Supplementary material for: Thompson, M. G. K., Walker, S. W. C., and Parnis, J. M.

"*Identification and reactivity of allylvanadium hydride*"

Item listing:

The figures that are presented in this supplementary material focus on the significant regions of infrared absorption for the allylvanadium hydride species.   These have been given in the form of difference spectra, using the original spectra provided in Figure 1 of the main document.   These additional spectra are provided to give greater detail than in the original figures, for clarity.
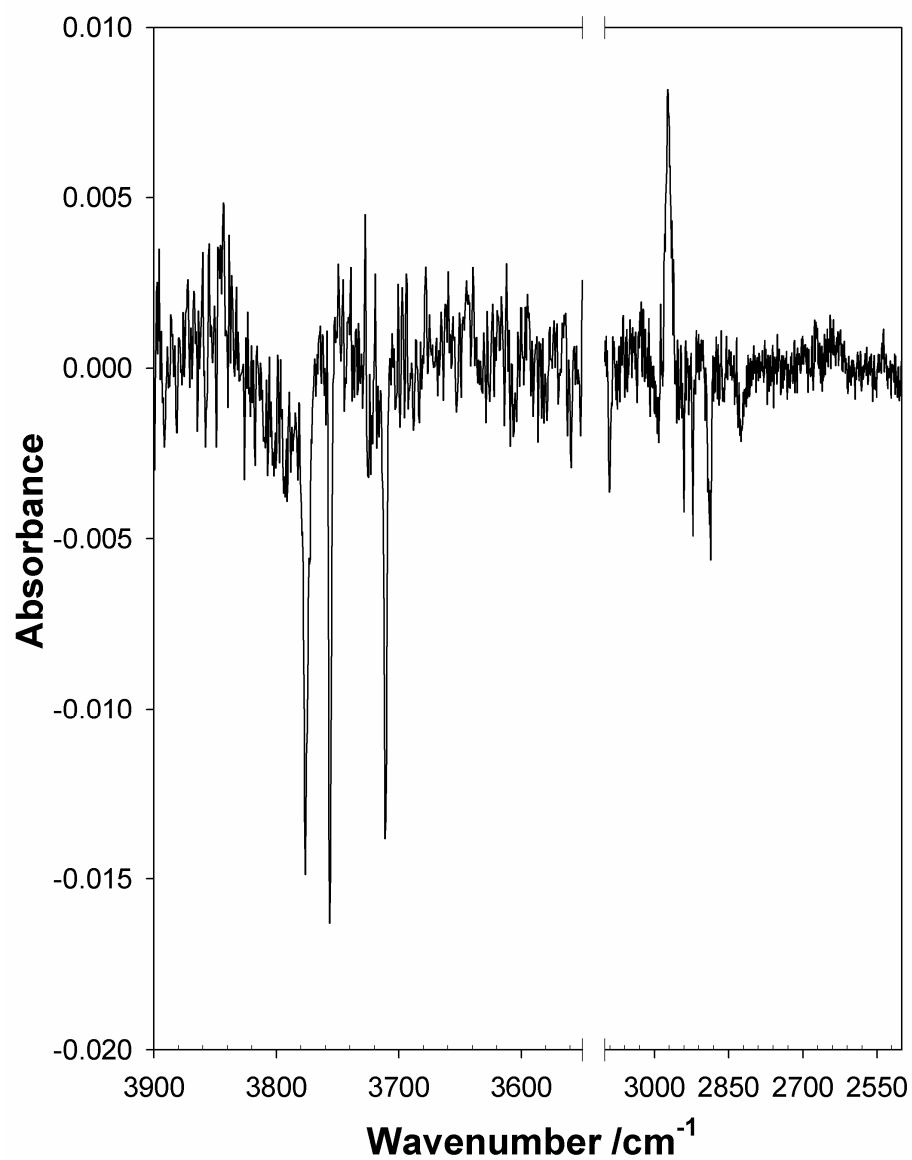
Figure S1: Portions of the difference infrared spectrum in the O-H and C-H region for V atoms reacting with 1 to 1000 propene to Ar under matrix isolation conditions. Exact wavenumber positions for major product absorptions are given in Table 1.

Figure S2: Portions of the difference infrared spectrum in selected hydrocarbon absorption regions for V atoms reacting with 1 to 1000 propane to Ar under matrix isolation conditions. Exact wavenumber positions for major product absorptions are given in Table 1.

