Nature of the Metal–Carbon Triple Bond. A Reevaluation of the $M\equiv C$ Stretching Frequency and Force Constant

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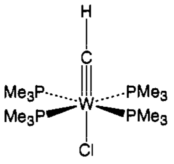
Fischer's landmark discovery of transition-metal alkylidyne complexes two decades ago[1] initiated an extensive research effort that has resulted in the development of a large, diverse class of molecules that exhibit fascinating reaction chemistry.[2] Much of the descriptive chemistry of these species hinges on the attribution of a formal bond order of 3 to the linkage between the alkylidyne ligand (CR) and the metal. This bonding description was initially based on the required valency of the ligated carbon atom[1] and on X-ray crystallographic studies, the latter of which yielded the expected findings of a short M–C bond and a nearly linear M–C–R linkage.[3] Direct evidence for the high multiplicity of the M–C bond order was ultimately provided by the sizable M–C force constant ($k(W\equiv C) = 7.00$–7.40, $k(Cr\equiv C) = 5.18$ mdyn Å^{-1}), which was determined, together with the $M\equiv C$ stretching frequency ($\nu(M\equiv C) = 1300$–1400 cm^{-1}), from an elegant series of vibrational spectroscopic experiments undertaken by Dao, Fischer, and co-workers on the archetypal $M(\equiv CR)(CO)_4X$ (M = Cr, Mo, W; R = Me, Ph; X = anionic ligand) complexes.[4] Although $\nu(M\equiv CR)$ bands with similar frequencies have subsequently been observed for other alkylidyne compounds,[2e,5] an acknowledged complication with the determination of $\nu(M\equiv C)$ and $k(M\equiv C)$ for $M(CR)(CO)_4X$ complexes arises from the vibrational complexity of their R groups; the $M\equiv C$ stretching coordinate is strongly coupled with other symmetry coordinates, especially the MC–C stretch and deformations of the R group, vitiating the $M\equiv C$ diatomic-oscillator character of the mode. Normal-coordinate calculations reveal that the contribution of the $M\equiv C$ symmetry coordinate to the normal mode responsible for the $\nu(M\equiv C)$ band is less than 50%.[4f,k]

Given the importance of these fundamental physical parameters to characterizing the nature of the metal–carbon triple bond, we believed a new determination of $\nu(M\equiv C)$ and $k(M\equiv C)$ was justified in view of the availability of the complex $W(CH)(PMe_3)_4Cl$ (**1**),[6] which is a rare example of a compound that possesses the parent methylidyne ligand.[7] Methylidyne complexes are spectroscopically superior to the previously studied $M(CR)(CO)_4X$ compounds with respect to the identification of $\nu(M\equiv C)$ because the methylidyne ligand will exhibit only two modes (C—H stretching and $M\equiv C$—H bending) in addition to $\nu(M\equiv C)$.[8] Our studies of the Raman spectra of **1** and its isotopomers indicate that the pure $M\equiv C$ stretching frequency and force constant are substantially smaller than the presently accepted values.



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The Raman spectrum of $W(CH)(PMe_3\text{-}d_9)_4Cl$ (**1**-d_{36})[9] is displayed in Figure 1. The bands in this spectrum are clustered in three distinct regions, with ranges of ca. 50–1050, 1950–2250, and 2950–3000 cm^{-1}. Significantly, the featureless 1100–1900 cm^{-1} region includes that region reported by Fischer and Dao as containing the band attributable to $\nu(W\equiv C)$ in the spectra of $W(CR)(CO)_4X$ complexes (1300–1400 cm^{-1}).[4] We assign the strong band at 911 cm^{-1} in the spectrum of **1**-d_{36} as $\nu(W\equiv C)$ and the weak doublet at 2979/2993 cm^{-1} as ν(C–H) of the methylidyne ligand,[10] based on the behavior of these bands upon isotopic substitution. Shown in Figure 2 are the Raman spectra of **1**, **1**-d_{36}, and $W(CD)(PMe_3)_4Cl$ (**1**-d_1)[9] in the region 50–950 cm^{-1}. Substitution of natural abundance PMe_3 for deuterated PMe_3 results in a shift of all of the bands observed in the spectrum of **1**-d_{36} (Figure 1) to higher frequencies, with the exception of the 911 cm^{-1} band and the 2979/2993 cm^{-1} doublet, the latter of which becomes obscured in the spectrum of **1** by bands arising from C–H stretching modes of PMe_3. This behavior indicates that only these three features are associated with the WCH moiety. Deuterium labeling of the methylidyne ligand (**1**-d_1) results

