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Infrared Spectra, Structure, and Bonding of the $GeH_3{-}CrH$, $HGe{\equiv}MoH_3$, and $HGe{\equiv}WH_3$ Molecules in Solid Neon and Argon

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Laser ablated chromium, molybdenum, and tungsten atoms react with germane during condensation in excess noble gases. The chromium reaction stopped at the germyl metal hydride, molybdenum gave some hydride but mostly germylidyne, and tungsten reacted spontaneously to give only the germylidyne species. These molecules were identified by isotopic shifts, density-functional theory product energy and frequency calculations, and comparison to the analogous methane and silane reaction products. Effective bond orders for the $HGe{\equiv}MoH_3$ and $HGe{\equiv}WH_3$ molecules are 2.82 and 2.87 using the B3LYP density functional, and are slightly lower than their silicon and carbon analogues. Our calculated $Ge{\equiv}M$ triple bond lengths for these simple trihydride complexes are 0.05 to 0.10 Å shorter than those measured for larger group 6 organometallic complexes.

Introduction

Carbon is well-known for yielding multiple bonds,[1,2] and a large number of organometallic complexes containing carbon−metal double and triple bonds are known, particularly the alkylidene and alkylidyne complexes of group 6 metals.[3,4] However, heavier members of the carbon family are less effective in multiple bonding. As a result only one silylyne complex with Mo−Si triple bond character[5] and several examples of germylyne group 6 metal complexes have been reported by the Power and Filippou groups.[6−9]

Laser-ablated metal atoms have been employed in our laboratory to react with small molecules and form simple compounds of particular interest for their chemical bonding.[10−12] Such is the case for the simplest group 6 methylidyne molecules $HC{\equiv}MoH_3$ and $HC{\equiv}WH_3$, which are major products of the methane activation reaction whereas only $CH_3{-}CrH$ is formed with the lightest member of the family. The chemistry of group 6 metals (Cr, Mo, W) reveals an interesting trend. Because different d orbitals participate in bonding, the tungsten and molybdenum compounds favor high oxidation states while chromium counterparts form low oxidation states. For example group 6 metal atoms react with H_2O_2 to give high oxidation state H_2WO_2 and H_2MoO_2, and low oxidation state $Cr(OH)_2$, respectively.[13] In addition tungsten and molybdenum atoms react with H_2 in solid neon to produce trigonal prismatic C_{3v} hexahydride, WH_6, and MoH_6, while only the dihydride complex, $CrH_2(H_2)_2$ is obtained for chromium.[14] Of particular interest to the present

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(1) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley: New York, 1999.

(2) Massey, A. G. *Main Group Chemistry*, 2nd ed.; John Wiley and Sons: New York, 2000.

(3) McLain, S. J.; Wood, C. D.; Messerle, L. W.; Schrock, R. R.; Hollander, F. J.; Youngs, W. J.; Churchill, M. R. *J. Am. Chem. Soc.* **1978**, *100*, 5962; (carbyne synthesis)

(4) (a) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145. (b) Herndon, J. W. *Coord. Chem. Rev.* **2004**, *248*, 3. (c) Herndon, J. W. *Coord. Chem. Rev.* **2005**, *24*, 999. (d) Herndon, J. W. *Coord. Chem. Rev.* **2006**, *250*, 1889.

(5) Mork, B. V.; Tilley, T. D. *Angew. Chem.* **2003**, *115*, 371.

(6) Simons, R. S.; Power, P. P. *J. Am. Chem. Soc.* **1996**, *118*, 11966.

(7) Pu, L.; Twamley, B.; Haubrich, S. T.; Olmstead, M. M.; Mork, B. V.; Simons, R. S.; Power, P. P. *J. Am. Chem. Soc.* **2000**, *122*, 650.

(8) Filippou, A. C.; Philippopoulos, A. I.; Portius, P.; Neumann, D. U. *Angew. Chem.* **2000**, *112*, 2881.

(9) (a) Filippou, A. C.; Portius, P.; Philippopoulos, A. I. *Organometallics* **2002**, *21*, 653. (b) Balazs, G.; Gregoriades, L. J.; Scheer, M. *Organometallics* **2007**, *26*, 3058.

(10) Cho, H.-G.; Andrews, L. *J. Am. Chem. Soc* **2005**, *127*, 8226; (Mo + CH_4)

(11) Cho, H.-G.; Andrews, L.; Marsden, C. *Inorg. Chem.* **2005**, *44*, 7634; (Cr, W + CH_4)

(12) Andrews, L.; Cho, H.-G. *Organometallics* **2006**, *25*, 4040; and references therein (Review article)

(13) Wang, X.; Andrews, L. *J. Phys. Chem. A* **2006**, *110*, 10409; (M + H_2O_2)

(14) (a) Wang, X.; Andrews, L. *J. Am. Chem. Soc.* **2002**, *124*, 5636; (WH_6). (b) Wang, X.; Andrews, L. *J. Phys. Chem. A* **2003**, *107*, 570; (Cr + H_2). (c) Wang, X.; Andrews, L. *J. Phys. Chem. A* **2005**, *109*, 9021; (Mo + H_2)

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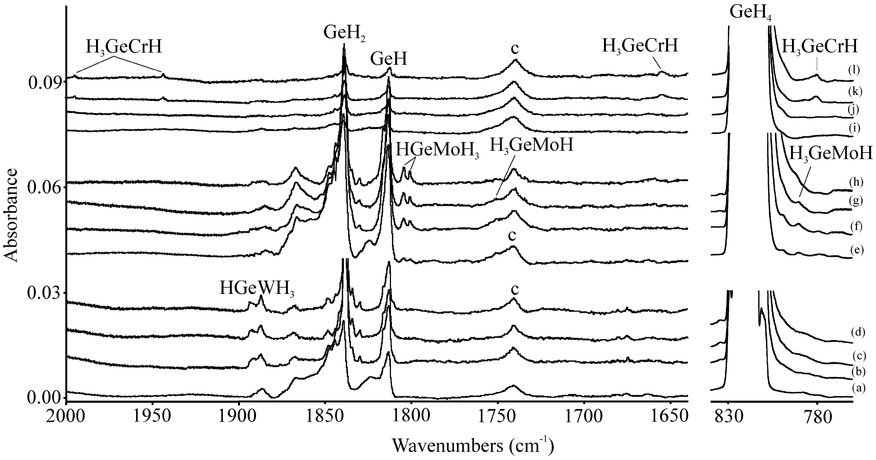

