

Photochemical Activation of Ethene C–H Bonds of $(\eta^5\text{-C}_5\text{H}_5)\text{Ir}(\text{C}_2\text{H}_4)_2$ in Low-temperature Matrices and in Solution

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A series of vinyl hydride complexes, $\text{cpIr}(\text{L})(\eta^1\text{-C}_2\text{H}_3)\text{H}$ ($\text{cp} = \eta^5\text{-C}_5\text{H}_5$), have been characterised on photolysis of $\text{cpIr}(\text{C}_2\text{H}_4)_2$ by i.r. spectroscopy in low-temperature matrices ($\text{L} = \text{C}_2\text{H}_4, \text{CO}$) and by n.m.r. spectroscopy in solution ($\text{L} = \text{C}_2\text{H}_4, \text{PPh}_3, \text{Me}_2\text{SO}$); $\text{cpIr}(\text{C}_2\text{H}_4)(\eta^1\text{-C}_2\text{H}_3)\text{H}$ undergoes secondary photolysis in matrices to form the vinylidene complex, $\text{cpIr}(\text{C}=\text{CH}_2)(\text{H})_2$.

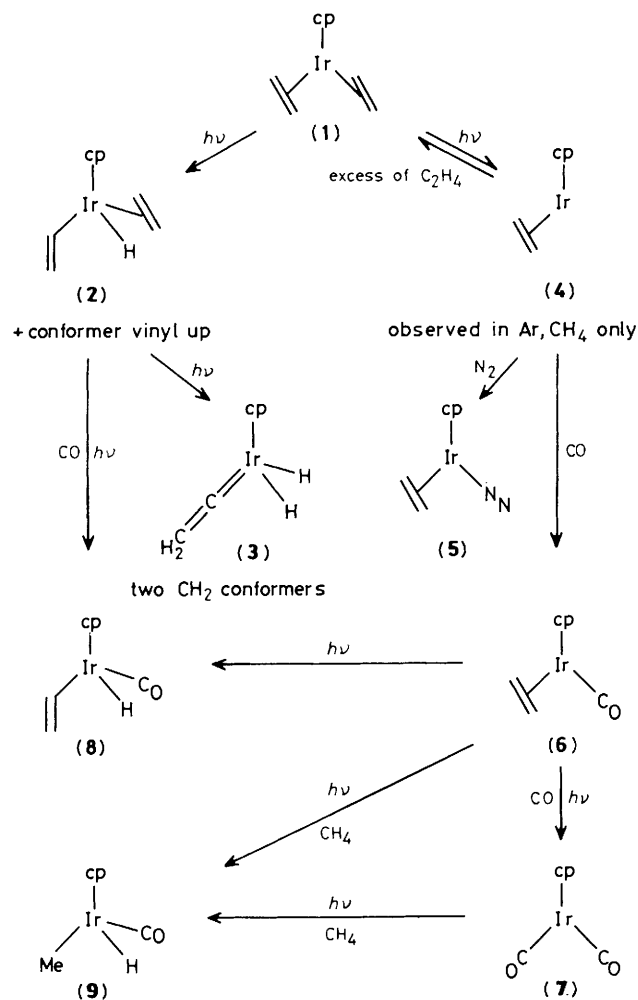
Following our demonstration of the photodissociation of ethene from $\text{cpRh}(\text{C}_2\text{H}_4)_2$ and $\text{cpRh}(\text{C}_2\text{H}_4)\text{CO}$ ($\text{cp} = \eta^5\text{-C}_5\text{H}_5$),¹ we now report the contrasting photochemical conversions of the iridium analogue, $\text{cpIr}(\text{C}_2\text{H}_4)_2$, (**1**), into vinyl hydride complexes (Scheme 1). Until 1985, insertions into ethene C–H bonds to form vinyl hydrides² or vinylidene dihydrides³ were confined to dinuclear and polynuclear complexes. However, last year witnessed the reversible photoisomerisation of hydrogen-bonded $\text{Fe}(\text{C}_2\text{H}_4)$ to $\text{HFe}(\text{C}_2\text{H}_3)$,⁴ and the reaction of an iridium complex with ethene yielding both a π -complex and a vinyl hydride ($\eta^5\text{-C}_5\text{Me}_5$) $\text{Ir}(\text{PMe}_3)(\eta^1\text{-C}_2\text{H}_3)\text{H}$;⁵ the latter is converted into the π -complex on thermolysis.^{5,6} Meanwhile, evidence for vinylic activation of alkenes in catalytic processes has accumulated.⁷

