Matrix Infrared Spectra and Quantum Chemical Calculations of Ti, Zr, and Hf Dihydride Phosphinidene and Arsinidene Molecules

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FREQUENCIES IN cm^{-1} and INTENSITIES (km/mol) CALCULATED BY THE B3LYP FUNCTIONAL FOR THE SINGLET MH2=EH, **mp,** and TRIPLET MH-EH2,**i,** REACTION PRODUCTS FOR GROUP 4 METALS AND E=N, P, and As.

TiH2=NH(S): 3570.2(100), 1689.3 (254), 1654.4 (485), 1021.1 (203), 630.4 (83), 540.3 (239), 498.8 (1), 418.0 (142), 393.7 (136).

TiH-NH2(T): 3580.6 (21), 3483.7 (20), 1571.8 (432), 1535.4 (36), 663.1 (184), 495.4 (143), 480.2 (36), 353.2 (14), 328.8 (49).

TiH2=PH(S): 2078.8 (5), 1691.3 (321), 1671.1 (379), 847.3 (28), 676.0 (103), 503.0 (24), 477.5 (65), 319.9 (134), 261.8 (11).
TiD2=PD(S): 1491.9 (3), 1204.1 (169), 1200.4 (196), 610.4 (11), 552.2 (62), 431.3 (18), 348.0 (30), 233.7 (74), 187.6 (4).

TiH-PH2(T): 2353.1 (26), 2298.8 (46), 1582.5 (429), 1025.7 (15), 445.2 (73), 335.4 (13), 268.8 (51), 232.3 (2), 132.8 (28).

TiH-AsH2(T): 2129.3 (64), 2061.5 (89), 1582.8 (444), 972.7 (17), 402.5 (65), 273.2 (1), 200.3 (25), 109.3 (27), 61.7 (76).

TiH2=AsH(S): 1912.2 (19), 1692.7 (342), 1674.5 (346), 846.8 (33), 657.1 (97), 461.2 (60), 406.7 (7), 321.6 (71), 166.9 (14)

ZrH2-AsH(S): 1866.5 (23), 1659.8 (300), 1633.7 (385), 844.2 (31), 623.9 (116), 481.1 (44), 384.7 (124), 306.0 (12), 233.4 (6).

ZrH2-PH(S): 2066.2 (9), 1657.6 (284), 1631.6 (408), 831.8 (25), 633.2 (119), 492.3 (36), 458.9 (50), 351.2 (99), 272.9 (7).

ZrH-AsH2(T): 2026.1 (36), 1857.4 (34), 1599.9 (409), 969.6 (22), 493.3 (8), 357.7 (50), 317.4 (18), 191.5 (4), 144.8 (11).

ZrH-PH2(T): 2338.5 (20), 2253.8 (29), 1608.6 (404), 1068.2 (14), 453.1 (35), 327.2 (11), 216.3 (22), 175.2 (29), 124.0 (13).

HfH2-AsH(S): 1892.2 (29), 1711.4 (255), 1683.0 (316), 814.4 (31), 653.2 (95), 503.3 (35), 384.8 (119), 281.2 (3), 228.9 (6).

HfH2-PH(S): 2084.0 (13), 1710.1 (234), 1682.9 (335), 803.2 (26), 664.7 (91), 520.5 (29), 441.5 (56), 369.8 (74), 255.2 (7).

HfH-AsH2(T): 1778.9 (24), 1759.7 (13), 1635.4 (441), 975.8 (34), 647.8 (0), 552.4 (10), 311.4 (50), 239.1 (19), 200.2 (2).
HfH-PH2(T): 2337.8 (20), 2272.8 (24), 1650.3 (360), 1069.3 (13), 450.2 (17), 321.0 (12), 225.0 (20), 170.9 (8), 147.4 (15).

FREQUENCIES IN cm^{-1} and INTENSITIES (km/mol) CALCULATED BY THE B3LYP FUNCTIONAL

FOR THE NONAGOSTIC SINGLET H-P=TiH2 MOLECULE OPTIMIZED WITH THE

Ti-P-H ANGLE FIXED TO 170.0 DEGREES [structure given in Figure S1].

HP=TiH2: 2453.1 (0.3), 1697.7 (425), 1673.3 (350), 635.8 (169) [TiH2 bending, Ti-P-H bending],

519.1 (40), 366.8 (169), 351.4 (183), 168.2 (14), -188.0 (26) [P-H bending mode].

BPW91 calculations have been done for comparison. The agostic angles of HN=TiH2, HP=TiH2, and HAs=TiH2 are 173.1, 60.4, and 56.3 degrees. Below are the BPW91 frequencies in cm^{-1}
and intensities (km/mol) for HP=TiH2 and HAs=TiH2.

HP=TiH2: 1964.2 (2), 1642.3 (239), 1626.2 (301), 950.5 (18), 653.3 (115), 505.6 (63), 485.6 (28),
349.2 (109), 299.3 (13).

