

Figure 1. Molecular structure of $[\text{Pt}(\eta^3\text{-CH}_2\text{CMeCH}_2)(\text{PPh}_3)(\text{CH}_2=\text{CHPh})]\text{PF}_6$ (**1c**).¹⁰ Atoms are represented by thermal ellipsoids at the 30% probability level. Selected bond lengths (Å) and bond angles (deg) not cited in the text are Pt-P = 2.309 (3), C(1)-C(2) = 1.341 (17), C(2)-C(3) = 1.512 (17), C(12)-C(14) = 1.535 (21); P-Pt-C(1) = 88.2 (3), C(1)-Pt-C(2) = 34.6 (4), C(2)-Pt-C(13) = 79.8 (5).

tropically by the block-diagonal least-squares procedure to $R = 0.053$ for 4919 reflections ($|F_o| > 3\sigma(|F_o|)$).⁹

The molecular structure of **1c** is shown in Figure 1. The internal geometry of the η^3 -allyl ligand and its mode of coordination to Pt^{II} seem to be normal when compared to those¹² in other η^3 -allyl(phosphine) complexes of Pt(II) and Pd(II). Very remarkable is nearly in-plane coordination of the C=C bond with the phenyl substituent on the same side as that of the allyl methyl with respect to the coordination plane. The angle between the C=C axis and the approximate coordination plane, defined by the Pt, P, and the center of gravity of the allyl triangle, is only 10.0° (the corresponding angle in **2** is ca. 90°) with C(2) being displaced farther from the plane (0.32 Å) than C(1) (0.08 Å). The intrinsically small bite angle of the bidentate ligand (η^3 -allyl) and the smaller angle of C(11)-Pt-P [92.1 (4)°] than usual C(allyl)-metal-cis-ligand angles appear to help make enough room for the in-plane coordination of the styrene in **1c**, even though both Pt-C(olefin) lengths [Pt-C(1) = 2.203 (12) Å, Pt-C(2) = 2.301 (12) Å] are somewhat longer than those in other styrene complexes of Pt(II) [2.16-2.19 and 2.20-2.24 Å, respectively].¹³

¹H NMR data^{4a,14} of **1c**, when compared with those^{5,14} of **2**, seem to be consistent with preservation of the in-plane configuration or one close to it even in solutions.¹⁵ Thus, in **2** the resonances due to H^{gem} and H^{tr}, located close to PPh₃, receive

considerable upfield shifts due to the magnetic anisotropy of the P-phenyl rings and exhibit ³¹P couplings, while in **1c** it is the H^{tr} and H^{cis} resonances that receive such anisotropy and exhibit ³¹P couplings. It should be pointed out that placing the styrene ligand in **1c** perpendicular to the coordination plane with the phenyl substituent on the allyl side, just as in **2**, requires no severe steric constraint.¹⁶

We presume that behind this contrast between the structures of **1c** and **2** are electronic demands of the ancillary hydrocarbon ligands. The nature of the metal atom seems less important in this argument, for ¹H NMR evidence unambiguously indicated⁵ the upright coordination of ethylene in $[\text{Pt}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{CH}_2=\text{CH}_2)]\text{ClO}_4$ (**3**). The role of the Cp ligand, a six-electron donor, in stabilizing the upright coordination of the olefin in **2** and **3** has already been pointed out.^{5,6} The structure of **1c** determined might be a manifestation of the notion,^{2,4c} in those complexes that lack severe steric constraints around the olefin, that the d π orbital used for π back-bonding in the in-plane coordination in square-planar complexes is slightly higher than that in the upright one. Or it is also possible that the lowest filled MO (π type) of the allyl ligand extending to the central carbon raised the in-plane d π orbital effectively, which is pointing near to this carbon.

The square-planar metal complexes simultaneously containing the η^3 -allyl and olefin ligands have often been regarded as key intermediates in various metal-catalyzed synthetic reactions.¹⁷ The results described above may thus be useful in planning and explaining the steric outcome of such synthetic reactions.