The i.r. spectrum of (**1**)⁸ isolated in an Ar matrix at high dilution at 20 K shows that it is essentially transparent in the 2800–1450 cm^{-1} region. Irradiation† ($\lambda > 290 \text{ nm}$) causes growth of product bands at 2184, 1680, 1576, and 1379 cm^{-1} [Figure 1(a),(b)] together with further bands at lower frequency.‡ At this stage there is slight release of C_2H_4 (1438, 952 cm^{-1} , Figure 1). Selective photolysis (most effectively with $\lambda = 308 \text{ nm}$, XeCl laser) differentiates two groups of bands: the 1680 cm^{-1} feature and the bands of C_2H_4 continue to grow whereas those at 1576 and 1379 cm^{-1} soon decrease [Figure 1(c),(d)]. Meanwhile, loss of (**1**) continues; indeed we have been unable to effect a decrease in C_2H_4 or increase in (**1**) (cf. Rh experiments).¹ We assign the primary photoproduct as the vinyl hydride isomer of (**1**), $\text{cpIr}(\text{C}_2\text{H}_4)(\eta^1\text{-C}_2\text{H}_3)\text{H}$, (**2**) with bands at 2184, 1576, and 1379 cm^{-1} and the secondary product as the vinylidene complex, $\text{cpIr}(\text{C}=\text{CH}_2)(\text{H})_2$, (**3**) with bands at 2184 and 1680 cm^{-1} . These assignments account for the positions and intensities of the bands of Figure 1§ whereas other possible products such as alkyne complexes or metallocyclopentanes could not.

According to this postulate both (**2**) and (**3**) are 18-electron complexes which should be little affected by excess of C_2H_4 , whereas any 16e complexes should react.¹⁰ Production of (**2**)

and (**3**) was unaffected by doping the matrix with C_2H_4 (10%), but four product bands below 1300 cm^{-1} were reduced substantially. We assign these bands‡ to a second primary product $\text{cpIr}(\text{C}_2\text{H}_4)$, (**4**), the analogue of the only Rh photoproduct.¹

On photolysis of $\text{cpIr}(\text{C}_2\text{D}_4)_2$, [$^2\text{H}_8$] (**1**), in solid Ar [Figure 1(e)], we observe product bands at 1512 and 1660 cm^{-1} with the growth behaviour of (**2**) and (**3**) respectively. These shifts are consistent with $\nu(\text{C}=\text{C})$ modes;§ a weaker band at 1572



Scheme 1

† Complex (**1**) is white with u.v. absorptions at 202, 234 (sh), and 261 (sh) nm.

‡ I.r. bands in Ar matrices at 20 K (cm^{-1}). Bands marked with an asterisk overlap with those of (**1**) or [$^2\text{H}_8$](**1**). (**2**): 2216 sh, 2200 sh, 2184 [$\nu(\text{IrH})$], 1579 [$\nu(\text{CC vinyl})$], 1573 [$\nu(\text{CC vinyl})$], 1378 [$\delta(\text{CH}_2 \text{ vinyl})$], 1266 [$\delta(\text{CH}_2) + \nu(\text{CC ethene})$], 1190, 1002, [$\delta(\text{CH}_2 \text{ vinyl})$], 865, 845*, 834, 756, 748, 680, 431, [$\nu(\text{IrC vinyl})$]; [$^2\text{H}_8$](**2**): 1580 [$\nu(\text{IrD})$], 1572 [$\nu(\text{IrD})$], 1512 [$\nu(\text{CC vinyl})$], 1502 [$\nu(\text{CC vinyl})$], 1049 [$\delta(\text{CH}_2 \text{ vinyl})$], 949*, 824, 687, 549, 411 [$\nu(\text{IrC vinyl})$]; (**3**): 2216 sh, 2200 sh, 2184 [$\nu(\text{IrH})$], 1680 [$\nu(\text{CC vinylidene})$], 1188 (not assigned), 818, 711, 593, 555; [$^2\text{H}_8$](**3**): 1580 [$\nu(\text{IrD})$], 1572 [$\nu(\text{IrD})$], 1661 [$\nu(\text{CC vinylidene})$], 832, 816, 595; (**4**): 1281, 1276, 846, 762; (**6**): 1980 [$\nu(\text{CO})$], 587 [$\delta(\text{IrCO})$]; (**7**): 2040 [$\nu_{\text{sym}}(\text{CO})$], 1974 [$\nu_{\text{asym}}(\text{CO})$], 599 [$\delta(\text{IrCO})$], 574 [$\delta(\text{IrCO})$]; (**8**): 2021 [$\nu(\text{CO})$], 558 [$\delta(\text{IrCO})$], 504 [$\delta(\text{IrCO})$].