Figure 1. Infrared spectra for the Cr, Mo, and W atom and GeH_4 reaction products in the 2000−1640 and 840−760 cm^{-1} regions in solid argon at 4 K. (a) W + GeH_4 deposition for 60 min, (b) after annealing to 20 K, (c) after >470 nm irradiation, (d) after annealing to 30 K. (e) Mo + GeH_4 deposition for 60 min, (f) after annealing to 20 K, (g) after >380 nm irradiation, (h) after annealing to 30 K. (i) Cr + GeH_4 deposition for 60 min, (j) annealing to 20 K, (k) after >470 nm irradiation, (l) after annealing to 30 K. Bands labeled "c" are common to different metals and thus not due to a unique metal reaction product.

investigation, silane activation by group 6 metals gave the $SiH_3{-}MH$ hydride for Cr and Mo and the $HSi{\equiv}MH_3$ silylidyne for Mo and W.[15]

We present here a matrix infrared spectroscopic study of laser-ablated Cr, Mo, and W atom reactions with GeH_4 in solid argon and neon. The most interesting new products, $HGe{\equiv}MoH_3$ and $HGe{\equiv}WH_3$, are isoelectronic to the above silylidynes and the methane reaction product methylidynes $HC{\equiv}MoH_3$ and $HC{\equiv}WH_3$.[10−12]

Experimental and Computational Methods. Matrix isolation experiments involving laser-ablated Cr, Mo and W atom reactions with small molecules and germane (Matheson) reactions with ozone in excess argon have been described in previous papers.[13−17] The Nd:YAG laser fundamental (1064 nm, 10 Hz repetition rate with 10 ns pulse width) was focused onto a rotating metal target (Johnson Matthey), which gave a bright plume spreading uniformly to the 4 K CsI window. The metal targets were polished to remove the oxide coatings and immediately placed in the vacuum chamber. The laser energy was varied about 10−20 mJ/pulse. Fourier transform infrared spectroscopy (FTIR) spectra were recorded at 0.5 cm^{-1} resolution on a Nicolet 750 with 0.1 cm^{-1} measurement accuracy using an MCTB detector. Isotopic samples (GeD_4 and GeH_xD_{4-x} ($x = 0{-}4$)) were prepared as described, and the sample was frozen and degassed before use.[16] Matrix samples were annealed at different temperatures, and selected samples were subjected to photolysis by a medium pressure mercury arc lamp (Philips, 175W, globe removed) and glass filters.

Complementary density-functional theory (DFT) calculations were performed using the Gaussian 03 program,[18] the B3LYP and BPW91 density functionals, 6−311+G(3df,3pd) basis set for hydrogen and germanium atoms, and SDD for the metal atoms.[19−22] All of the geometrical parameters were fully optimized, and the optimized geometry was confirmed by vibrational analysis. Harmonic vibrational frequencies were calculated analytically with zero-point energy included for the determination of reaction energies. Natural bond orbital (NBO)[18,23] analysis was also done to explore the bonding in new germylidyne molecules.

Results and Discussion

Infrared spectra of products formed in the reactions of laser-ablated chromium, molybdenum, and tungsten atoms with GeH_4 in excess argon and neon during condensation at 4 K will be presented in turn. DFT calculations were performed to support the identifications of new reaction products. Common species, such as GeH_x intermediates, hydrogen species, and metal oxides have been identified in previous papers.[24−26]

Infrared Spectra. Figure 1 compares spectra of reaction products for three group 6 metal atoms and germane in argon, and the product absorptions are listed in Tables 1 and 2. In this manner common bands can be identified and eliminated from consideration for new metal reaction products. For example GeH_2 and GeH are produced[24b] at 1839 and 1813 cm^{-1} in all laser ablated metal experiments with germane.

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(15) Wang, X.; Andrews, L. *J. Am. Chem. Soc.* **2008**, *130*, 6766; (Cr, Mo, W and SiH_4)

(16) Withnall, R.; Andrews, L. *J. Phys. Chem.* **1990**, *94*, 2351; (GeH_4)

(17) (a) Andrews, L. *Chem. Soc. Rev.* **2004**, *33*, 123. (b) Andrews, L.; Citra, A. *Chem. Rev.* **2002**, *102*, 885.

(18) Kudin, K. N., et al. *Gaussian 03*, Revision D.01; Gaussian, Inc.: Pittsburgh, PA, 2004.

(19) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, Y.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(20) Perdew, J. P.; Burke, K.; Wang, Y. *Phys. Rev. B* **1996**, *54*, 16533; and references therein.

(21) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265.

(22) Andrae, D.; Haeussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta.* **1990**, *77*, 123.

(23) (a) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. (b) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev* **1988**, *88*, 899.

