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Ground-State and Excited-State C≡C Stretching Frequencies of Dimetallapolyyne Redox Congeners. Direct Evidence for Metal→Alkynyl π-Back-Bonding

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Summary: Paramagnetic [K(crypt-222)][$\mathrm{Mo_2(C\equiv CSiMe_3)_4(PMe_3)_4}$] ([K(crypt-222)]**1**) is prepared by one-electron reduction of $\mathrm{Mo_2(C\equiv CSiMe_3)_4(PMe_3)_4}$ (**1**) by $\mathrm{K(C_{10}H_8)}$ in the presence of crypt-222. The ν(C≡C) frequencies for **1** and [K(crypt-222)]**1** in their ground states and δ → δ* electronic excited states are controlled by the occupancy of the $\delta(\mathrm{M_2})$ and $\delta^*(\mathrm{M_2})$ orbitals, lying in the order **1** (δ^2) > **1*** ($\delta^1\delta^{*1}$) > [K(crypt-222)]**1** ($\delta^2\delta^{*1}$) > [K(crypt-222)]**1*** ($\delta^1\delta^{*2}$); this order indicates that M→$\mathrm{C\equiv CSiMe_3}$ π-back-bonding is of increasing importance across this series.

A general description of the metal−carbon bond in transition-metal−alkynyl compounds has not yet been developed.[1,2] This is despite the fact that understanding the nature of this bond is a logical prerequisite for the rational design of electronic materials composed of metal−alkynyl building blocks[3−7] and for interpreting their physical properties. Particular uncertainty surrounds the contribution of M→CCR π-back-bonding to the metal−carbon interaction. Although the degree to which alkynyl ligands act as π-acceptors has often been inferred from comparisons among C≡C stretching frequencies of $\mathrm{ML}_m\mathrm{(C\equiv CR)}_n$ compounds, such interpretations are problematic because ν(C≡C) typically varies so little (a few tens of $\mathrm{cm^{-1}}$) as a function of oxidation state and ancillary ligand that electronic effects other than M−CCR π interactions cannot be excluded from consideration.[1] Moreover, Lichtenberger and co-workers have recently reported definitive evidence from photoelectron-spectroscopic studies that alkynyl ligands are π-donors in $\mathrm{FeCp(C\equiv CR)(CO)_2}$ complexes and that their π-acceptor character is negligible,[2,8] although, as they noted, more electron-rich compounds might exhibit M→CCR π-back-bonding. Herein, we report the synthesis of an electron-rich compound, $\mathrm{[Mo_2(C\equiv CSiMe_3)_4(PMe_3)_4]^-}$, that together with its one-electron-oxidized congener $\mathrm{Mo_2(C\equiv CSiMe_3)_4(PMe_3)_4}$ (**1**)[9,10] possess unique electronic attributes for testing this hypothesis: their $\delta(\mathrm{M_2})$ and $\delta^*(\mathrm{M_2})$ orbitals are of π-symmetry with respect to the π*(C≡CR) orbitals, so changing the δ,δ* occupancy chemically and photochemically allows broad and systematic variation of the M−CCR π-electron configuration. The ground-state and $\delta(\mathrm{M_2}) \rightarrow \delta^*(\mathrm{M_2})$ excited-state C≡C stretching frequencies of these compounds provide the first unambiguous evidence for M→CCR π-back-bonding.

The cyclic voltammogram of $\mathrm{Mo_2(C\equiv CSiMe_3)_4(PMe_3)_4}$ exhibits a reversible, one-electron reduction wave at

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(1) Manna, J.; John, K. D.; Hopkins, M. D. *Adv. Organomet. Chem.* **1995**, *38*, 79−154.

(2) Lichtenberger, D. L.; Renshaw, S. K.; Bullock, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 3276−3285.

(3) For references prior to 1994 on metal−alkynyl electronic materials, see ref 1. Recent leading references are given in refs 4−7.