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[8] The only prior reports of vibrational spectra of metal methylidyne compounds have been for matrix-isolated fragments (Chang S.-C.; Hauge, R. H.; Kafafi, Z. H.; Margrave, J. L.; Billups, W. E. *J. Chem. Soc., Chem. Commun.* **1987**, 1682–1684; *J. Am. Chem. Soc.* **1988**, *110*, 7975–7980) whose electronic structures bear little resemblance to those of discrete, isolable alkylidyne complexes (McKee, M. L. *J. Am. Chem. Soc.* **1990**, *112*, 2601–2607. Hamilton, T. P.; Schaefer, H. F., III. *J. Chem. Soc., Chem. Commun.* **1991**, 621–622. Granucci, G.; Persico, M. *J. Mol. Struct.* **1993**, *283*, 111–116).

[9] The compounds **1**-d_{36} and **1**-d_1 were prepared analogously to **1** (ref 6), substituting $PMe_3\text{-}d_9$ and $AlMe_3\text{-}d_9$, respectively, for the natural abundance starting materials. Based on ^{1}H NMR spectroscopy of concentrated solutions, the isotopic purity of **1**-d_{36} is 99.6%, and that of **1**-d_1 is 96.6%. The ^{1}H (where observable), ^{13}C, and ^{31}P NMR chemical shifts for **1**-d_{36} and **1**-d_1 are identical to those reported previously for **1**. ^{2}D NMR (76.8 MHz, C_6H_6) for **1**-d_{36}: δ 1.45 (br, PC*D*). ^{2}D NMR (76.8 Hz, C_6H_6) for **1**-d_1, δ 6.63 (br, WC*D*).

[10] (a) The observation of two ν(C—H) bands is presumably the result of the presence of two crystallographically distinct molecules of **1** in the solid state (ref 10b). The absence of a site splitting of the $\nu(W\equiv C)$ band may reflect the fact that this mode does not involve atoms located at the periphery of the molecule. The infrared spectrum of **1**-d_{36} in benzene solution exhibits a single band at 2979 cm^{-1}. (b) Churchill, M. R.; Rheingold, A. L.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 3392–3399.

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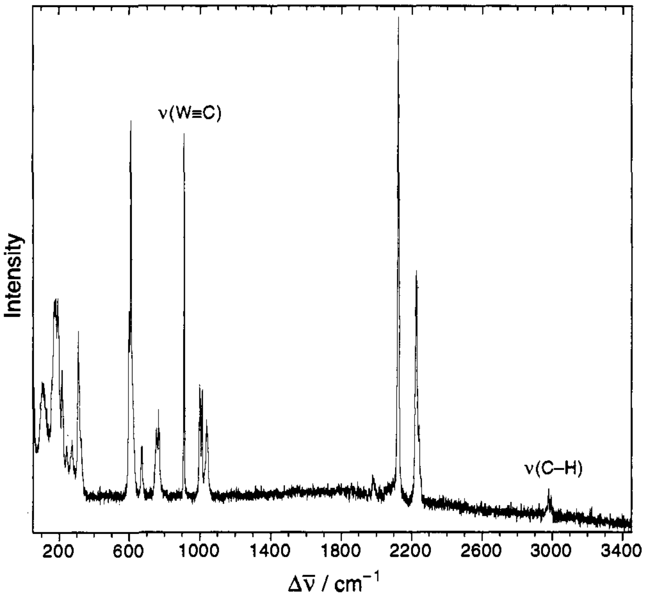

Figure 1. Raman spectrum of microcrystalline **1**-d_{36}, recorded under nonresonant conditions (λ_{ex} = 632.8 nm).