(24) (a) Smith, G. R.; Guillory, W. A. *J. Chem. Phys.* **1972**, *76*, 3208; (photolysis of GeH_4). (b) Wang, X.; Andrews, L.; Kushto, G. P. *J. Phys. Chem. A* **2002**, *106*, 5809; (Ge + H_2)

(25) (a) Wight, C. A.; Ault, B. S.; Andrews, L. *J. Chem. Phys.* **1976**, *65*, 1244. (b) Milligan, D. E.; Jacox, M. E. *J. Mol. Spectrosc.* **1973**, *46*, 460; (Ar_nH^+)

(26) Bare, W. D.; Souter, P. F.; Andrews, L. *J. Phys. Chem. A* **1998**, *102*, 8279; (metal oxides)

Table 1. Observed and Calculated Fundamental Frequencies of the GeH_3—CrH Germyl Metal Hydride in the Ground $^5A'$ Electronic State with the C_s Structure[a]

	GeH_3—CrH					GeD_3—CrD				
approximate description	obs	calc(L)	int	calc(W)	int	obs	calc(L)	int	calc(W)	int
Ge—H str, a″	1996	2090	144	2059	123	1440	1490	73	1468	62
Ge—H str, a′		2085	127	2050	111		1483	70	1459	60
Ge—H str, a′	1944	2059	144	2016	116	1404	1463	69	1432	57
Cr—H str, a″	1656[b]	1713	185	1701	133	1194	1224	96	1215	69
GeH_2 bend, a′		884	38	852	33		628	19	605	16
GeH_2 bend, a′		881	40	845	33		626	20	6101	16
GeH_3 def, a′	781[b]	781	356	749	288	covered	561	182	538	147
HCrGe bend, a″		437	84	411	82		325	43	308	41
GeH_2 rock, a″		343	0	321	0		248	0	232	0
HCr,GeH_3 rock, a′		281	28	256	25		220	1	214	0
Cr—Ge str, a′		219	2	218	4		194	15	179	16
HCrGe def, a″		84	78	88	61		60	41	63	33

[a] Frequencies and intensities are in cm^{-1} and km/mol. Observed in an argon matrix. Frequencies and intensities computed with B3LYP/6−311++G(3df,3pd) in the harmonic approximation using the SDD core potential and basis set for Cr noted (L) and using BPW91 noted (W). Symmetry notations are based on the C_s structure. [b] Neon matrix values 1677 and 792 cm^{-1}.

Table 2. Observed and Calculated Fundamental Frequencies of HGe≡MoH_3 and HGe≡WH_3 Complexes in the Ground $^1A_1$ Electronic States with the C_{3v} Structures[a]

	HGe≡MoH_3			DGe≡MoD_3			HGe≡WH_3			DGe≡WD_3		
approx. mode description	obs	calc	int	obs	calc	int	obs	calc	int	obs	calc	int
Ge—H str, a_1		2079	63		1482	33		2107	42		1502	22
M—H str, e	1804.8[b]	1895	247 × 2	1292.3[c]	1352	125 × 2	1894.0[d]	1951	204 × 2	masked[f]	1386.7	103 × 2
M—H str, a_1	1801.0[b]	1891	218	masked[c]	1337	109	1887.5[d]	1961	222	masked[f]	1387.3	111
MH_2 bend, e		853	36 × 2		605	17 × 2		829	29 × 2		588	14 × 2
MH_2 def, e		587	61 × 2		424	32 × 2		529	33 × 2		379	17 × 2
MH_3 def, a_1		535	48		429	11		578[e]	51		429[d]	20
Ge≡M str, a_1		371	6		339	16		347[e]	3		331[d]	7
HGeM def, e		305	13 × 2		218	7 × 2		326	6 × 2		235	3 × 2

[a] Frequencies and intensities are in cm^{-1} and km/mol. Observed in an argon matrix. Frequencies and intensities computed with B3LYP/6−311++G(3df,3pd) in the harmonic approximation using the SDD core potential and basis set for Mo and W. Calculations using the BPW91 functional gave similar frequencies. The mode symmetry notations are based on the C_{3v} structure. [b] Neon matrix band positions 1827.3, 1822.5 cm^{-1}. [c] Neon matrix band positions masked by methane impurity. [d] Neon matrix band positions 1917.4, 1911.2 cm^{-1}. [e] These nondegenerate modes are mixed internal coordinates. [f] Argon matrix counterpart masked by a common band, but neon matrix position is 1373.5 cm^{-1}. The 1340 cm^{-1} band in the GeH_xD_{4-x} experiment is close to this band position for the all-D species.

A unique chromium product is formed on >470 nm irradiation and includes bands at 1996, 1968, 1944, 1656, and 781 cm^{-1}. A possible molybdenum counterpart gives a weak shoulder absorption at 1751 cm^{-1} on a broad 1741 cm^{-1} band that is common to all metals and a new 790 cm^{-1} band. The major molybdenum product increases on annealing to 20 and 30 K, on >380 and >290 nm irradiation and gives rise to sharp bands at 1804.8 and 1801.0 cm^{-1}. The tungsten product is masked by a common germane combination band on sample deposition, which decreases to reveal sharp new product absorptions at 1894.0 and 1887.5 cm^{-1} with a 1:2 relative intensity. These bands increase on >470 nm irradiation, and also on annealing to 30 K so this reaction appears to be spontaneous. Recall that recent silane reactions gave similar bands at 1806.2 and 1802.1 cm^{-1} for Mo and at 1894.9 and 1887.8 cm^{-1} for W with the same reversed 2:1 and 1:2 relative intensity pattern.[15]

The reaction with GeD_4 in excess argon gave the 1194.1 cm^{-1} counterpart of the chromium product with H/D frequency ratio 1.387 for a Cr—H stretching mode and two weaker bands at 1440 and 1404 cm^{-1}. The Mo counterparts for this product were not observed. The major Mo product also increased on near uv irradiation at 1292.3 and 1284.0 cm^{-1} (Figure 2) and defined 1.397 and 1.403 H/D ratios for two different Mo—H stretching modes. Unfortunately the W product counterparts were covered by precursor combination bands. However, the W reaction with mixed isotopic GeH_xD_{4-x} sample gave new peaks at 1894, 1890, 1888, and 1340 cm^{-1}. The mixed isotopic precursor and Mo produced new peaks at almost the same positions, 1804 and 1292 cm^{-1}, as the pure isotopic precursors.