§ Bergman's vinyl hydride has $\nu(\text{CC})$ at 1553 cm^{-1} , $\text{Fe}(\text{C}_2\text{H}_3)\text{H}$ at 1556 cm^{-1} ; $\text{Fe}(\text{C}_2\text{D}_3)\text{D}$ at 1477 cm^{-1} . C=C stretching vibrations of other mononuclear vinylidene complexes occur in the range 1590–1660 cm^{-1} (ref. 9).

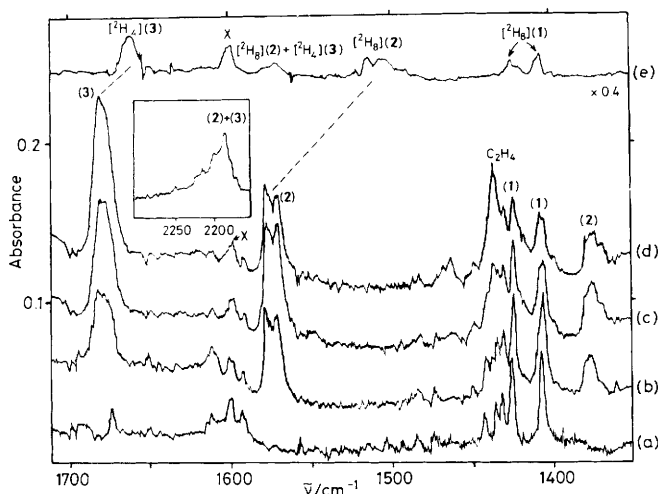


Figure 1. (a) Partial i.r. spectrum of (1) in Ar matrix at 20 K (230 min deposition, sublimation temperature 290 K, 10.2 mmol Ar); (b) after 60 min u.v. photolysis (Hg arc 125 W, $\lambda > 290$ nm); (c) after 130 min further photolysis ($\lambda > 290$ nm); (d) after 30 min photolysis (defocused XeCl laser pulsed at 5 Hz, av. power 150 mW, $\lambda = 308$ nm), notice inset of 2200 cm^{-1} region at this stage; (e) spectrum of $\text{cpIr}(\text{C}_2\text{D}_4)_2$, $[\text{}^2\text{H}_8](1)$, after similar photolysis treatment to (b)–(d). Bands marked according to Scheme 1, \times due to residual matrix-isolated water. Notice the structure on the product bands which is absent in the spectrum of (1). This structure varies with the matrix material and indicates the existence of two conformers of (2) and (3).

cm^{-1} is assigned as the counterpart of the 2184 cm^{-1} band of (2) and (3) [$\nu(\text{IrH})/\nu(\text{IrD}) = 1.39$]. The positions of the other vinyl bands \ddagger of (2) and $[\text{}^2\text{H}_8](2)$ correlate with those of $\text{HFe}(\text{C}_2\text{H}_3)/\text{DFe}(\text{C}_2\text{D}_3)$.⁴

When (1) is photolysed in a N_2 matrix, products (2), (3), and C_2H_4 are observed as in Ar, but an additional intense band (2134 cm^{-1}) indicates the presence of $\text{cpIr}(\text{C}_2\text{H}_4)\text{N}_2$, (5). Use of a CO matrix still allows production of (2), but (3) and (4) are substantially reduced compared to Ar matrices and several $\nu(\text{CO})$ bands are observed. The features due to $\text{cpIr}(\text{C}_2\text{H}_4)\text{CO}$, (6), and $\text{cpIr}(\text{CO})_2$, (7) are identified readily,^{1,11,12} but an additional $\nu(\text{CO})$ band (2021 cm^{-1}) is observed 41 cm^{-1} above the band of (6), even after short photolysis times [Figure 2(e)]. \ddagger This product, (8), continues to grow when (6) is decreasing and makes a small contribution to the $\nu(\text{C}=\text{C})$ mode at 1570 cm^{-1} . The position of $\nu(\text{CO})$ and the contribution to the 1570 cm^{-1} mode lead us to assign (8) as $\text{cpIr}(\text{CO})(\eta^1\text{-C}_2\text{H}_3)\text{H}$. \S