Registry No. **1c**, 79730-88-4.

Supplementary Material Available: Table of fractional atomic coordinates and anisotropic thermal parameters for **1c** (1 page). Ordering information is given on any current masthead page.

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Observation of High-Resolution Oxygen-17 NMR Spectra of Inorganic Solids

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Oxygen is the most abundant element on earth, comprising over 60% of the atoms in the earth's crust, and is thus of considerable geological interest. We report in this communication the first observation of high-resolution oxygen-17 nuclear magnetic resonance spectra of several oxides and oxyanions, obtained at 11.7 T by using the techniques of magic-angle sample spinning (MASS^{1,2}) and variable-angle sample spinning (VASS^{3,4}) NMR

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(11) Bond lengths (Å): C(11)-C(12) = 1.449 (19); C(12)-C(13) = 1.380 (19); Pt-C(11) = 2.175 (13); Pt-C(12) = 2.196 (14); Pt-C(13) = 2.226 (14). Bond angles (deg): C(11)-C(12)-C(13) = 116.4 (12); C(11)-Pt-C(13) = 66.3 (5). The dihedral angle between the approximate coordination plane (see below) and the η^3 -allyl plane is 115.5°, and C(14) is displaced from the latter plane toward Pt by 0.34 Å.

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(14) The coordination shifts ($\delta_{\text{free}} - \delta_{\text{complex}}$) for H^{gem}, H^{tr}, and H^{cis} (with respect to Ph) of styrene are as follows: **1c**, 0.17, 1.41, 1.49 ppm; **2**, 1.46, 1.97, 0.15 ppm. J_p values (Hz) are as follows: **1c**, 3.0 (H^{tr}), 7.2 (H^{cis}); **2**, 3.0 (H^{gem}), 2.6 (H^{tr}).

(15) The following discussion is valid for the NMR data due to the major diastereoisomer^{4a} in solutions. The olefinic proton resonances due to the minor isomer could not be resolved well.

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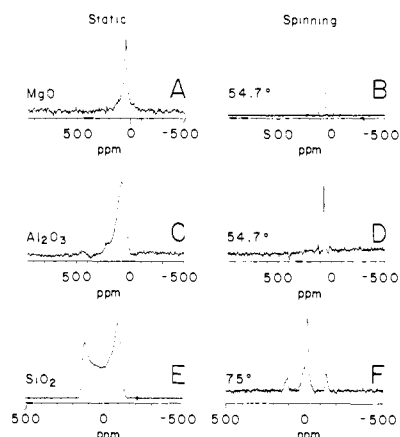


Figure 1. Static and spinning oxygen-17 Fourier transform NMR spectra of several oxides at 11.7 T (corresponding to an ^{17}O Larmor frequency of 67.8 MHz): (A) static MgO, 39 scans, recycle time = 10 s; (B) MASS MgO at 4.5 kHz, 12 scans, recycle time = 30 s; (C) static Al_2O_3 , 1350 scans, recycle time = 30 s; (D) MASS Al_2O_3 at 3.4 kHz, 195 scans, recycle time = 30 s; (E) static SiO_2 , 10 scans, recycle time = 120 s; (F) VASS SiO_2 ($\theta = 75^\circ$) at 4.1 kHz, 47 scans, recycle time = 60 s. Values of between 10- and 100-Hz exponential line broadening were used to improve spectral signal-to-noise ratios. The scale is referenced to an external sample of tap water.

spectroscopy. The results indicate considerable potential for these methods in structural analyses of inorganic solids.