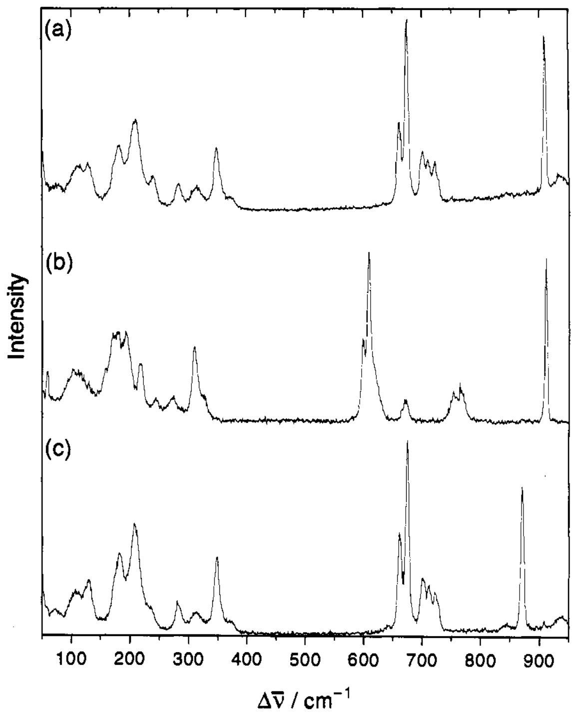

Figure 2. Raman spectra of tungsten methylidyne complexes in the 50–950 cm^{-1} region: (a) **1**; (b) **1**-d_{36}; (c) **1**-d_1.

in a spectrum identical to that of **1** save the 911 and 2979/2993 cm^{-1} features, which are shifted to 871 and 2235/2244 cm^{-1}, respectively. The 40 cm^{-1} shift of the ν(W≡C) band upon methylidyne deuteration is close to the value of 31 cm^{-1} predicted by allowing the CH unit to vibrate harmonically against W as a pseudodiatomic. The frequency shift between ν(C–H) and ν(C–D) of **1** and **1**-d_1 is in good agreement with expectation.

We have not been able to identify bands attributable to the ν(W—Cl) mode or the two δ(W≡C—H) modes (nondegenerate under C_{2v} symmetry) in the Raman spectra of **1** or its isotopomers. We expect the frequency of the former mode to be <275 cm^{-1} for **1** based on the long W–Cl bond distance for this compound[10b] and thus that it is energy factored from coupling strongly with ν(W≡C). This prediction is borne out by the Raman spectra of the series of related methylidyne complexes W(CH)($Me_2PCH_2CH_2PMe_2)_2$X (X = Cl, Br, I), for which the frequencies of the strong ν(W≡C) bands (920 cm^{-1}) are independent of X. Based on this observation, as well as the energy factoring of the ν(C–H) mode from the ν(W≡C) mode and the insensitivity of the frequency of ν(W≡C) to the isotopic formulation of the PMe_3 ligands, it is clear that the ν(W≡C) modes of these methylidyne complexes lack the extensive coupling that is present in M(CR)-$(CO)_4$X complexes[4] and thus that 910–920 cm^{-1} represents a much better estimate of the pure W≡C strengthing frequency than that available from the latter compounds. Consistent with this is the fact that these ν(W≡C) frequencies are comparable to the ν(W≡E) frequencies of the isoelectronic metal–oxo and -nitrido compounds [W(≡E)($Ph_2PCH_2CH_2PPh_2)_2X]^{n+}$ (E = O, n = 1, ν = 955 cm^{-1};[11a] E = N, n = 0, ν = 980 cm^{-1}).[11b] The W≡(CH) force constant for **1** in the diatomic harmonic oscillator approximation is 5.9 mdyn Å^{-1}; this is considerably smaller than previous estimates (7.00–7.40 mdyn Å^{-1}).[4a–c,f]

It has been previously reported that the trans ligand in the complexes W(CH)L_4X and Ta(C-*t*-*Bu*)HL_4X can significantly perturb the spectroscopic signatures, length, and basicity of the M≡C bond.[12,13] In closing, we note that the ν(W≡C) and ν(C—H) frequencies of W(CH)L_4X complexes are important parameters for quantifying such ancillary ligand effects. An interesting observation in this regard is that the methylidyne ν(C—H) frequency of **1** is 300 cm^{-1} lower than those of terminal alkynes.[14] This suggests that the carbon p orbital character in the methylidyne C–H bond is larger than that of a pure sp hybrid, consistent with inferences made from NMR spectroscopic and structural studies of this and related methylidyne compounds.[7b,12]

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