In solid neon the stronger chromium product bands were observed at 1677.3 and 792.1 cm^{-1}, which are shown in Figure S1 (Supporting Information), and the deuterium counterpart of the former was observed at 1209 cm^{-1}. Figure 3 compares the neon matrix spectra for the Mo and W reactions: the common GeH_2 and GeH bands were observed at 1862.5 and 1831.5 cm^{-1}. The sharp major W product is observed at 1917.4 and 1911.2 cm^{-1} and the sharp major Mo product at 1827.3 and 1822.5 cm^{-1}. With GeD_4, the W product gave a single absorption at 1373.5 cm^{-1}.

Calculations. Following our investigation of group 6 metal reactions with methane, which progressed through insertion followed by hydrogen transfer,[10−12] calculations were done for the series of products GeH_3—MH, GeH_2=MH_2, HGe≡MH_3, and the bridged species Ge(H)=MH_3. The energy profile is shown in Figure 4. As for the methane and silane reactions, the global minimum energy species for chromium is the first insertion product GeH_3—CrH, and the energies of subsequent H-transfer species are significantly higher. With Mo the initial GeH_3—MoH intermediate is low in energy, the germylidene is 8 kcal/mol higher, the germylidyne is 4 kcal/mol higher, but the bridged species is 8 kcal/mol lower. However for tungsten, the product energy

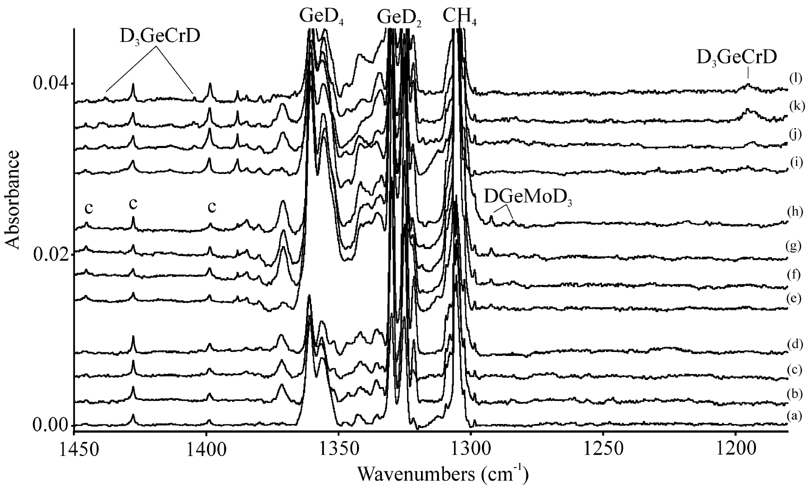

Figure 2. Infrared spectra for the Cr, Mo, and W atom and GeD_4 reaction products in the 1450−1180 cm^{-1} region in solid argon at 4 K. (a) W + GeD_4 deposition for 60 min, (b) after annealing to 20 K, (c) after >470 nm irradiation, (d) after annealing to 30 K. (e) Mo + GeD_4 deposition for 60 min, (f) after annealing to 20 K, (g) after >470 nm irradiation, (h) after annealing to 30 K. (i) Cr + GeD_4 deposition for 60 min, (j) annealing to 20 K, (k) after >470 nm irradiation, (l) after annealing to 30 K.

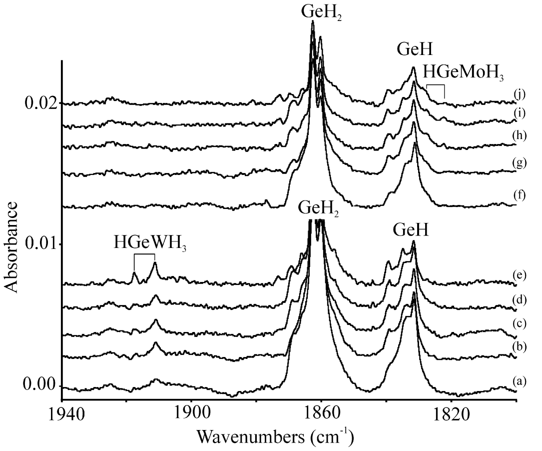

Figure 3. Infrared spectra for the Mo and W atom and GeH_4 reaction products in the 1940−1800 cm^{-1} region in solid neon at 4 K. (a) W + GeH_4 deposition for 60 min, (b) after annealing to 8 K, (c) after >470 nm irradiation, (d) after >380 nm irradiation, (e) after annealing to 10 K. (f) Mo + GeH_4 deposition for 60 min, (g) after annealing to 8 K, (h) after >470 nm irradiation, (i) after >380 nm irradiation, (j)after annealing to 10 K.

decreases steadily with the number of hydrogen atoms transferred to the metal center, and the bridged trihydride species is the global minimum. We also performed intrinsic reaction coordinate calculations[18] to locate the transition state between the singlet state $HGe{\equiv}MH_3$ and $Ge(H){=}MH_3$ molecules and found such an intermediate with one imaginary H−Ge−M bending frequency for each (i611 and i507) and 14 and 11 kcal/mol higher energy than the germylidyne species for M = Mo and W, respectively. Product structures calculated for each metal are illustrated in Figure 5.

GeH_3−CrH. New absorptions appeared at 1996, 1944, 1656, and 781 cm^{-1} on >470 nm irradiation and sharpened on annealing in experiments with chromium (Figure 1). Only the two strongest and lowest of these were observed in solid neon, at 1677 and 792 cm^{-1} (Figure S1, Supporting Information). Similar absorptions were assigned to SiH_3−CrH molecules in our silane investigation.[15] The Ge−H stretching modes are about 100 cm^{-1} lower than the corresponding Si−H modes, and the very strong GeH_3 deformation mode is about 70 cm^{-1} lower than the SiH_3 analogue, which are in agreement with calculations. Two corresponding Ge−D modes were observed at 1440 and 1404 cm^{-1} in solid argon (Figure 2, c denotes bands common to all experiments), and the H/D ratios, 1.385, for these bands are near that for germane itself, 1.387. The Cr−H stretching mode is, however, higher by 10 cm^{-1} in the germane species following the increase in the Cr−H stretching mode from CH_3−CrH to SiH_3−CrH. The deuterium counterpart is found at 1194 cm^{-1} for the Cr−D stretching mode, and the H/D ratio for the present Cr−H stretching mode, 1.387, is near this ratio for the silicon, 1.386, and carbon, 1.385, species.[11,15] The unique identifying mode for this molecule is the symmetric GeH_3 deformation (umbrella mode), which is observed spot on the calculated value at 781 cm^{-1} (Table 1, Figure 1). Correlation between strong calculated and observed frequencies supports the identification of GeH_3−CrH following the observation of the silicon analogue.[15] We observe only two of the three computed Ge−H stretching modes: according to our calculations, the third mode may not be resolved from the observed higher frequency band.