(4) Electroactive "molecular wires": (a) Lavastre, O.; Plass, J.; Bachmann, P.; Guesmi, S.; Moinet, C.; Dixneuf, P. H. *Organometallics* **1997**, *16*, 184. (b) Lavastre, O.; Even, M.; Dixneuf, P. H.; Pacreau, A.; Vairon, J.-P. *Organometallics* **1996**, *15*, 1530. (c) Bradshaw, J. D.; Guo, L.; Tessier, C. A.; Youngs, W. J. *Organometallics* **1996**, *15*, 2582. (d) Sato, M.; Mogi, E. *J. Organomet. Chem.* **1996**, *508*, 159. (e) Le Narvor, N.; Lapinte, C. *Organometallics* **1995**, *14*, 634. (f) Sato, M.; Mogi, E.; Kumakura, S. *Organometallics* **1995**, *14*, 3157. (g) Colbert, M. C. B.; Hodgson, D.; Lewis, J.; Raithby, P. R.; Long, N. J. *Polyhedron* **1995**, *14*, 2759. (h) Colbert, M. C. B.; Ingham, S. L.; Lewis, J.; Long, N. J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1994**, 2215. (i) Colbert, M. C. B.; Edwards, A. J.; Lewis, J.; Long, N. J.; Page, N. A.; Parker, D. G.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1994**, 2589. (j) Sato, M.; Hayashi, Y.; Shintate, H.; Katada, M.; Kawata, S. *J. Organomet. Chem.* **1994**, *471*, 179. (k) Russo, M. V.; Furlani, A.; Licoccia, S.; Paolesse, R.; Villa, A. C.; Guastini, C. *J. Organomet. Chem.* **1994**, *469*, 245. (l) Sato, M.; Shintate, H.; Kawata, Y.; Sekino, M.; Katada, M.; Kawata, S. *Organometallics* **1994**, *13*, 1956. (m) Osella, D.; Gambino, O.; Nervi, C.; Ravera, M.; Russo, M. V.; Infante, G. *Inorg. Chim. Acta* **1994**, *225*, 35. (n) Onitsuka, K.; Tao, X.-Q.; Sonogashira, K. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 2611.

(5) Metal-capped carbon chains: (a) Falloon, S. B.; Arif, A. M.; Gladysz, J. A. *Chem. Commun.* **1997**, 629. (b) Brady, M.; Weng, W.; Zhou, Y.; Seyler, J. W.; Amoroso, A. J.; Arif, A. M.; Böhme, M.; Frenking, G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1997**, *119*, 775. (c) Bruce, M. I.; Ke, M.; Low, P. J. *Chem. Commun.* **1996**, 2405. (d) Bunz, U. H. F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 969. (e) Bartik, T.; Bartik, B.; Brady, M.; Dembinski, R.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 414. (f) Coat, F.; Lapinte, C. *Organometallics* **1996**, *15*, 477. (g) Yam, V. W.-W.; Lau, V. C.-Y.; Cheung, K.-K. *Organometallics* **1996**, *15*, 1740. (h) Weng, W.; Bartik, T.; Brady, M.; Bartik, B.; Ramsden, J. A.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1995**, *117*, 11922. (i) Le Narvor, N.; Toupet, L.; Lapinte, C. *J. Am. Chem. Soc.* **1995**, *117*, 7129. (j) Brady, M.; Weng, W.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1994**, 2655. (k) Lang, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 547. For a review of $\mathrm{M{-}C_2{-}M}$ compounds, see: Beck, W.; Niemer, B.; Wieser, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 923.

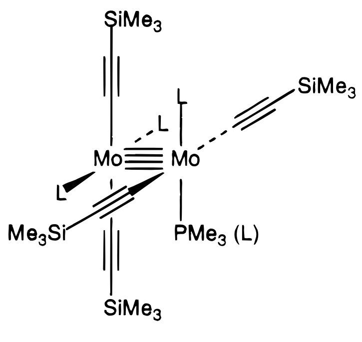
(6) Polymers, oligomers, and networks: (a) Springborg, M.; Albers, R. C. *Phys. Rev. B* **1996**, *53*, 10626. (b) Irwin, M. J.; Jia, G.; Payne, N. C.; Puddephatt, R. J. *Organometallics* **1996**, *15*, 51. (c) Markwell, R. D.; Butler, I. S.; Kakkar, A. K.; Khan, M. S.; Al-Zakwani, Z. H.; Lewis, J. *Organometallics* **1996**, *15*, 2331. (d) Faust, R.; Diederich, F.; Gramlich, V.; Seiler, P. *Chem. Eur. J.* **1995**, *1*, 111. (e) Yang, M.; Zhang, L.; Cai, Z.; Yang, P.; Xu, Z. *J. Polym. Sci., Polym. Chem.* **1995**, *A33*, 2203. (f) Khan, M. S.; Kakkar, A. K.; Long, N. J.; Lewis, J.; Raithby, P.; Nguyen, P.; Marder, T. B.; Wittmann, F.; Friend, R. H. *J. Mater. Chem.* **1994**, *4*, 1227. (g) Tykwinski, R. K.; Stang, P. J. *Organometallics* **1994**, *13*, 3203. (h) Faulkner, C. W.; Ingham, S. L.; Khan, M. S.; Lewis, J.; Long, N. J.; Raithby, P. R. *J. Organomet. Chem.* **1994**, *482*, 139. (i) Khan, M. S.; Kakkar, A. K.; Ingham, S. L.; Raithby, P. R.; Lewis, J.; Spencer, B.; Wittmann, F.; Friend, R. H. *J. Organomet. Chem.* **1994**, *472*, 247. (j) Diederich, F.; Faust, R.; Gramlich, V.; Seiler, P. *J. Chem. Soc., Chem. Commun.* **1994**, 2045. (k) Wittmann, H. F.; Friend, R. H.; Khan, M. S.; Lewis, J. *J. Chem. Phys.* **1994**, *101*, 2693.