HAs=TiH2: 1718.8 (11), 1638.0 (247), 1624.5 (285), 967.7 (21), 635.5 (114), 489.0 (67), 399.4 (87), 328.9 (59), 260.7 (4).

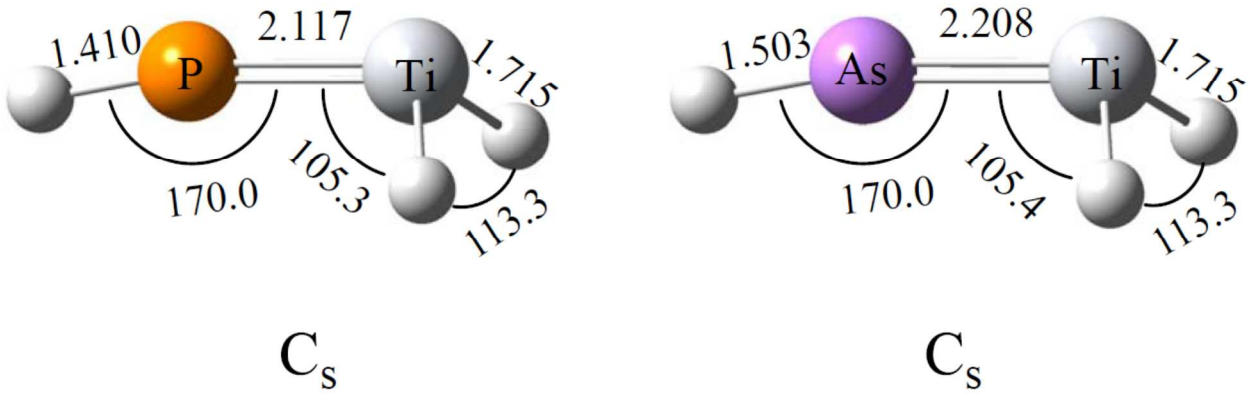

Figure S1. Structures computed for the fixed obtuse agostic angle isomers of $HP{=}TiH_2$ and $HAs{=}TiH_2$.

Table S1: Parameters from Natural Bond Order Analysis for the E-M Bond of the H_2E-MH Products[a]

Product	r(E-M)	Occupancy	Bond Order	% E	% M
H_2N-TiH	1.919	σ (0.999), σ* (0.004) α π (0.999), π* (0.000) α σ (0.999), σ* (0.004) β	1.495	86.12 [s (40.66), p (59.32)] 88.00 [s (0.00), p (99.93)] 87.94 [s (42.16), p (57.82)]	13.88 [s (25.72), p (6.17), d (68.04)] 12.00 [s (0.00), p (10.36), d (89.53)] 12.06 [s (17.44), p (6.71), d (75.77)]
H_2N-ZrH	2.209	σ (0.999), σ *(0.006) α π (0.999), π* (0.001) α σ (0.999), σ *(0.006) β	1.492	86.86 [s (40.49), p (59.48)] 88.77 [s (0.38), p (99.55)] 87.87 [s (40.56), p (59.41)]	31.47 [s (17.04), p (2.22), d (80.37)] 11.23 [s (0.11), p (6.37), d (93.18)] 12.13 [s (16.24), p (2.39), d (80.97)]
H_2N-HfH	2.005	σ (0.999), σ *(0.005) α π (0.999), π* (0.001) α σ (0.999), σ* (0.006) β	1.493	87.47 [s (41.03), p (59.94)] 89.65 [s (0.87), p (99.07)] 87.99 [s (41.90), p (58.07)]	12.53 [s (14.46), p (2.74), d (82.48)] 10.35 [s (0.26), p (8.19), d (91.20)] 12.01 [s (20.56), p (3.07), d (76.05)]
H_2P-TiH	2.507	σ (0.997), σ* (0.003) α π (0.997), π* (0.003) β	0.994	72.67 [s (8.33), p (91.35)] 80.18 [s (13.03), p (86.71)]	27.33 [s (42.31), p (7.27), d (50.25)] 19.82 [s (38.17), p (11.27), d (50.37)]
H_2P-ZrH	2.597	σ (0.997), σ* (0.003) α σ (0.997), σ* (0.003) β	0.994	74.14 [s (10.25), p (89.43)] 77.78 [s (12.20), p (87.53)]	25.86 [s (28.21), p (4.23), d (67.27)] 22.22 [s (31.99), p (5.25), d (62.46)]
H_2P-HfH	2.581	σ (0.996), σ* (0.005) α σ (0.995), σ* (0.007) β	0.990	76.34 [s (12.44), p (86.76)] 76.76 [s (12.10), p (87.25)]	23.66 [s (20.47), p (6.87), d (72.56)] 23.24 [s (38.79), p (7.32), d (53.82)]
H_2As-TiH	2.603	σ (0.996), σ* (0.003) α σ (0.995), σ* (0.004) β	0.992	71.70 [s (6.85), p (92.96)] 79.85 [s (11.18), p (88.66)]	28.30 [s (45.18), p (8.69), d (46.04)] 20.15 [s (40.00), p (13.29), d (46.61)]
H_2As-ZrH	2.629	σ (0.996), σ* (0.003) α σ (0.995), σ* (0.003) β	0.993	74.00 [s (9.71), p (89.73)] 78.01 [s (12.09), p (87.41)]	26.00 [s (29.67), p (7.58), d (62.66)] 21.99 [s (24.25), p (8.17), d (67.48)]
H_2As-HfH	2.572	σ (0.996), σ* (0.002) α π (0.996), π* (0.002) β	0.994	74.28 [s (12.23), p (87.11)] 76.34 [s (12.06), p (87.44)]	25.72 [s (17.43), p (8.26), d (74.23)] 23.66 [s (29.82), p (7.17), d (62.94)]