Complexes (6), (7), and (8) may also be generated in a CO–Ar (1 : 9) matrix, but use of a CO– CH_4 (1 : 9) matrix gives an additional product with $\nu(\text{CO})$ at 2005 cm^{-1} , close to that of (8) (now at 2017 cm^{-1} [Figure 2(a–d)]). This complex (9), is readily assigned as $\text{cpIr}(\text{CO})(\text{Me})\text{H}$.^{11,12}

\S Comparison of spectra in Ar and CO matrices indicates that the relative intensities of $\nu(\text{CO})$ and $\nu(\text{C}=\text{C})$ for (8) exceeds 25. The observed intensity ratio of I_{2021}/I_{1571} of ca. 5 on initial photolysis and the presence of at least 6 other product bands in CO matrices which fall within 6 cm^{-1} of the positions of (2) in Ar, show that both (2) and (8) are formed in CO matrices. Even when the 2021 cm^{-1} band of (8) has reached absorbance > 1 , no other $\nu(\text{CO})$ bands are detected with which it can be associated. Use of a $^{12}\text{CO}\text{-}^{13}\text{CO}\text{-Ar}$ (1 : 1 : 18) matrix confirms that (8) is a monocarbonyl complex. Rest and Whitwell have identified a closely related molecule $(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{CO})(\eta^1\text{-C}_2\text{H}_3)\text{H}$ on photolysis of $(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{CO})_2$ in C_2H_4 -doped matrices.¹²

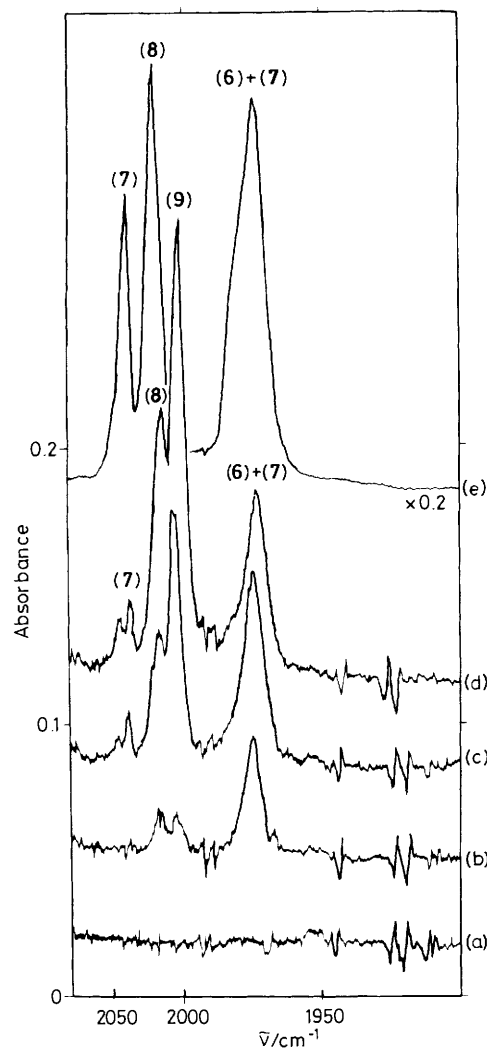


Figure 2. (a) I.r. spectrum of (1) in CO– CH_4 (1 : 9) matrix at 17 K in CO stretching region (195 min deposition, sublimation temperature 286 K, 7.7 mmol CO– CH_4); (b) after 20 min u.v. photolysis (Cd arc, $\lambda = 229$ nm); (c) after 95 min further photolysis ($\lambda = 229$ nm); (d) after 25 min near u.v. photolysis (Hg arc, $\lambda > 370$ nm); (e) spectrum obtained after similar treatment of (1) in CO–Ar (1 : 9) matrix. Bands are labelled according to Scheme 1.