(7) Nonlinear-optical materials: (a) Nguyen, P.; Lesley, G.; Marder, T. B.; Ledoux, I.; Zyss, J. *Chem. Mater.* **1997**, *9*, 406. (b) Whittall, I. R.; Humphrey, M. G.; Persoons, A.; Houbrechts, S. *Organometallics* **1996**, *15*, 1935. (c) Whittall, I. R.; Humphrey, M. G.; Samoc, M.; Swiatkiewicz, J.; Luther-Davies, B. *Organometallics* **1995**, *14*, 5493. (d) Whittall, I. R.; Humphrey, M. G.; Hockless, D. C. R.; Skelton, B. W.; White, A. H. *Organometallics* **1995**, *14*, 3970. (e) Myers, L. K.; Ho, D. M.; Thompson, M. E.; Langhoff, C. *Polyhedron* **1995**, *14*, 57.

(8) Lichtenberger, D. L.; Renshaw, S. K.; Wong, A.; Tagge, C. D. *Organometallics* **1993**, *12*, 3522−3526.

(9) (a) Stoner, T. C.; Dallinger, R. F.; Hopkins, M. D. *J. Am. Chem. Soc.* **1990**, *112*, 5651. (b) Stoner, T. C.; Geib, S. J.; Hopkins, M. D. *J. Am. Chem. Soc.* **1992**, *114*, 4201. (c) Stoner, T. C.; Geib, S. J.; Hopkins, M. D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 409.

(10) Stoner, T. C.; Schaefer, W. P.; Marsh, R. E.; Hopkins, M. D. *J. Cluster Sci.* **1994**, *5*, 107−124.



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−2.13 V (vs $FeCp_2/FeCp_2^+$) in tetrahydrofuran (THF),[11] which suggested that $[Mo_2(C{\equiv}CSiMe_3)_4(PMe_3)_4]^-$ could be synthesized and isolated. Accordingly, addition of a THF solution of $K(C_{10}H_8)$ (1 equiv) to an equimolar mixture of royal blue, diamagnetic **1** and 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (crypt-222) in THF at −78 °C results in a red-brown solution, from which paramagnetic, orange-brown [K(crypt-222)]-$[Mo_2(C{\equiv}CSiMe_3)_4(PMe_3)_4]$ ([K(crypt-222)]**1**) can be isolated in ca. 65% yield upon removal of solvent and extraction of naphthalene with pentane.[12] [K(crypt-222)]**1** reacts instantly with air in both the solid state and solution to form a dark blue product that consists primarily of **1**, as indicated by UV−vis and infrared spectroscopy. The infrared spectrum of [K(crypt-222)]-**1** exhibits a single, strong band in the ν(C≡C) region at 1954 cm^{-1}; for **1**, the corresponding band appears at 1991 cm^{-1}.[10,13] We expect that the structure of $\mathbf{1}^-$ possesses idealized D_{2d} symmetry, like that of **1**, based on the fact that the D_{2d} symmetry of related compounds of the type $[Re_2Cl_4(PR_3)_4]^{2+}$ is maintained upon both one- and two-electron reduction.[14]

