This is a remarkable correlation in view of the differences mentioned above and the fact that the data are from different sources. Also, K_{enol} for the α-aryl-substituted **1** are at 94.6 °C whereas the data for the α-H and the α-Me enols are at 80.6 °C. Nevertheless, we would expect a linear relationship, possibly with a different slope, even if all the data were at the same temperature,[14] but we did not try to correct for this effect since the literature values for system **2** are in the process of minor revision as a result of either better measurements or modification in rate constants used for the calculation.[15]

Although the linearity in Figure 1 may partially result from the fact that the data correlated covers only 2 orders of magnitude in each series,[16] it certainly reflects a proportionality between the substituent effects in both systems. The difference in the solvents used (hexane for compounds **1**, hydrogen-bonding water for compounds **2**) and the partial conjugation of the mesityl groups with the double bond of **1** should increase and decrease, respectively, the sensitivity to a change in the substituent in series **1**. These effects should be reflected in the magnitude of the slope, and we note that for series **3**, where the planarity is presumably higher, the change of R from H to Me reduces K_{enol} more than the parallel change in series **1** and **2**.[17] However, the data available are insufficient for a meaningful analysis of the slope.
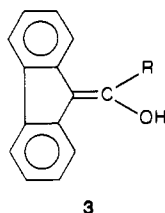
3

The linearity involving the *meta* and *para* aromatic substituents is not surprising since both Hammett correlations for **1** and **2** (R = *meta*- and *para*-substituted aryl) are linear.[6a,9c] However, the more interesting question as to whether steric effects in series **2** are also playing a dominant role as in series **1**[9a,b] cannot be answered since only R = H and Me appear in Figure 1.

Assuming that Figure 1 applies beyond the limited data, we calculated two K_{enol} values for two extreme cases in series **2**. These are given in Table I. For the α-mesityl compound (**2**, R = Mes) the enol is predicted to be relatively stable with a pK_{enol} of 5.4 ± 0.2, whereas the α-*tert*-butyl enol (**2**, R = *t*-Bu) is predicted to be the least stable with a pK_{enol} of 11 ± 0.2 (points A and B in the figure). The latter value is of special interest since MO calculations on series **2** (R = H, alkyl) do not show a large difference in pK_{enol} between **2** (R = Me) and **2** (R = *t*-Bu).[18] A direct measurement should resolve this discrepancy.

(14) This is based on the fact that the main point which determines the slope is that for the H derivative since it is relatively remote from all the other points. Since the enol content in series 1 for R = H at equilibrium is already 95%, even a large change in the equilibrium constants (e.g., to 97% enol) at a different temperature is most likely to be within the experimental error, due to the limitation of NMR integration. Trial shifts of this point indeed still give linear relationships but with different slopes.

(15) For example, a factor of 2 was recently introduced into the calculation of K_{enol} values[6a,b] due to a change in the value of the diffusion-controlled second-order rate constant. The pK_{enol} value for acetophenone has been recently revised from 7.90 to 7.96.[6d] Also, when the previous pK_{enol} value of 6.55 reported by Capon for **2** (R = H)[4b] is used, a linear correlation with a slope of 1.16 still prevails.

(16) The data for each series are more extensive, but the data for common substituents cover only 2 orders of magnitude in K_{enol}.

(17) For **3** (R = H), pK_{enol} = -1.23 (Harcourt, M.; More O'Ferrall, R. A. *J. Chem. Soc., Chem. Commun.* **1987**, 822. For **3** (R = Me), pK_{enol} = 2.3 (Argile, A.; Carey, A. R. E.; Harcourt, M.; Murphy, M. G.; More O'Ferrall, R. A. *Isr. J. Chem.* **1985**, *26*, 303).