Figure S3: Portion of the difference infrared spectrum for V atoms reacting with 1 to 1000 propene to Ar under matrix isolation conditions. Exact wavenumber positions for major product absorptions are given in Table 1.
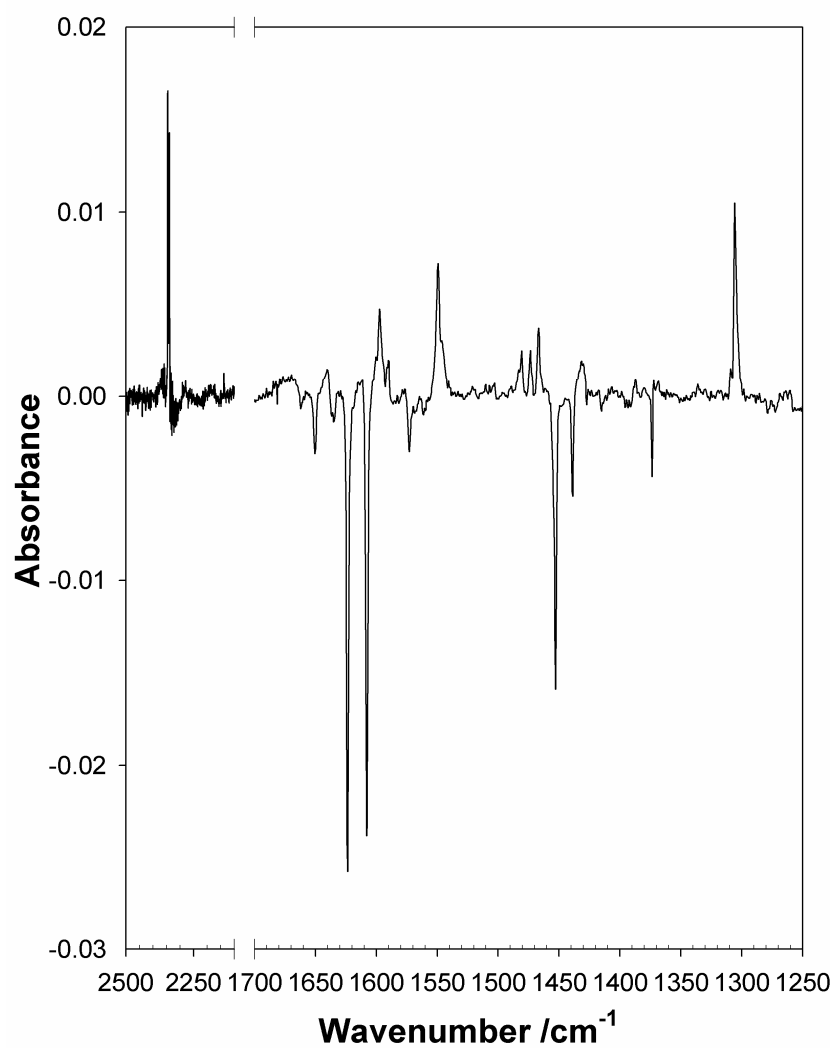