Frequencies for ν(C≡C) in the δ → δ* electronic excited states of **1** and [K(crypt-222)]**1** were determined from electronic absorption spectra of the compounds at 10 K. These spectra exhibit vibronically structured bands attributable to the $^1(\delta \rightarrow \delta^*)$ and $^2(\delta \rightarrow \delta^*)$ transitions of **1** (Figure 1) and [K(crypt-222)]**1** (Figure 2), respectively, as the lowest-energy features. Aside from the fact that the $^2(\delta \rightarrow \delta^*)$ transition of [K(crypt-222)]**1** is red shifted by ca. 7000 cm^{-1} from the $^1(\delta \rightarrow \delta^*)$ transition of **1**, as a result of the larger spin-pairing energy contributions to the latter,[15] the two bands are qualitatively similar: both are dominated by a 350−370 cm^{-1} vibronic progression that is attributable to nominal ν(Mo−Mo)/ν(Mo−C) modes[16] and, additionally, exhibit weaker, lower frequency vibronic origins (ca. 160/170, 240 cm^{-1}). Near the high-energy edge of each band—beyond the point at which features attributable to combinations of the lower-frequency fundamentals are still clearly resolved—an additional, weak vibronic

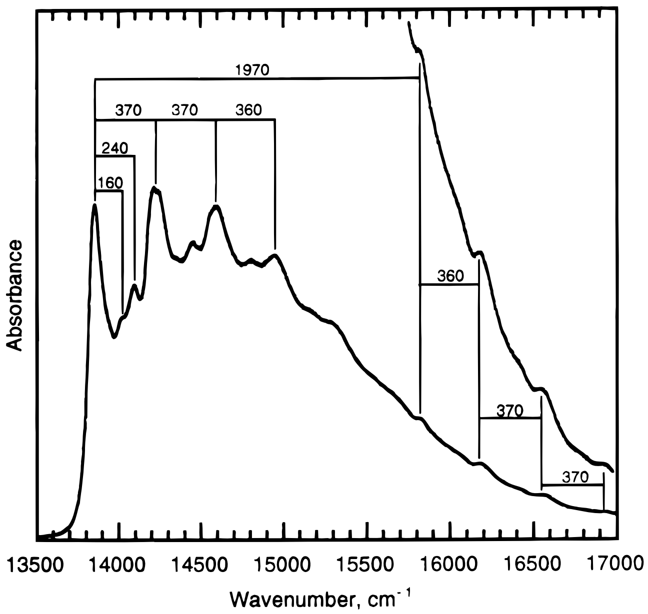

Figure 1. Electronic absorption spectrum of a polycrystalline film of **1** at ca. 10 K. Vibronic spacings are given in cm^{-1}. The trace in the upper right corner is an expansion of the ν(C≡C) origin and associated features.

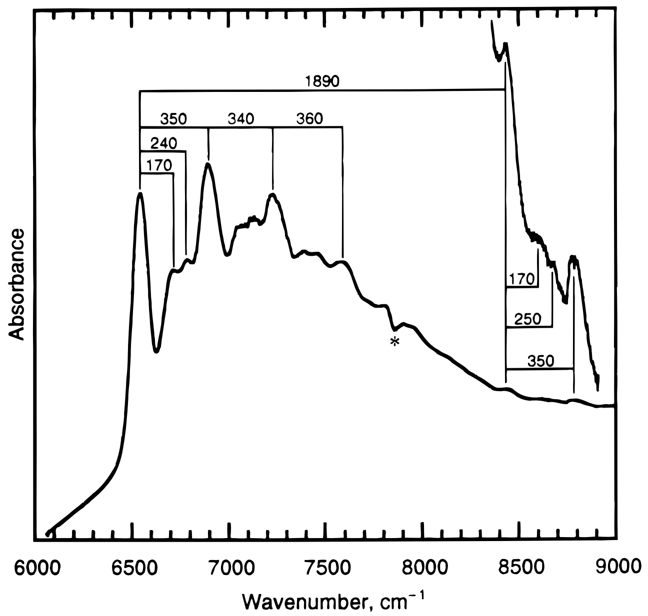

Figure 2. Electronic absorption spectrum of a polycrystalline film of [K(crypt-222)]**1** at ca. 10 K. Vibronic spacings are given in cm^{-1}. The trace in the upper right corner is an expansion of the ν(C≡C) origin and associated features. The dip in intensity at 7850 cm^{-1}, marked by an asterisk, is an instrumental artifact.