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Preparation and Structure of [(Me3CO)3W≡C—Ru(CO)2(Cp)], a Heteronuclear, μ2-Carbide Complex

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Carbon monoxide dissociates to reactive carbide and oxide fragments on many catalytically active metal surfaces. Dissociation is believed to be the first step in the reductive hydrogenation of CO via the Fischer-Tropsch synthesis and related reactions.[1] The remarkable reactivity of these surface carbides is probably due to the fact that they are highly "exposed", with a low coordination number. Most organometallic carbide complexes contain carbon atoms surrounded by at least five metal atoms.[2] However, $[Fe_4C(CO)_{12}]^{2-}$ and related tetranuclear carbide clusters studied by Bradley, Muetterties, and Shriver show high reactivity at the carbide ligand.[3] The chemistry of $[Fe_3(CCO)(CO)_9]^{2-}$ suggests the intermediacy of a very reactive Fe_3C cluster.[4] The sole fully characterized example of a two-coordinate metal carbide complex is $[Fe_2(\mu_2-C)(5,10,15,20\text{-tetraphenylporphyrinate})_2]$.[5-7] A dinuclear bicarbide complex, $[Ta_2(\mu_2-C_2)\{OSi(CMe_3)_3\}_6]$, has recently been reported by Wolczanski and co-workers.[8] We report here the first heterodinuclear complex with a two-coordinate carbide ligand.

Schrock, Chisholm, and their co-workers have shown that tungsten-alkylidyne complexes efficiently catalyze alkyne metathesis according to eq 1.[9,10] In general, the largest alkyne

$$[W(\equiv CR)(OCMe_3)_3] + R^1C\equiv CR^2 \rightarrow$$
$$[W(\equiv CR^1)(OCMe_3)_3] + RC\equiv CR^2 \quad (1)$$
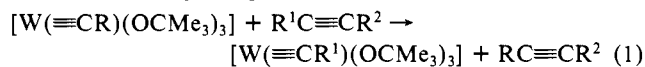
substituent in the system (R^1) remains on the alkylidyne, and the

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most volatile alkyne is eliminated. The reaction of [W($\equiv$ CCH$_2$CH$_3$)(OCMe$_3$)$_3$]^{9,10} (1.70 g, 3.83 mmol) with [Ru(C$\equiv$ CMe)(CO)$_2$(Cp)]^{11} (1.00 g, 3.83 mmol) in *n*-pentane/benzene (5/1) for 24 h at room temperature proceeds with elimination of 2-pentyne (eq 2). Evaporation and subsequent recrystallization

$$[W(\equiv CEt)(OCMe_3)_3] + [M(C\equiv CMe)(CO)_2(Cp)] \rightarrow$$
$$[(Me_3CO)_3W\equiv C-M(CO)_2(Cp)] + MeC\equiv CEt \quad (2)$$
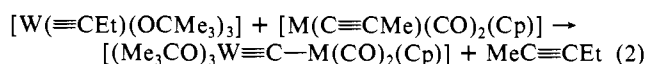
from toluene/pentane (1/10) leads to 1.33 g (54.5%) of [(Me$_3$CO)$_3$W$\equiv$C—Ru(CO)$_2$(Cp)] (1) as yellow, needlelike crystals. Attempts to prepare the congeneric iron–tungsten carbide complex [(Me$_3$CO)$_3$W$\equiv$C—Fe(CO)$_2$(Cp)] by using [Fe(C$\equiv$ CMe)(CO)$_2$(Cp)]^{12} led to mixtures containing [Fe$_2$(CO)$_4$(Cp)$_2$] upon attempted purification. Spectroscopic properties of 1,^{13} including an alkylidyne resonance at 237.3 ppm with $^1J_{CW}$ = 290.1 Hz in its ^{13}C NMR spectrum, support its formulation as a μ_2-carbide complex.$^{2-4}$ The range of reported alkylidyne ^{13}C resonances for [W($\equiv$CR)(OCMe$_3$)$_3$] complexes is 223–292 ppm.^{9,10} In general, electron π-donor substituents such as SCMe$_3$ (222.7 ppm) shift the alkylidyne ^{13}C resonance to higher field, whereas electron-withdrawing substituents such as SiMe$_3$ (292.1 ppm) have the opposite effect, consistent with the strong donor ability of the [Ru(CO)$_2$(Cp)] group. The large W–C coupling constant reflects considerable s-character in the bonding orbitals of the carbide carbon in 1.