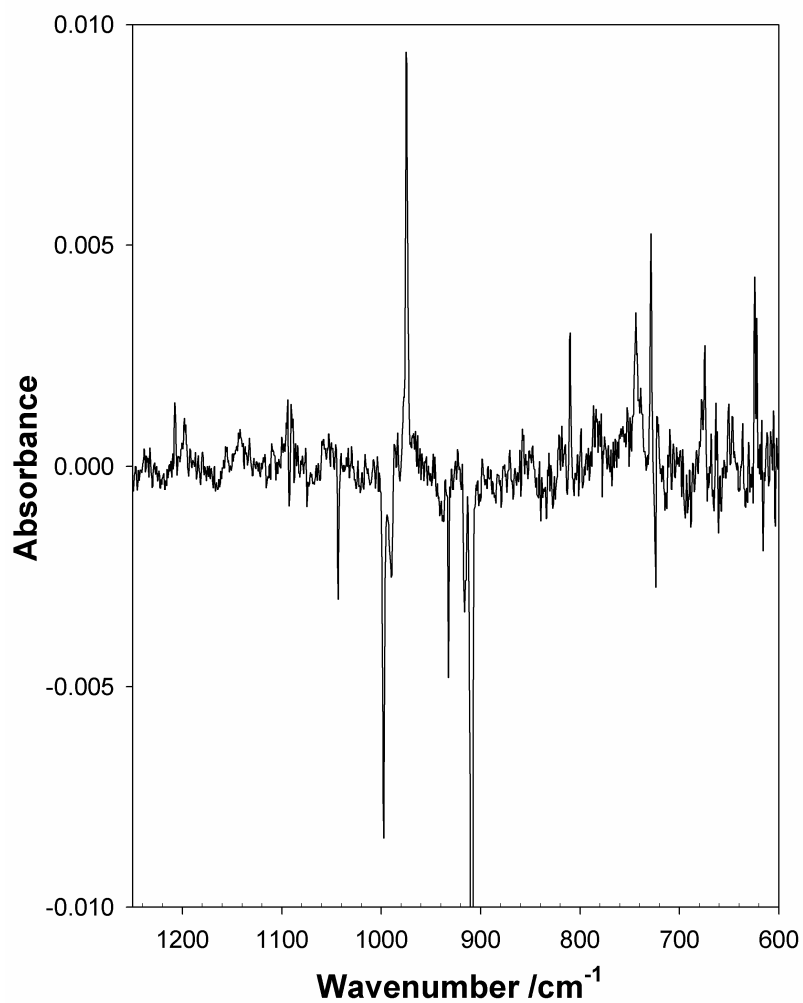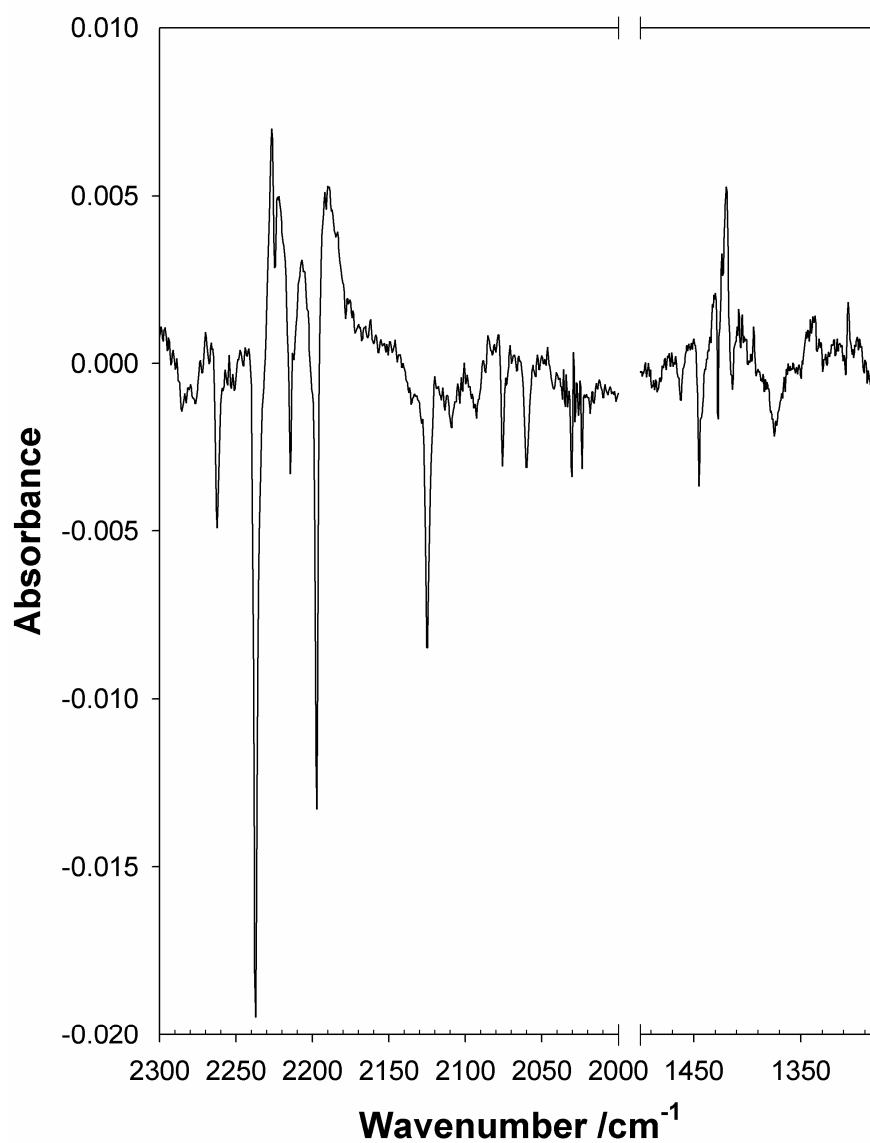
Figure S4: Portions of the difference infrared spectrum obtained for the reaction of V atoms with 1 to 1000 d_6-propene to Ar. Exact wavenumber positions for major product absorptions are given in Table 1.