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(11) Haines, D. E.; Smith, W. E.; Hopkins, M. D. Unpublished results.

(12) Anal. Calcd (found) for $C_{50}H_{108}KMo_2N_2O_6P_4Si_4$: C, 46.18 (46.46); H, 8.37 (8.06); N, 2.15 (2.09). IR, ν(C≡C) region (neat film): 1954 cm^{-1} (s). EPR (solid, 295 K): $g = 2.05$.

(13) The C≡C stretching coordinates of D_{2d}-symmetric $M_2(CCR)_4(PMe_3)_4$ transform according to $a_1 + b_2 + e$, of which b_2 and e are allowed in the infrared spectrum. The infrared bands of **1** and [K(crypt-222)]**1** at 1991 and 1954 cm^{-1}, respectively, are assigned to e-symmetric C≡C stretches on the basis that these should be more intense than the b_2-symmetric modes; a vector-sum model predicts $[I(e)/I(b_2)] = {}^1/_2(\tan^2 \theta) \cong 2$ (where θ is the angle between the Mo−Mo and the C≡C bonds, taken from the structure of $Mo_2(CCH)_4(PMe_3)_4$ in ref 9c). The FT-Raman spectrum of **1** exhibits a band at 1999 cm^{-1} attributable to the a_1-symmetric ν(C≡C) mode. Repeated attempts to measure the ν(C≡C) frequency for [K(crypt-222)]**1** by Raman spectroscopy have been unsuccessful due to decomposition of the sample upon laser excitation.

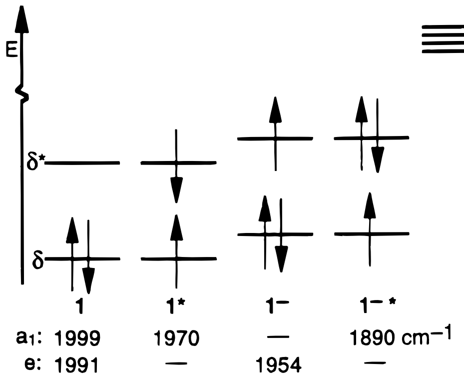
(14) Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; Tomas, M.; Walton, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 4950−4954.

(15) (a) Hopkins, M. D.; Gray, H. B.; Miskowski, V. M. *Polyhedron* **1987**, *6*, 705−714. (b) Bursten, B. E.; Clayton, T. W., Jr. *J. Cluster Sci.* **1994**, *5*, 157−171.

(16) Normal-coordinate calculations on **1** and the isotopomers $Mo_2(C{\equiv}CSiMe_3\text{-}d_9)_4(PMe_3)_4$ and $Mo_2(^{13}C{\equiv}^{13}CSiMe_3)_4(PMe_3)_4$ (John, K. D.; Miskowski, V. M.; Vance, M. A.; Dallinger, R. F.; Wang, L. C.; Geib, S. J.; Hopkins, M. D. Manuscript in preparation) indicate that there is significant coupling between the symmetric ν(Mo−Mo) and ν(Mo−C) stretching modes, but that ν(C≡C) is uncoupled from other modes (>90% C≡C stretching in character).

origin is observed, the spacing of which relative to the 0–0 band is 1970 cm^{-1} for **1** and 1890 cm^{-1} for [K(crypt-222)]**1**. Progressions built on these origins arising from the 350/370 cm^{-1} mode are resolved, as are features attributable to the lower-frequency modes. Isotopic labeling of the alkynyl ligands of **1** with ^{13}C allows the 1970 cm^{-1} origin of this compound to be unambiguously assigned to one quantum of the ν(C≡C) stretching mode, as this origin is shifted to 1900 cm^{-1} in the spectrum of $Mo_2(^{13}C{\equiv}^{13}CSiMe_3)_4(PMe_3)_4$; this frequency is in close agreement with what is expected from the diatomic-oscillator approximation (1890 cm^{-1}). By analogy, the 1890 cm^{-1} origin observed in the spectrum of [K(crypt-222)]**1** is also assigned to ν(C≡C).