The structure of carbide complex 1 was confirmed by a X-ray crystal structure determination (Figure 1).^{14} The most striking structural feature of 1 is the single carbon atom bridging tungsten and ruthenium in a linear fashion. The 1.75 (2) Å tungsten-carbon triple bond length in 1 is comparable to those in related tungsten–alkylidyne complexes [W($\equiv$CPh)(OCMe$_3$)$_3$] (1.758 (5) Å)^{15} and [W($\equiv$CR)(OCMe$_3$)$_3$]$_2$ (R = Me, NMe$_2$, 1.75–1.77 Å).^{16} The Ru–C1 bond length of 2.09 (2) Å is slightly longer than most ruthenium to CO bonds (1.74–2.00 Å)^{17} but falls in the range of other ruthenium-to-carbon σ-bond lengths (e.g., [Ru-(CONH$_2$)(CO)$_2$(Cp)],^{18} d = 2.082 (7) Å and [Ru(C$\equiv$CPh)-(PPh$_3$)$_2$(Cp)],^{17} d = 2.016 (3) Å). The W–C–Ru bond angle is linear, 177 (2)°, consistent with the prediction that the hybridization of surface carbide fragment should be determined solely by the number of metal–carbon bonds.^{7e} The relative conformation of the two metal atoms is anti, i.e., the ligands are "staggered" (Figure 1b). The shortest intramolecular, non-hydrogen atom contact between ligands (excluding the carbide) on tungsten and
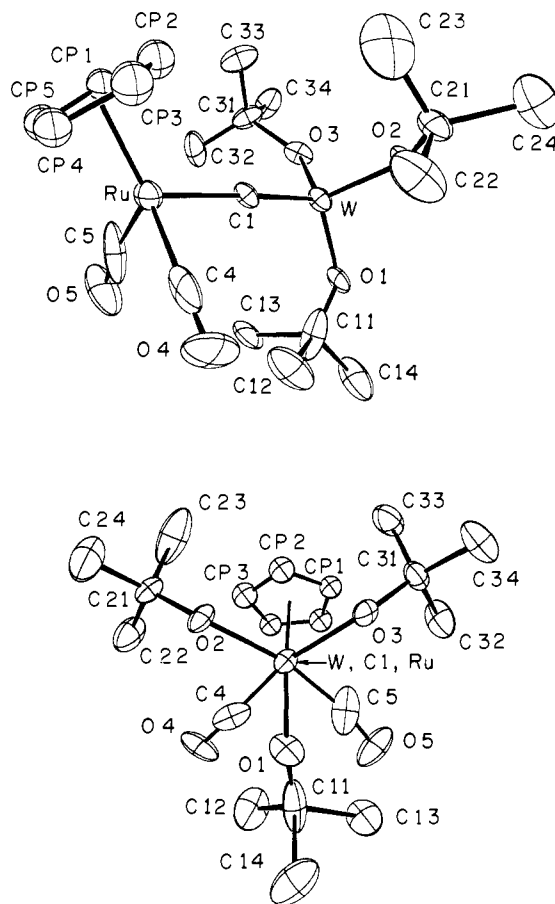

Figure 1. ORTEP^{23} plot of the structure of 1 showing 50% probability ellipsoids. Selected bond distances (Å): W–C1, 1.75 (2); W–O1, 1.80 (2); W–O2, 1.89 (2); W–O3, 1.90 (2); Ru–C1, 2.09 (2); Ru–C4, 1.96 (5); Ru–C5, 2.00 (6); Ru–Cp(centroid), 1.95; C4–O4, 1.12 (5); C5–O5, 1.18 (6). Selected bond angles (deg): W–C1–Ru, 177 (2); C1–W–O1, 113 (1); C1–W–O2; 107 (1); C1–W–O3, 107 (1); O1–W–O2, 108.1 (9); O1–W–O3, 109.6 (9); O2–W–O3, 112.7 (8); C1–Ru–C4 88 (1); C1–Ru–C5 89 (1); C1–Ru–CpO^a, 120; C4–Ru–C5, 95 (2); Ru–C4–O4, 177 (4); Ru–C5–O5, 168 (6).