Figure S5: Portions of the difference infrared spectrum showing major product absorptions for the reaction of V atoms with 1 to 1000 d_6-propene to Ar. Exact wavenumber positions for major product absorptions are given in Table 1.

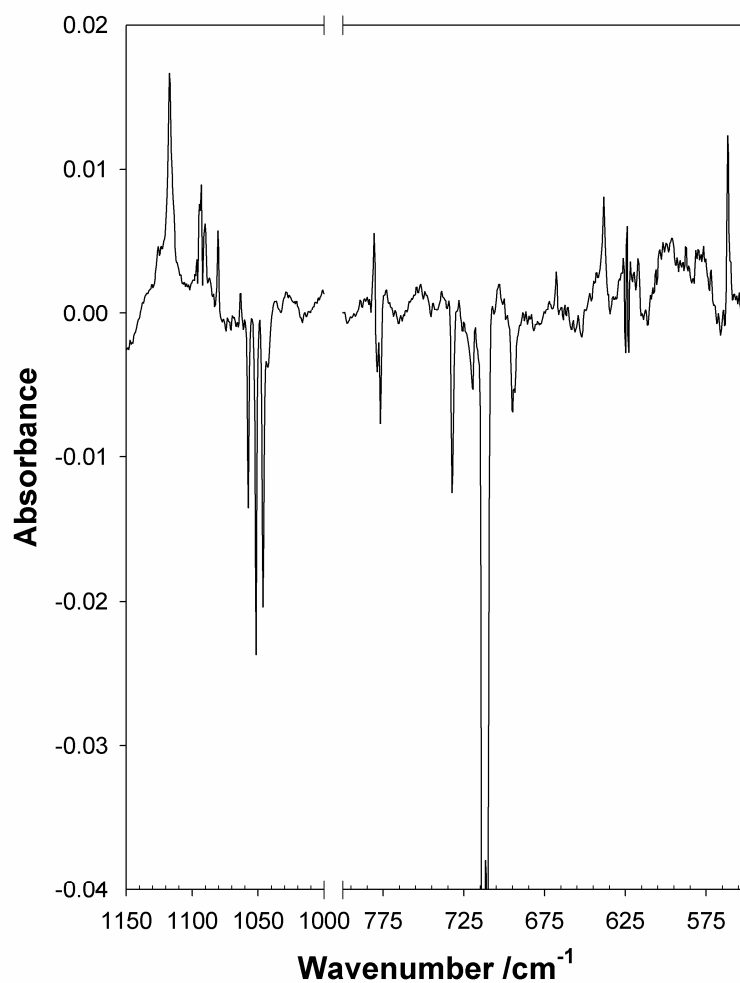From the main results, the observed features corresponding to species A have been compared with calculated frequencies for both a doublet and quartet H-V-allyl species. Of these two, only the doublet insertion species provides a good match for the calculated wavenumber values (see main paper). This conclusion is based on the matching of the observed and calculated relative intensity patterns as well as a comparison of the ratio of the observed and calculated wavenumber values to typical correction factors for harmonically approximated wavenumber positions for the method and basis set that has been used. The comparison of the experimental data with the isotopomers of the quartet structure is given here.

Table S1: Comparison of the predicted wavenumber values (unscaled) for isotopomers of quartet (η^3-allyl) vanadium hydride