GeH_3−MoH. Weak new absorptions were observed at 1751 and 790 cm^{-1} on sample deposition with molybdenum in excess argon. The band labeled "c" is common to all metal experiments with germane. These bands relate with the strongest calculated frequencies for the molybdenum hydride counterpart (Table S1, Supporting Information), but the weaker Ge−H stretching modes and deuterium counterparts were not observed. These bands were not observed in solid neon. This evidence supports a tentative identification of the GeH_3−MoH species, but most of this reaction product continues to other species during relaxation of the laser-ablated Mo atom reaction product with germane.

$HGe{\equiv}MH_3$ (M = W, Mo). The new 1804.8, 1801.0 cm^{-1} 2:1 relative intensity pair of bands in the Mo experiment are slightly lower than a similar pair at 1806.2, 1802.1 cm^{-1} using silane[15] and a single band at 1830 cm^{-1} in the methane reaction.[10] These bands shifted to 1292.3 and 1284.0 cm^{-1}

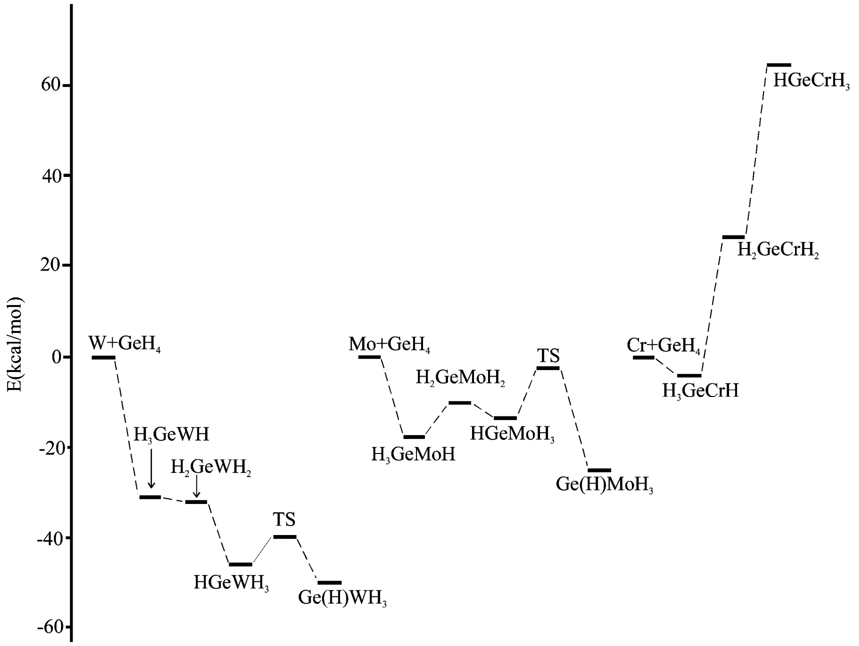

Figure 4. Energy profiles for group 6 metal atom and germane reaction products computed at the B3LYP level of theory.

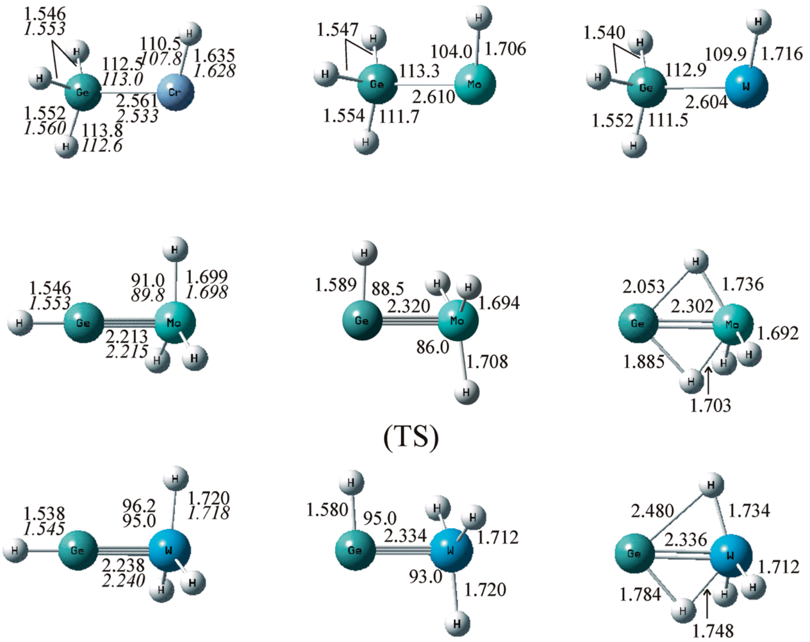

Figure 5. Optimized structures for products of group 6 metal and germane reaction. Parameters, bond lengths in angstroms, and angles in degrees, given for B3LYP, BPW91.