ruthenium is 3.21 Å between O4 and C12, suggesting that the anti conformation is favored electronically. Related [(μ-Ge)-{Mn(CO)$_2$(C$_5$H$_4$Me)}$_2$] also has an anti conformation, as rationalized by Kostić and Fenske.^{6b,7d}

Reaction 2 is unique in producing a *mono*carbide-bridged dinuclear complex. Related reactions of [W$_2$(OCMe$_3$)$_6$] with *trans*-[Pt(C$\equiv$CH)$_2$(PMe$_2$Ph)$_2$] lead, via Me$_3$COH elimination, to tungsten–platinum complexes with bridging bicarbide ligands.^{19a}

(11) Previously unreported [Ru(C$\equiv$CMe)(CO)$_2$(Cp)] was prepared in 78% yield by the reaction of [Ru(Cl)(CO)$_2$(Cp)]^{20} with Me$_3$SiC$\equiv$CMe and KF in methanol:^{24} IR (pentane, cm^{-1}) 2051 (v (C$\equiv$C)), 1985, 1956 (v (C$\equiv$O)); ^{1}H NMR (CDCl$_3$, 90 MHz) δ 5.40 (s, 5 H, Cp), 2.00 (s, 3 H, Me); MS, 261 (M$^+$), 234 (M$^+$ – CO), 206 (M$^+$ – 2CO). Anal. Calcd for C$_{10}$H$_8$O$_2$Ru: C, 45.95; H, 3.10. Found: C, 45.30; H, 3.31.

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(14) Crystal data for 1: Data were collected on an Enraf-Nonius CAD4 diffractometer by using Mo Kα radiation. Reflections (5108) were measured, and of these 2803 with (F_o)$^2 \geq 3\sigma(F_o)^2$ were used. Space group P1̄, Z = 2, a = 10.981 (3) Å, b = 14.766 (2) Å, c = 9.699 (2) Å, α = 105.70 (1)°, β = 110.32 (2)°, γ = 74.50 (2)°, V = 1393.27 Å^3, ρ_{calcd} = 1.519 g·cm^{-3}, μ = 47.66 cm^{-1}. The tungsten atom was located by using Patterson methods, and the remaining non-hydrogen atoms by using DIRDIF^{21} or difference Fourier methods. The cyclopentadienyl group was refined as a rigid group with individually varied isotropic thermal parameters on carbon atoms and fixed thermal parameters on hydrogen atoms. All other atoms were refined with anisotropic thermal parameters. An empirical absorption correction (CAMEL^{22}) was applied to the data. Full-matrix least-squares refinement led to R = 6.9%, R_w = 9.5%.

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Similarly, [W$_2$(OCMe$_3$)$_6$] reacts with EtC≡C—C≡CEt to give [(Me$_3$CO)$_3$W≡C—C≡W(OCMe$_3$)$_3$] which resembles a μ_2-bicarbide complex.[9]

In summary, we have prepared the first fully characterized heterodinuclear μ_2-carbide complex. We are investigating the reaction chemistry of this complex, which we hope will provide insights into the reactivity of carbides on catalyst surfaces.

Supplementary Material Available: Tables of positional and thermal parameters, bond distances, bond angles, and least-squares planes for the structure of **1** (5 pages); tables of observed and calculated structure factors for the structure of **1** (18 pages). Ordering information is given on any current masthead page.