[a] Computed with B3LYP/aug-cc-pVTZ. Bond order = [occ – occ*]/2.

Table S2: Parameters from Natural Bond Order Analysis for the E-M Bond of the HE=MH_2 Products[a]

Product	r(E-M)	Occupancy	Bond Order	% E	% M
HN=TiH_2	1.663	σ (1.982), σ* (0.042) π (1.991), π* (0.012) π (1.977), π* (0.035)	2.975	77.32 [s (55.49), p (44.49)] 73.06 [s (2.87), p (97.07)] 74.97 [s (0.00), p (99.93)]	22.68 [s (17.97), p (5.46), d (76.50)] 26.94 [s (0.10), p (4.75), d (95.06)] 25.13 [s (0.00), p (5.34), d (94.58)]
HN=ZrH_2	1.799	σ (1.987), σ *(0.043) π (1.995), π* (0.008) π (1.989), π* (0.017)	2.952	79.67 [s (53.42), p (46.54)] 78.08 [s (4.73), p (95.20)] 79.13 [s (0.00), p (99.93)]	20.33 [s (17.96), p (1.44), d (80.29)] 21.92 [s (0.14), p (3.35), d (96.22)] 20.87 [s (0.00), p (3.01), d (96.68)]
HN=HfH_2	1.791	σ (1.994), σ *(0.028) π (1.995), π* (0.008) π (1.988), π* (0.020)	2.961	81.51 [s (58.86), p (41.11)] 78.14 [s (0.07), p (99.88)] 80.90 [s (0.00), p (99.94)]	18.49 [s (19.45), p (3.08), d (77.27)] 21.86 [s (0.57), p (2.96), d (96.22)] 19.10 [s (0.00), p (4.37), d (95.37)]
HP=TiH_2	2.176	σ (1.995), σ* (0.004) π (1.960), π* (0.038)	1.957	60.55 [s (1.99), p (97.70)] 58.14 [s (11.64), p (87.59)]	39.45 [s (1.72), p (10.50), d (87.46)] 41.86 [s (22.67), p (3.77), d (73.32)]
HP=ZrH_2	2.323	σ (1.995), σ* (0.004) π (1.981), π* (0.026)	1.973	64.91 [s (2.25), p (97.20)] 62.78 [s (12.18), p (87.11)]	35.09 [s (1.50), p (8.08), d (90.30)] 37.22 [s (24.88), p (1.41), d (73.63)]
HP=HfH_2	2.318	σ (1.994), σ* (0.005) π (1.992), π* (0.015)	1.982	62.66 [s (2.95), p (96.52)] 67.81 [s (12.24), p (86.98)]	37.34 [s (2.59), p (11.16), d (86.13)] 32.19 [s (28.95), p (1.49), d (69.50)]
HAs=TiH_2	2.285	σ (1.991), σ* (0.006) π (1.955), π* (0.037)	1.952	59.73 [s (1.26), p (98.63)] 57.22 [s (10.84), p (89.03)]	40.27 [s (1.15), p (11.15), d (87.4)] 42.78 [s (24.79), p (4.51), d (70.38)]
HAs=ZrH_2	2.431	σ (1.993), σ* (0.005) π (1.980), π* (0.022)	1.973	63.93 [s (1.71), p (98.09)] 61.66 [s (10.93), p (88.93)]	36.07 [s (1.27), p (8.88), d (89.56)] 38.34 [s (27.06), p (2.06), d (70.77)]
HAs=HfH_2	2.427	σ (1.993), σ* (0.005) π (1.991), π* (0.012)	1.984	67.20 [s (2.61), p (97.06)] 61.20 [s (10.32), p (89.16)]	32.80 [s (2.75), p (12.50), d (84.63)] 38.80 [s (30.39), p (2.10), d (67.45)]

[a] Computed with B3LYP/aug-cc-pVTZ. Bond order = [occ – occ*]/2.Bond lengths in .