We show in Figure 1 static and 4.5-kHz MASS NMR spectra of MgO, enriched with ^{17}O .⁵ MgO crystallizes in the rock salt structure and has O^{2-} ions in high symmetry environments.⁶ As a result, at 11.7 T the (67.8 MHz) ^{17}O NMR spectrum of a static sample consists of a narrow absorption (Figure 1A) broadened primarily by weak quadrupolar and dipolar (^{17}O - ^{17}O and ^{25}Mg - ^{17}O) interactions. On rapid magic-angle spinning, an extremely narrow resonance at 46 ± 1 ppm relative to liquid H_2^{17}O is obtained (Figure 1B). This resonance is the narrowest ^{17}O absorption we have observed in solids, being even narrower than that of liquid H_2^{17}O ,⁷ and is much better resolved than that reported in 1963 at ≈ 70 ppm relative to H_2^{17}O .⁸ Such narrow oxide absorptions are likely to be rare, and a more typical result is shown in Figure 1C and D. Here, we show static and 3.4-kHz MASS NMR spectra of α - Al_2O_3 , enriched in ^{17}O basically as in ref 5. Previous dynamic polarization studies of ruby (Al_2O_3 ; Cr^{3+})⁹ have indicated an electric quadrupole coupling constant (e^2qQ/h) and asymmetry parameter (η) of 2.167 MHz and 0.517, for α - Al_2O_3 . If this is correct, then the observed relatively narrow resonance in Figure 1C must arise solely from the $1/2, -1/2$ transition.² The observed line shape is not that expected for a second-order quadrupole interaction, which strongly suggests a dominant effect of ^{27}Al - ^{17}O (and ^{17}O - ^{17}O) dipolar interactions on line broadening, as observed previously with the ^{27}Al nuclei in α - Al_2O_3 .² As a result of a small second-order quadrupolar broadening, a conventional MASS NMR experiment is therefore successful in yielding a high-resolution spectrum (Figure 1D) since the dominant dipolar interactions are averaged under magic-angle rotation.¹ The oxide chemical shift is 66 ± 2 ppm relative to water.

By contrast to the relatively narrow ^{17}O spectra of the essentially ionic oxides MgO and α - Al_2O_3 , the static spectrum of Si^{17}O_2 , prepared as in ref 10, is very broad (Figure 1E) and exhibits a well-resolved second-order quadrupolar powder pattern line

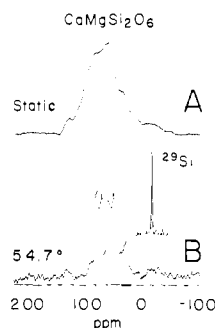


Figure 2. 67.8-MHz ^{17}O Fourier transform (A) static and (B) MASS NMR spectra of diopside ($\text{CaMgSi}_2\text{O}_6$). Static spectrum was obtained with 496 scans and an exponential line broadening of 100 Hz. The spinning spectrum was obtained at a spinning rate of 4.7 kHz, 45 scans, and 50-Hz exponential line broadening. A recycle time of 120 s with 90° ($7.0 \mu\text{s}$) pulse excitation was used for both spectra. The inset shows a 71.5-MHz ^{29}Si spectrum of diopside, for comparison. The scale is referenced to an external sample of tap water.

shape²⁻⁴ characterized by $e^2qQ/h = 5.8 \pm 0.5$ MHz and $\eta = 0 \pm 0.05$, in good agreement with recent results of Bray and co-workers.¹¹ Because the second-order quadrupole interaction dominates the line shape, VASS NMR (at $\theta = 75^\circ$ since $\eta = 0^3$) is the method of choice for NMR line narrowing, as shown in Figure 1F.