with deuterium substitution and gave 1.397 and 1.403 H/D isotopic frequency ratios. Neon matrix counterparts were observed at 1827.3 and 1822.5 cm^{-1} for the hydrogen species. Likewise, the 1894.0, 1887.5 cm^{-1} 1:2 relative intensity pair of bands in the W experiment are also lower than the corresponding 1894.9, 1887.8 cm^{-1} pair with silane and the 1907, 1896 cm^{-1} set from the methane reaction. The neon matrix counterparts at 1917.4, 1911.2 cm^{-1} shift on deuterium substitution into a single band at 1373.5 cm^{-1}, which gives 1.396 and 1.392 H/D ratios for the two modes. We note that the present new neon matrix bands are just 2−3 cm^{-1} below the values observed for MoH_4 and WH_4, respectively, with comparable H/D isotopic frequency ratios, 1.390 and 1.387, which verifies the observation of new Mo−H and W−H stretching modes.[14] Although the deuterium product is masked in solid argon with GeD_4, the mixed precursor has a window at the appropriate place, and we observe the strong deuterium counterpart at 1341 cm^{-1}, which gives the H/D frequency ratio 1.412. Furthermore, the 1894, 1890, 1888 cm^{-1} band profile shows that two or more H atoms are bonded to the W center.

Our calculations for harmonic symmetric and antisymmetric W−H stretching modes for HGe≡WH_3 (Table 2) find 1.413 and 1.407 H/D ratios, respectively, which support assignment of the two above bands to symmetric and antisymmetric W−H stretching modes as the symmetric mode involves less metal and more hydrogen motion for an obtuse angle between the equivalent W−H bonds.

Table 3. Calculated Fundamental Frequencies for the Bridged $Ge(H){=}MoH_3$ and $Ge(H){=}WH_3$ Germylidene Complexes[a]

	$Ge(H){=}MoH_3$		$Ge(H){=}WH_3$	
approximate description	calc	int	calc	int
M−H str, a′	1906	249	1966	124
M−H str, a″	1904	131	1960	213
M−H str, a′	1811	16	1902	150
M−(H) str, a′	1754	101	1717	10
(H)−Ge str, a′	1015	5	1219	11
MH_2 bend, a′	904	2	874	8
MH_2 rock, a″	833	90	860	34
MH_2 twist, a″	719	19	674	31
M−H def, a″	598	72	594	32
Ge−M str, a′	452	45	436	53
M−H def, a′	345	9	297	7
MH_2 tors, a″	337	21	264	8

[a] Ground states $^1A'$. Frequencies and intensities are in cm^{-1} and km/mol computed with B3LYP/6−311++G(3df,3pd) in the harmonic approximation using the SDD core potential and basis set for Mo and W. Symmetry notations are based on the C_s structure. Calculations with the BPW91 density functional gave similar frequencies.

The assignments to $HGe{\equiv}WH_3$ and $HGe{\equiv}MoH_3$ follow those for $HSi{\equiv}WH_3$ and $HSi{\equiv}MoH_3$ and are based on B3LYP harmonic frequency calculations.[15] For $HGe{\equiv}MoH_3$ we find a strong degenerate Mo−H antisymmetric mode at 1895 cm^{-1} and a half as strong Mo−H symmetric mode at 1891 cm^{-1} (Table 2), and we observe only two bands at 1804.8 and 1801.0 cm^{-1} with 2:1 relative intensity (frequencies overestimated by 5.0%). In addition the strong band is 25 cm^{-1} lower than the strong band for $HC{\equiv}MoH_3$ and the calculated value for $HGe{\equiv}MoH_3$ is 16 cm^{-1} lower than the calculated value for the methylidyne. However, the calculated value for the bridged species is only 5 cm^{-1} lower (Table 3), which is not as good agreement by 11 cm^{-1}, and the bridged species has an observable bridge bond stretching mode predicted 150 cm^{-1} lower, but this band is not observed. Hence, our 1804.8 and 1801.0 cm^{-1} bands are best assigned to the $HGe{\equiv}MoH_3$ germylidyne, which is separated from the lower energy bridged species by a 14 kcal/mol higher energy transition state.

For the $HGe{\equiv}WH_3$ molecule our calculation predicted a strong degenerate W−H antisymmetric mode at 1961 cm^{-1} and a half as-strong W−H symmetric mode at 1951 cm^{-1}, and the two predictions are in very good agreement with the 1894.0 and 1887.5 cm^{-1} experimental values (overestimated by 3.5% and 3.3%). The two bands are observed 13 and 8 cm^{-1} lower than the corresponding bands for $HC{\equiv}WH_3$, and our calculation predicts them 10 and 9 cm^{-1} lower. For the bridged species, the two higher modes are predicted to fall 5 and 0 cm^{-1} lower than for the methylidyne, and a comparable bridge bond stretching mode at 58 cm^{-1} lower. Hence, the two higher bands for the bridged species are not predicted as accurately as those for the germylidyne, but the clincher is the absence of the observable bridged stretching mode. The unobserved lower energy bridged species is separated from $HGe{\equiv}WH_3$ by an 11 kcal/mol higher energy transition state. The new peaks observed with the GeH_xD_{x-4} reagent are in agreement with our calculations for the $HGe{\equiv}MHD_2$ and $DGe{\equiv}MH_2D$ species, but these band positions are not sufficiently unique to rule out the bridged species in their own right.