The relationship between the frequency of ν(C≡C) and the [δ,δ^*(M_2)] electron configuration of **1** and [K(crypt-222)]**1** provides direct evidence for M→CCR π-back-bonding. The ground states and $\delta \rightarrow \delta^*$ excited states (**1***, [K(crypt-222)]**1***) of the two compounds are described by four different configurations of the δ and δ^* orbitals: **1**, [$\sigma^2\pi^4\delta^2$]; **1***, [$\sigma^2\pi^4\delta^1\delta^{*1}$]; [K(crypt-222)]**1**, [$\sigma^2\pi^4\delta^2\delta^{*1}$]; [K(crypt-222)]**1***, [$\sigma^2\pi^4\delta^1\delta^{*2}$]. The b_1-symmetry δ and a_2-symmetry δ^* orbitals are of π symmetry with respect to the ligands and, hence, are capable of interacting with the π(CCR) and π^*(CCR) orbitals ($a_2 + b_1 + e$), with the δ^* orbital being closer in energy to the π^*(CCR) levels than is the δ orbital. Importantly, increasing the occupancy of the δ^* orbital and raising the energy of δ and δ^* by reduction of Mo_2^{4+} to Mo_2^{3+} results in a significant, systematic reduction in the frequency of ν(C≡C), indicating that M→$CCSiMe_3$ π-back-bonding increases concomitantly. Context for these frequencies and the differences among them is provided by the ca. 80 previously reported ν(C≡C) frequencies for $[ML_m(C{\equiv}CSiMe_3)_n]^{z+}$ complexes (M = group 4 to group 10, d^0–d^8; z = +1 to −2; Figure 3), all but three of which lie in a narrow 80 cm^{-1} range (1990–2070 cm^{-1}). In contrast, the ν(C≡C) frequencies of **1** and [K(crypt-222)]**1*** differ by >100 cm^{-1}, with that for [K(crypt-222)]**1*** being, by >50 cm^{-1}, the lowest yet reported; the latter frequency is suggestive of significant double-bond character in the alkynyl C–C linkages.



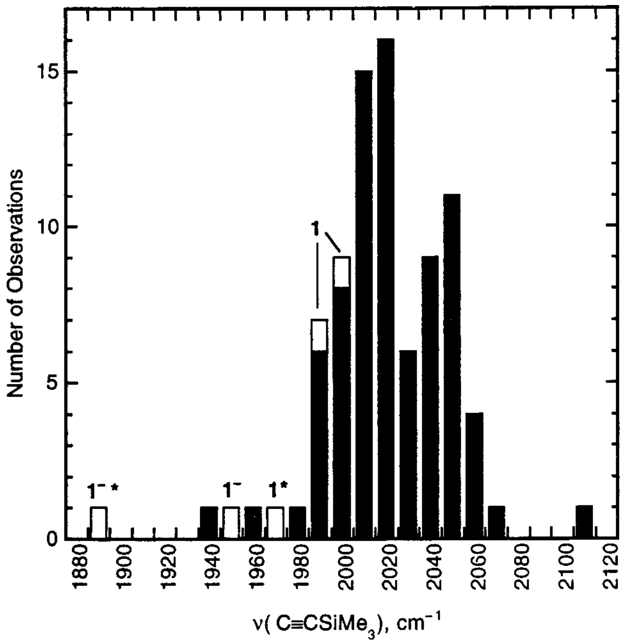


Figure 3. Distribution of ν(C≡C) stretching frequencies for $ML_m(C{\equiv}CSiMe_3)_n$ complexes. A listing of compounds, frequencies, and references is available as Supporting Information. Ground-state and excited-state frequencies for **1** and [K(crypt-222)]**1** are shown by unshaded bars.

In summary, we have demonstrated that M→CCR π-back-bonding can contribute substantially to the metal–carbon interaction in metal–alkynyl compounds. It is important to note that the present data do not rule out contributions from M←CCR π-bonding in these compounds; unfortunately, attempts to prepare $[Mo_2(C{\equiv}CSiMe_3)_4(PMe_3)_4]^+$, for which such interactions could be particularly important, have not been successful. The observation that the extent of M→CCR π-back-bonding is markedly different in the ground and excited states of **1** and **1**$^-$ has important implications for metal–alkynyl electronic materials, as this opens the possibility of photochemically switching those properties that are electronically governed by the M–CCR π interactions.

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Supporting Information Available: Tables of ν(C≡C) frequencies for $ML_m(C{\equiv}CSiMe_3)_n$ complexes, with references (6 pages). Ordering information is given on any current masthead page.

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