We have also investigated the possible utility of high-field solid-state ^{17}O NMR spectroscopy in investigating the structures of a variety of oxyanions. The results of Figure 2A and B were obtained on the ^{17}O -enriched¹² pyroxene diopside ($\text{CaMgSi}_2\text{O}_6$), which contains single chains of SiO_3 silicate tetrahedra. There are two nonbridging and one bridging oxygens per silicon. All three oxygens are crystallographically distinct.¹³ The 67.8-MHz ^{17}O NMR spectrum of a stationary sample of diopside is a rather broad resonance (Figure 2A). The overall spectral breadth is considerably less than that of SiO_2 (Figure 1E). On rapid (~ 5 kHz) MASS, there is considerable narrowing of the broad static powder pattern, and what we believe are three ^{17}O resonances are observed (Figure 2B). The peaks indicated do not originate from spinning side bands, and our tentative assignment of the observed features is that the two narrow doublets arise from the two nonbridging oxygens, and the high-field feature arises from the bridging oxygen. The structure on the two narrow doublets arises from partially averaged second-order quadrupole interactions,³ corresponding to $e^2qQ/h \approx 3$ MHz and $\eta \approx 0.35$. The high-field peak is more difficult to characterize since it is much broader and weaker, but it presumably arises from the single bridging oxygen and has a larger e^2qQ/h value (≈ 4 MHz). These rather preliminary assignments are consistent with our interpretation of the static line shape, together with other results on a variety of neso-, soro-, and phyllosilicates,¹⁴ and if correct, our ^{17}O solid-state NMR results imply a general increase in e^2qQ/h (or covalency) for all oxygens with increase in branching ($Q^0 \rightarrow Q^4$, Figures 1, E and F, and 2, A and B).¹⁴

The results we have presented in this communication clearly indicate that high-field oxygen-17 NMR spectroscopy is a potentially very powerful method for determination of the structures of a wide variety of inorganic oxides and oxyanions. Especially promising appear to be the possibilities of investigating the structures of silicate minerals (and their glasses), where ^{17}O enrichment may be carried out either synthetically or by exchange.¹⁵ For example, in diopside there is only a single ^{29}Si resonance in

(5) MgO was prepared by calcination of ^{17}O -labeled $\text{Mg}(\text{OH})_2$, which was formed on addition of concentrated NH_4OH solution to $\text{Mg}(\text{NO}_3)_2$ in 40% ^{17}O H_2O .

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a silicon MASS NMR experiment (insert in Figure 2B) compared to *three* sets of ^{17}O resonances. This permits, in principle, a far more detailed structural analysis using ^{17}O NMR, since isotropic chemical shifts, chemical shift tensors,¹⁴ electric quadrupole coupling constants, and electric-field gradient tensor asymmetry parameters for *each* nonequivalent oxygen appear to be measurable.

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Registry No. MgO, 1309-48-4; $\alpha\text{-Al}_2\text{O}_3$, 1344-28-1; cristobalite, 14464-46-1; diopside, 14483-19-3; ^{17}O , 13968-48-4.

Metal Formyl Complex via Hydride Transfer from $\text{HRu}(\text{CO})_4^-$: Model for Catalytic Hydrogenation of Carbon Monoxide

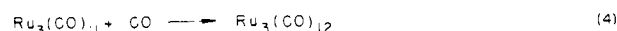
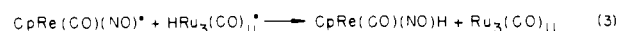
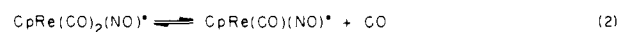
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Catalytic systems for homogeneous hydrogenation of the carbon monoxide molecule have been postulated to proceed through initial formation of a metal formyl complex,^{1,2} although the intramolecular migration of a hydride ligand to coordinated CO has been shown in several complexes to be a difficult process.³⁻⁵ Intermolecular hydride donation from boron hydride reagents has been used as a general synthetic route to metal formyl complexes.⁴ Reactions of early transition-metal hydrides (groups 4A and 5A) with CO or metal carbonyls have also been reported; many of these processes are known or postulated to involve intermolecular hydride transfer to a carbonyl ligand.^{7,8} These reactions, however, require the stoichiometric use of powerful hydride donors that are not readily regenerable in a catalytic process. Here we report the generation of a metal formyl complex by hydride transfer from

Scheme I



a group 8 metal complex, $\text{HRu}(\text{CO})_4^-$, which is plausibly regenerable from H_2 and CO in a catalytic system. We also suggest that this intermolecular hydride-transfer process is a model for the initial activation of carbon monoxide in a catalytic system for CO reduction.