High-Symmetry, High-Temperature Zeolite Lattice Structures

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Considerable progress has been made in recent years in the investigation of the structures of zeolite catalysts by solid-state high-resolution ^{29}Si MAS NMR techniques.[1] For low Si/Al ratio materials, the spectra give a description of the distribution of Si and Al throughout the lattice, while for completely siliceous analogues the spectra may be related directly to the lattice structures.[2] The effect of removing all of the aluminum from the lattice is to give very narrow resonances in the ^{29}Si MAS NMR spectrum which are all due to Si[4Si] environments and which reflect the number and populations of the crystallographically inequivalent lattice sites in the unit cell. These latter spectra have been used to probe various subtle effects on the lattice structures via the short-range ordering[2] and are a very useful complement in structural investigations to the more conventional powder XRD technique. In the present communication, we describe how these spectra combined with variable-temperature operation can be used to detect the existence of high-symmetry phases for various zeolites at elevated temperatures. It is only with materials of sufficiently high quality such as those investigated that the spectral resolution

ZSM 39

Figure 1. ^{29}Si MAS NMR spectra of zeolite ZSM-39 (79.5 MHz, 500 scans, 7-s delay, and 0-Hz line broadening) at the temperatures indicated. The cubic structure for ZSM-39 is shown also.[3]

is good enough to detect and characterize these phases.

ZSM-39 is a highly siliceous zeolite previously shown to be cubic by powder XRD measurements (Figure 1, inset).[3] However, the authors of the diffraction study pointed out that the existence of a number of very low intensity reflections indicated a deviation from cubic symmetry and termed it "pseudocubic". This was confirmed by ^{29}Si MAS NMR measurements[4] which showed five resonances of relative intensities 1:4:4:4:4 rather than three of 1:4:12 expected for a perfect cubic lattice and indicated that the deviation involved the loss of the 3-fold [1,1,1] axis of symmetry.[4]

Figure 1 shows variable-temperature ^{29}Si MAS NMR spectra for a perfectly crystalline, completely siliceous sample of this material over the temperature range of the phase transition. As the temperature is raised, the resonances all remain narrow but there is a clear change over a very small temperature range to a new spectrum of three peaks whose relative intensities of 1:4:12 clearly indicate cubic symmetry at least on a local basis and on the NMR time scale. The changes are completely reversible and are also shown by less crystalline materials with correspondingly reduced resolution.

Similar increases in lattice symmetry are also shown by ZSM-5[5] and ZSM-11. In the case of ZSM-5, the spectrum changes from a 24-line pattern at room temperature to a pattern of 12 lines (Figure 2A) consistent with a change in symmetry from monoclinic to orthorhombic. In the material studied, all 12 resonances can be detected at different temperatures. Figure 2B shows the limiting high-temperature spectrum (373 K) for a very highly siliceous sample of zeolite ZSM-11 and its resolution into seven Lorentzian peaks of relative intensities, 1:(2 + 2):2:1:2:2, exactly consistent with the postulated lattice structure.[6] The room-temperature spectrum shows more than seven resonances, again consistent with a lower symmetry,[7] and line broadening indicating a distorted lattice.

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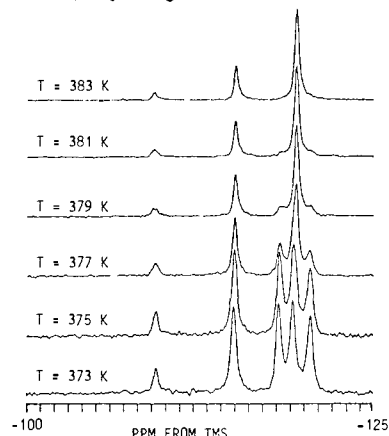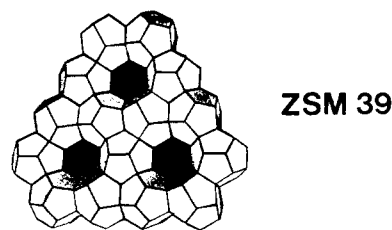
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