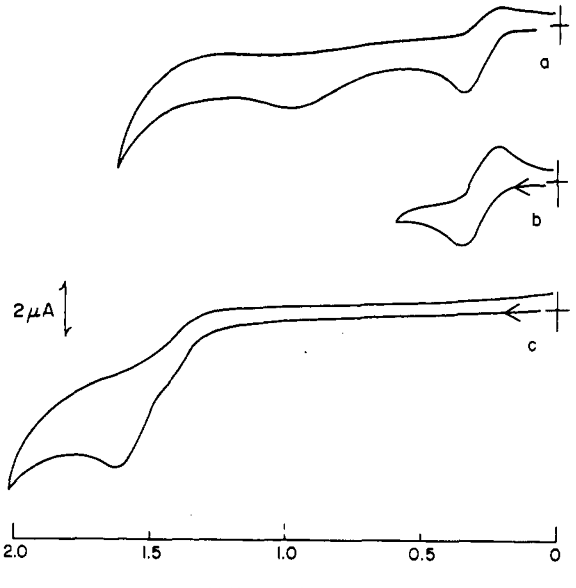

Figure 1. Single-scan cyclic voltammograms in 0.1 M TBAH–CH_2Cl_2: (a) $ReH_5(PPh_3)_3$ with a switching potential of +1.6 V; (b) $ReH_5(PPh_3)_3$ with a switching potential of +0.6 V; (c) $ReH_5(PPh_3)_3$ following bulk electrolysis at +0.5 V. All measurements are at a scan rate of 200 mV s^{-1}.

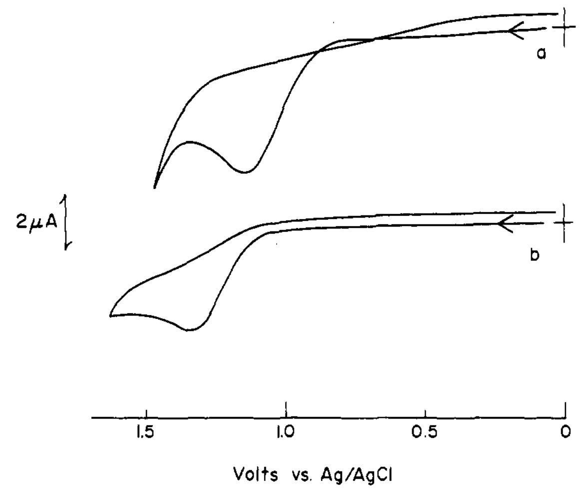

Figure 2. Single-scan cyclic voltammograms in 0.1 M TBAH–CH_2Cl_2: (a) $ReH_7(PPh_3)_2$; (b) PPh_3. All measurements are at a scan rate of 200 mV s^{-1}.

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(6) These complexes were prepared by the usual methods[7-9] and their ^1H NMR and IR spectral properties found to be in agreement with literature data.[7-9] A sample of $ReH_5(PCyPh_2)_3$, which has not been reported before, was obtained as a product in the reaction of $ReOCl_3(PCyPh_2)_2$ with $NaBH_4$ in ethanol: yield 17%; IR (Nujol) 2388 (vw), 2294 (m–w), 2226 (w) cm^{-1}; ^1H NMR (CD_2Cl_2) δ −6.44 [quartet, J(P–H) = 18 Hz, Re–*H*]; $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ +35.8 (singlet).

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