The matrix isolation results (Scheme 1) demonstrate (i) that (1) isomerises on photolysis to give (2) by insertion into ethene C–H bonds; (ii) that photodissociation of ethene also occurs [products (4)–(6)]; (iii) that secondary photolysis of (2) releases C_2H_4 and gives (3), a vinylidene complex; (iv) that formation of (3) is suppressed in CO, but a carbonyl(vinyl)-hydride complex, (8), is formed, probably by photolysis of (2); (v) that methane activation can be induced in CO– CH_4 matrices.

Photolysis ($\lambda > 290$ nm) of (1) in C_6D_6 solution in the presence of PPh_3 resulted in formation of two major products, one of which, (10), exhibited characteristic vinyl resonances in the ^1H n.m.r. spectrum (Figure 3). Decoupling difference spectra and selective ^{31}P decoupling were used to prove that (10) is $\text{cpIr}(\eta^1\text{-C}_2\text{H}_3)\text{H}(\text{PPh}_3)$. A related vinyl hydride product, $\text{cpIr}(\eta^1\text{-C}_2\text{H}_3)\text{H}(\text{Me}_2\text{SO})$, (11), was obtained by pho-

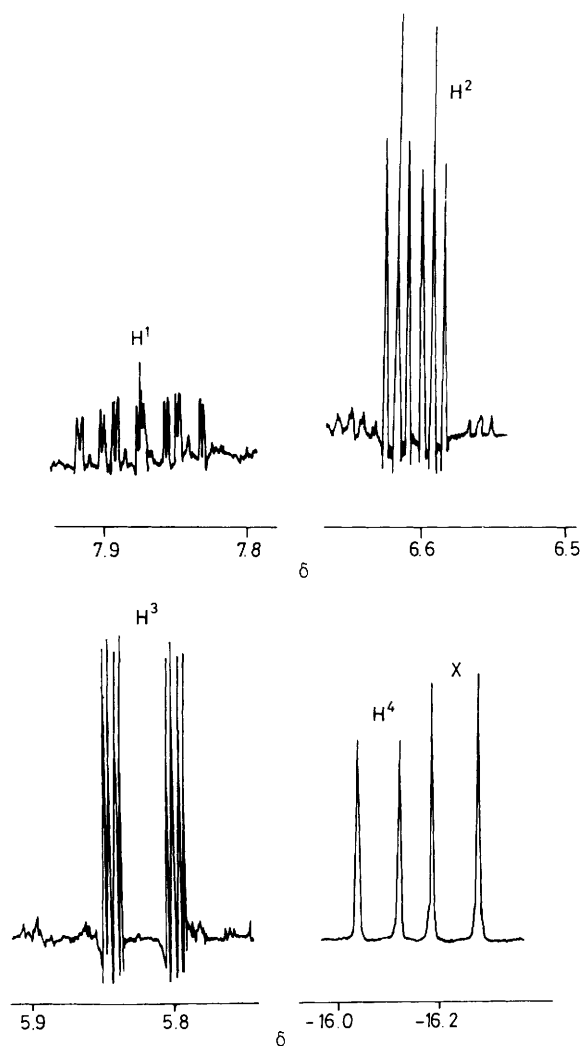
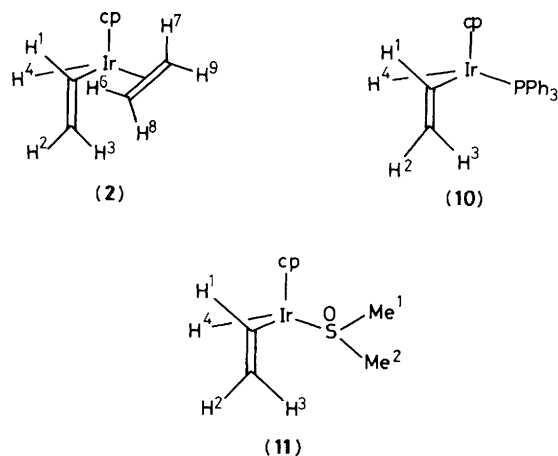


Figure 3. Solution ^1H n.m.r. spectrum of (10) showing vinyl and hydride signals obtained after 270 min photolysis ($\lambda > 290\text{ nm}$) of (1) in C_6D_6 (ca. 0.1 mol dm^{-3}). Notice that H^1 appears as a 16-line multiplet because of coupling to H^2 , H^3 , H^4 , and P. Each of these couplings has been removed by selective decoupling. The high field hydride doublet arises from the other product (X).

tolysis in the presence of Me_2SO . Photolysis of (1) in frozen $[\text{D}_6]\text{toluene}$ at 77 K followed by warming to 200 K allowed us to obtain ^1H and $^{13}\text{C}\{^1\text{H}\}$ n.m.r. spectra of a photoproduct formed in ca. 30% yield (cf. ref. 10).