We have also calculated (B3LYP) a triplet state butterfly-structured product $Ge(H)_2WH_2$, which has the same energy as singlet $HGe{\equiv}WH_3$, but the calculated W−H stretching frequencies 1800 cm^{-1} (287 km/mol) and 1968 cm^{-1} (102 km/mol) do not correlate with our observed germylidyne frequencies. In addition, the analogous triplet state butterfly-structured $Si(H)_2WH_2$ product is 1 kcal/mol higher in energy than singlet $HSi{\equiv}WH_3$. The calculated W−H stretching frequencies 1806 cm^{-1} (284 km/mol) and 1964 cm^{-1} (101 km/mol) for this butterfly structure do not match our observed silylidyne frequencies.[15]

Frequencies calculated with the BPW91 functional are slightly lower (Table S2, Supporting Information), and they correlate well with the B3LYP values, which substantiates the application of DFT to support vibrational assignments for these molecules.[27,28]

A close correlation between argon and neon matrix frequencies is expected as the less polarizable neon matrix host interacts less with the guest molecule than the more polarizable argon matrix,[29] and the 21−24 cm^{-1} differences (1.2%) observed here are appropriate for the vibration of metal hydrides with polar bonds.[14]

Reaction Mechanisms. The reaction of chromium, molybdenum, or tungsten atoms with GeH_4 gives the straightforward inserted metal hydride $GeH_3{-}MH$, which is trapped in the cold argon matrix for M = Cr, and some for M = Mo, but most continues further to $HGe{\equiv}MoH_3$ and with tungsten all goes to the lower energy $HGe{\equiv}WH_3$ final product. This is consistent with the product energy profile (Figure 4), which shows that the metal hydride is the only plausible product for chromium, one possibility for molybdenum, and most unlikely for tungsten. Remember that annealing increases the $HGe{\equiv}MoH_3$ and $HGe{\equiv}WH_3$ products,

$$M + GeH_4 \rightarrow GeH_3{-}MH \rightarrow GeH_2{=}MH_2 \rightarrow HGe{\equiv}MH_3 \tag{1}$$

which shows that reaction 1 is spontaneous for Mo and W atoms to give the final germylidyne product. Here, however, we are able to trap very little $GeH_3{-}MoH$ in solid argon and no $GeH_3{-}WH$, $GeH_2{=}MoH_2$, and $GeH_2{=}WH_2$ intermediates as the reaction goes on to the more stable final products.[30] We were not able to trap any $GeH_3{-}MoH$ in the more slowly condensing solid neon matrix at 4 K. In the silicon case, both $SiH_3{-}MoH$ and $HSi{\equiv}MoH_3$ are preserved as major products.[15] Finally, on the basis of reaction energies, $HGe{\equiv}WH_3$ is more stable than $HGe{\equiv}MoH_3$ as reaction 1 is 64 kcal/mol exothermic for W and 13 kcal/mol exothermic for Mo, computed at the B3LYP level of theory.

Structure and Bonding. The structures calculated for the three products of each group 6 metal atom reaction are collected in Figure 5. The three germyl metal hydrides have C_s structures comparable to those found for the methyl metal

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(27) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.
(28) Andersson, M. P.; Uvdal, P. L. *J. Phys. Chem. A* **2005**, *109*, 3937.
(29) Jacox, M. E. *Chem. Phys.* **1994**, *189*, 149.
(30) We would not be able to detect GeH_3-WH, even if it were trapped, as the two strongest infrared absorptions (Table S1) are likely to be masked by germane precursor and product bands.

hydrides,[10,11] and the silyl metal hydrides,[15] but of course, the Ge—M single bonds are longer than their silicon and carbon analogues. The calculated Ge—M single bond lengths range from 2.561 Å for Cr to 2.610 Å for Mo to 2.604 Å for the W compound, and they compare favorably to 2.590 Å and 2.681 Å values measured for Cr and W germylene complexes.[7] These open structures for germyl metal hydrides are in contrast to the butterfly hydrogen-bridged structure observed and calculated for Ge_2H_2.[31,32]

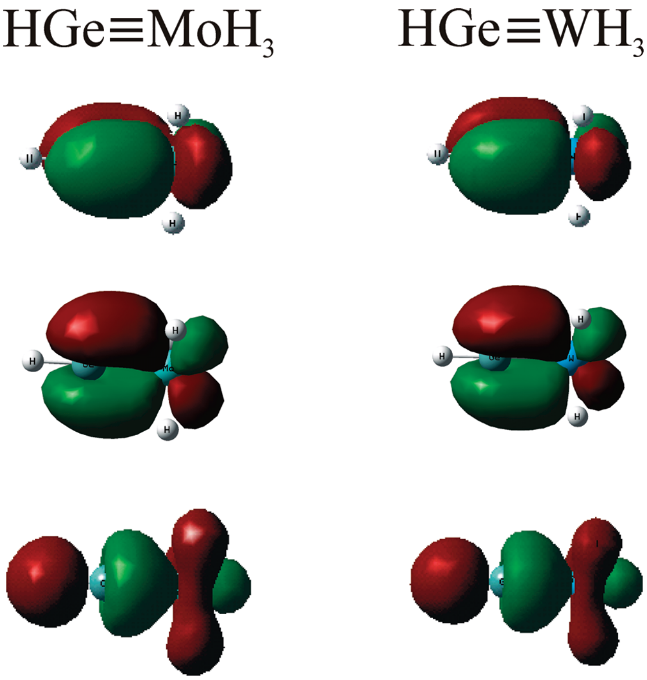
One of the most interesting comparisons with carbon is for the methylidene, silylidene,[15] and germylidene species. First, our computed Ge═Mo double-bond length 2.406 Å and Ge═W double-bond length 2.407 Å are near the median for the values computed for single bonds above and triple bonds below. Second, the computed GeH_2═MoH_2 and the GeH_2═WH_2 structures have a plane of symmetry, the two Ge—H bonds and the two M—H bonds are equivalent, and therefore no agostic distortion results. Agostic distortion was found for CH_2═MoH_2 at the B3LYP and even more at the CASPT2 level of theory[10,33] and for CH_2═WH_2 using CCSD.[11] It appears that the H bonded to Ge is too far away from the metal center for any interaction that can lead to distortion of these germylidene molecules. And third, notice that the dimensions for the three group 6 metal germylidenes are nearly the same.