quartet - HV(η^3-CH$_2$CHCH$_2$)			quartet - DV(η^3-CD$_2$CDCD$_2$)			quartet - DV(η^3-CD$_2$CHCH$_2$)		
6-311G(3df,3pd)	Rel.Int	Expt	6-311G(3df,3pd)	Rel.Int	Expt	6-311G(3df,3pd)	Rel.Int	Expt
94.6	0.52		72.1	0.58		72.7	0.60	
266.4	0.30		194.7	0.30		196.6	0.32	
341.2	0.06		290.5	0.06		318.2	0.05	
358.2	0.15		324.7	0.09		329.0	0.07	
372.6	0.01		338.0	0.00		359.5	0.01	
458.0	0.03		366.5	0.04		402.6	0.04	
613.6	0.07		439.4	0.07		512.8	0.07	
738.2	0.01	624.1	584.6	0.01		612.5	0.24	576.7
786.8	0.20	728.7	603.7	0.24	561.7	721.6	0.02	
863.5	0.12	810.1	673.3	0.18		792.6	0.01	
934.4	0.00		692.0	0.00		827.1	0.32	772.9
1019.9	0.04	974.5	814.1	0.00		947.3	0.01	
1033.8	0.00		859.7	0.02		1009.4	0.06	
1246.7	0.00		936.6	0.04		1082.1	0.01	
1253.2	0.07	1207.5	1028.4	0.00		1108.2	1.00	1117.6
1427.1	0.00		1069.1	0.01		1239.1	0.04	
1501.3	0.02		1108.0	1.00	1117.2	1262.4	0.15	
1548.3	0.16	1480.9	1254.4	0.03		1457.8	0.05	
1552.0	1.00	1549.2	1463.0	0.47	1406.6	1533.2	0.29	1475.9
3086.3	0.00		2248.2	0.02		2249.7	0.02	
3089.2	0.01		2249.2	0.02		2377.0	0.00	
3119.7	0.01		2303.6	0.01		3087.8	0.01	
3200.0	0.01		2376.8	0.00		3120.7	0.03	
3201.1	0.01		2378.6	0.01		3200.5	0.02	

To support the proposed mechanism accounting for the observed product distribution (See Scheme 1, in the discussion section of the main paper), we have undertaken preliminary calculations on potential structures of a VC_2 species. An isomer of this molecular formula is believed to be generated following the reactivity of H-V(η^3-allyl) with an additional propene unit, to form propane.

Several stable molecules are predicted for this molecular formula, and the two most stable molecules (the quartet (most stable), and doublet (+67 kJ.mol^{-1}, relative to the quartet) states of cyclic-VC_2) are predicted to each have one IR-active mode with significant intensity in the IR-range studied in the current work. However, comparing the predicted intensity for the expected VC_2 modes with the strongest predicted mode for the directly observed allyl complex (the V-H stretch) suggests that, at maximum, the VC_2 species would have ~15% of the absorption intensity. Since the final VC_2 product is not necessarily the sole organometallic product resulting from reactivity of the allyl species, the final VC_2 product may not contain 100% of the available V atoms, therefore leading to lower intensity for resulting VC_2 absorptions. Furthermore, the noise in the 500-600 cm^{-1} region is relatively high, and there is generally spectral broadening in this spectral range, suggesting that all of these factors may account for the low observed intensity. Related experiments which involve another spectroscopic technique such as UV-Visible spectroscopy could clarify the presence of such a species.

Table S2: B3LYP/6-311(3df,3pd) predicted values (unscaled) for isomers of doublet and quartet VC_2.

doublet		quartet		quartet		doublet		quartet	
linear C-V-C		linear C-V-C		bent C-V-C		cyclic VCC		cyclic VCC	
wavenumber (cm^{-1})	intensity	wavenumber (cm^{-1})	intensity	wavenumber (cm^{-1})	intensity	wavenumber (cm^{-1})	intensity	wavenumber (cm^{-1})	intensity
742.0	1.4	195.8	84.7	277.1	0.0	211.6	8.9	337.6	6.6
763.6	11.5	195.8	84.7	577.7	18.3	610.5	92.6	582.7	91.2
812.7	3.3	359.6	65.6	740.0	1.9	1618.3	3.1	1679.8	7.9
862.6	0.0	759.4	0.0						
CV bond length (Å)	1.639	CV bond length (Å)	1.693	CV bond length (Å)	1.727	CV bond length (Å)	1.875	CV bond length (Å)	1.916
				CVC bond angle	103.7	CC bond length (Å)	1.299	CC bond length (Å)	1.289
						CVC angle	40.54	CVC angle	39.31
						VCC angle	69.76	VCC angle	70.33
Raw Energy (hartrees)	-1019.798746	Raw Energy (hartrees)	-1019.835241	Raw Energy (hartrees)	-1019.838901	Raw Energy (hartrees)	-1020.0032	Raw Energy (hartrees)	-1020.0287
Relative Energy (kJ.mol^{-1})	603.92	Relative Energy (kJ.mol^{-1})	508.08	Relative Energy (kJ.mol^{-1})	498.47	Relative Energy (kJ.mol^{-1})	67.14	Relative Energy (kJ.mol^{-1})	0.00