In our study of a soluble iodide-promoted ruthenium catalytic system for CO hydrogenation,⁹ it was noted that catalyst concentration effects and the involvement of two essential catalyst components, $\text{HRu}_3(\text{CO})_{11}^-$ and $\text{Ru}(\text{CO})_3\text{I}_3^-$, indicated the operation of intermolecular processes. Since $\text{HRu}_3(\text{CO})_{11}^-$ is an apparent hydride donor in the presence of CO,¹⁰ a possible catalytic step could comprise transfer of the hydride ion to a carbonyl ligand in $\text{Ru}(\text{CO})_3\text{I}_3^-$ or, more probably, $\text{Ru}(\text{CO})_4\text{I}_2$ derived from the former complex by reaction with CO. This neutral Ru(II) complex contains highly electrophilic carbonyl ligands, as indicated by relatively high $\nu(\text{CO})$ frequencies.^{11,12} Reduction of a carbonyl ligand in this complex could be initiated by hydride transfer from $\text{HRu}_3(\text{CO})_{11}^-$ or from $\text{HRu}(\text{CO})_4^-$,¹³ a complex expected from fragmentation of the trinuclear hydride cluster under H_2/CO pressure. Reactions of $\text{Ru}(\text{CO})_4\text{I}_2$ with $\text{PPN}[\text{DRu}_3(\text{CO})_{11}]$ and $\text{PPN}[\text{DRu}(\text{CO})_4]$ ($\text{PPN} = \text{bis}(\text{triphenylphosphine})\text{iminium}$) were therefore investigated by ^2H NMR. (This technique was employed because of the possible greater stability of deuterioformyl complexes¹⁴ and the ease in identifying reduction products.) The complexes reacted at an observable rate at -60°C , but there was no evidence of metal formyl production. Only in a more rapid reaction of $\text{Ru}(\text{CO})_4\text{I}_2$ with $\text{LiDB}(\text{CH}_2\text{CH}_3)_3$ was evidence for a highly unstable formyl complex (a short-lived signal at β 13.65) observed. We therefore directed our attention toward reactions of the ruthenium hydride complexes with metal carbonyls such as $\text{Fe}(\text{CO})_5$ ¹⁵ and $[\text{CpRe}(\text{CO})_2(\text{NO})]\text{PF}_6$ ^{16,17} ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$), which are known to form relatively stable formyl complexes upon reaction with boron hydrides. Neither $\text{HRu}(\text{CO})_4^-$ nor $\text{HRu}_3(\text{CO})_{11}^-$ react with $\text{Fe}(\text{CO})_5$ at 25°C over many hours. The rhenium cation, however, is expected to be a better model for $\text{Ru}(\text{CO})_4\text{I}_2$, on the basis of its $\nu(\text{CO})$ frequencies.¹⁸

Reaction of $\text{HRu}_3(\text{CO})_{11}^-$ with $\text{CpRe}(\text{CO})_2(\text{NO})^+$ was complete within minutes under an N_2 atmosphere at 25°C , but a metal formyl complex could not be detected by IR or NMR spectroscopy. The major products were $\text{Ru}_3(\text{CO})_{12}$ and $\text{CpRe}(\text{CO})(\text{NO})\text{H}$.¹⁹ This reaction is *retarded* by an atmosphere of carbon monoxide, requiring several hours for completion; again, a metal formyl species could not be detected. Since hydride donation by $\text{HRu}_3(\text{CO})_{11}^-$ has previously been shown to be greatly accelerated by CO,¹⁰ it appears unlikely that a rhenium formyl complex is formed as an intermediate by hydride transfer in this reaction. (The $\text{CpRe}(\text{CO})(\text{NO})(\text{CHO})$ complex is reported to have a

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