Our calculated HGe≡MoH_3 and HGe≡WH_3 structures have C_{3v} symmetry, the same as their silicon and carbon analogues.[10−12,15] Our computed Ge≡Mo bond length of 2.213 Å may be compared to 2.271 Å and 2.318 Å values measured recently for germylyne complexes,[6,9] and our 2.238 Å Ge≡W computation may be considered with regard to 2.293 Å and 2.302 Å measurements for tungsten germylynes.[9] However, if our B3LYP calculation provides an accurate representation, the present simple trihydrido metal germylidyne complexes may have stronger triple bonds than the larger ligand stabilized complexes. Although we did not observe HGe≡CrH_3, our calculated bond length of 2.094 Å is also shorter than the 2.167 Å value reported for the Ge≡Cr bond in a representative organometallic complex.[7] Finally, our B3LYP calculated Ge≡M (M = Cr, Mo, W) triple bond lengths are 4, 3, and 2% shorter than these bond distances from the addition of tabulated triple bond covalent radii,[34] which is acceptable agreement considering the differences in these approaches.

Table 4. Natural Orbital Occupation Numbers for the HE≡MH_3 (E = C, Si, Ge, M = Mo, W) Molecules and the Resulting EBO[a]

molecule	σ	π	σ^*	π^*	EBO
HC≡MoH_3 (L)	1.96	3.94	0.07	0.04	2.89
HC≡MoH_3 (W)	1.96	3.97	0.07	0.04	2.90
HC≡WH_3 (L)	1.98	3.97	0.05	0.04	2.91
HC≡WH_3 (W)	1.98	3.95	0.05	0.04	2.92
HSi≡MoH_3 (L)	1.93	3.87	0.08	0.05	2.83
HSi≡MoH_3 (W)	1.92	3.90	0.09	0.04	2.84
HSi≡WH_3 (L)	1.96	3.88	0.04	0.04	2.88
HSi≡WH_3 (W)	1.95	3.91	0.05	0.04	2.89
HGe≡MoH_3 (L)	1.91	3.87	0.08	0.04	2.82
HGe≡MoH_3 (W)	1.90	3.90	0.09	0.04	2.83
HGe≡WH_3 (L)	1.94	3.88	0.05	0.04	2.87
HGe≡WH_3 (W)	1.93	3.91	0.06	0.04	2.87

[a] Values for π orbitals summed over both components. (L) denotes the B3LYP functional and (W) the BPW91 functional.



HGe≡MoH_3 HGe≡WH_3

Figure 6. Highest occupied molecular orbitals (HOMOs) for triple bonds in the HGe≡MoH_3 and HGe≡WH_3 molecules calculated with B3LYP/SDD/6−311++G(3df,3pd). Isoelectronic density level is 0.03 e/au^3.

The effective bond orders (EBOs) can be calculated from the orbital occupancies, namely total bonding minus total antibonding divided by two. The occupancies and EBOs are compared in Table 4 for methylidynes, silylidynes, and germylidynes of Mo and W. Notice that the EBO decreases more from C to Si than from Si to Ge, as the larger valence orbitals are less effective at bonding, and that the EBOs are slightly higher for W than corresponding Mo species. All are effectively triple bonds. The bonding sigma and pi molecular orbitals illustrated in Figure 6 for HGe≡MoH_3 and HGe≡WH_3 are almost the same to the eye. They may be compared to the analogous molecular orbitals for the silylidynes,[15] which are slightly more compact as expected.

It is also significant that the germylidynes HGe≡MH_3 are polarized similarly to the silylidynes and quite differently from the methylidynes.[15] Natural charges are compared in Table S3, Supporting Information. This polarization affects the Ge—H bond and reduces the s character (40.7%) with the balance (59.3%) in the sigma Ge—W bond whereas the C—H bond has more s character (45.3%) with the remainder (54.5%) in the sigma C—W bond. In these molecules the pi bonds are valence *n*p-tungsten 5d, as summarized in Table S2, Supporting Information.

It is also interesting to compare the product energy profile for methane reactions[11] with the products from germane (Figure 4). The chromium insertion product is the global minimum energy species for both reactions. With molybde-

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(31) Palagyi, Z.; Schaefer, H. F., III; Kapuy, E. *J. Am. Chem. Soc.* **1993**, *115*, 6901.

(32) Ricca, A.; Bauschlicher, C. W., Jr *J. Phys. Chem. A* **1999**, *103*, 11121.

(33) Roos, B. O.; Lindh, R. H.; Cho, H.-G.; Andrews, L. *J. Phys. Chem. A* **2007**, *111*, 6420; (theoretical study of CH_2═MH_2 complexes)

(34) Pyykkö, P.; Riedel, S.; Patzschke, M. *Chem.—Eur. J.* **2005**, *11*, 3511; (triple bond covalent radii)

num, all products are closer in energy but the insertion product is lowest for methane and germane (except for the bridged species). With tungsten, the strength of the W−H bond contributes to promote maximum hydrogen transfer and make the triple bonded species the global minimum for both precursors (again except for the bridged species).

Conclusions

Reactions of laser ablated chromium, molybdenum, and tungsten atoms with germane during condensation in excess argon start with the $GeH_3{-}MH$ insertion product, which is trapped for Cr, some for Mo, but most continues to $HGe{\equiv}MoH_3$, and all is believed to rearrange to lower energy $HGe{\equiv}WH_3$ for W. The subject molecules were isolated in solid argon and neon and identified by isotopic shifts and DFT frequency and structure calculations. The intermediate $GeH_2{=}MoH_2$ and the $GeH_2{=}WH_2$ structures have a plane of symmetry, and therefore no agostic distortion. The simple $HGe{\equiv}MoH_3$ and $HGe{\equiv}WH_3$ molecules contain fully developed triple bonds with effective bond orders of 2.82 and 2.87 using the B3LYP density functional, which are slightly lower than their silicon and carbon analogues. Finally, our calculated triple bond lengths for these simple Mo and W trihydride germylidyne complexes are 0.05 to 0.10 Å shorter than those measured for larger ligand-stabilized organometallic complexes.

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Supporting Information Available: Tables S1, S2, and S3 comparing calculated frequencies and molecular properties and Figure S1 of neon matrix spectra for the chromium reaction with germane. This material is available free of charge via the Internet at http://pubs.acs.org.

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