Selective decoupling and DEPT experiments demonstrated

\parallel N.m.r. data for (2), (10), and (11) (400 or 360 MHz for ^1H). Missing integrations unavailable because of overlap. Numbering shown in displayed formulae. (2): ^1H ($\text{C}_6\text{D}_5\text{CD}_3$): δ 7.26 (dd, 1H, $J_{\text{H}^1\text{H}^2}$ 9.9, $J_{\text{H}^1\text{H}^3}$ 17.4 Hz, H^1), 6.33 (dd, 1H, $J_{\text{H}^2\text{H}^3}$ 2.5 Hz, H^2), 5.34 (dd, 1H, H^3), 4.60 (s, C_5H_5), 2.30 (dd, 1H, $J_{\text{H}^6\text{H}^8}$ 8.8, $J_{\text{H}^6\text{H}^9}$ 11.5 Hz, H^6), 2.7 (overlaps with 1, H^8 and H^9), 1.40 (dd, 1H, $J_{\text{H}^7\text{H}^8}$ 8.4, $J_{\text{H}^7\text{H}^9}$ 11.0 Hz, H^7), -16.14 (s, 1H, H^4); $^{13}\text{C}\{^1\text{H}\}$ and DEPT: δ 120.0 (CHCH_2), 116.4 (CHCH_2), 84.4 (C_5H_5), 25.6 (CH_2CH_2), 17.6 (CH_2CH_2). (10): ^1H (C_6D_6): δ 7.88 (dddd, $J_{\text{H}^1\text{H}^2}$ 10, $J_{\text{H}^1\text{H}^3}$ 17, $J_{\text{H}^1\text{H}^4}$ 1, $J_{\text{H}^1\text{P}}$ 7 Hz, H^1), 6.61 (ddd, 1H, $J_{\text{H}^2\text{H}^3}$ 3, $J_{\text{H}^2\text{P}}$ 3 Hz, H^2), 5.82 (ddd, 1H, $J_{\text{H}^3\text{P}}$ 1.5 Hz, H^3), 4.98 (d, 5H, J_{PH} 1 Hz, C_5H_5), -16.08 (d, 1H, J_{PH} 33.1 Hz, H^4); ^{31}P (selective ^1H decoupling) δ 14.85 p.p.m. (d, J_{PH} 30.6 Hz, IrP). (11): ^1H (C_6D_6): δ 7.20 (dd, $J_{\text{H}^1\text{H}^2}$ 10, $J_{\text{H}^1\text{H}^3}$ 17 Hz, H^1), 6.47 (dd, $J_{\text{H}^2\text{H}^3}$ 3 Hz, H^2), 5.15 (dd, H^3), 5.06 (s, 5H, C_5H_5), 2.95 (br s, 3H, SMe^1), 2.67 (br s, 3H, SMe^2), -15.96 (s, 1H, IrH, H^4).



that this photoproduct was indeed (2). It proves to be stable at 200 K but slowly decomposes thermally at 0°C , probably to give (1); photolysis of room-temperature solutions yields only small amounts of (2) detectable *via* the hydride and cp resonances.

Taken together, the n.m.r. and i.r. experiments provide unequivocal evidence for the isomerisation of (1), the first time that a stable ethene π -complex has been converted into a metal(vinyl)hydride complex. Moreover, matrix isolation has again proved to be an effective guide to solution photochemistry.

Added in proof. The identity of the dinitrogen complex, (5), has been confirmed by use of a $^{14}\text{N}_2$ - $^{15}\text{N}_2$ (1:1) matrix [$\nu(^{14}\text{N}^{14}\text{N}) = 2133.7$, $\nu(^{15}\text{N}^{15}\text{N}) = 2062.7\text{ cm}^{-1}$]. Since submitting this paper, another example of photoinduced isomerisation of an ethene complex to a (η^1 -vinyl)hydride complex has been reported.¹³

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