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Low-Temperature Hydrogenation of Triplet Carbenes and Diradicaloid Biscarbenes—Electronic State Selectivity

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Addition of H_2 is one of the simplest carbene reactions imaginable. Yet, this fundamental reaction has seen little experimental study.[1] Theory suggests that singlet carbenes can insert directly into the H−H bond; reaction of singlet methylene is practically barrierless, according to calculation.[2] Triplet carbenes, in contrast, should add H_2 via an abstraction−recombination mechanism, which calculations indicate might have a larger barrier than singlets.[3] Recently, Sander and co-workers have described additions of a singlet[4] and a triplet[5] "super electrophilic" carbene to H_2 under cryogenic conditions. Spurred by these accounts, we wish to report our matrix isolation studies which indicate that H_2 additions not only may be more general for triplet carbenes than previously suggested but also may offer an electronic-state specific probe for diradicaloid biscarbenes.

We have reported that *p*-bis(chloromethylene)phenylene (**2**) exhibits spectroscopy and reactivity consistent with a $\sigma^2\pi^2$ quinonoid diradical electronic state.[6,7] In contrast, fluoro analogue **6** has a bis-closed shell singlet carbene ($\sigma^2\sigma^2$) electronic configuration.[8] Calculations support these assignments.[7,9] Seeking chemical probes that might distinguish these disparate electronic extremes, we explored the possibility of H_2 addition. Hence, irradiation (366 nm, 90 m) of *p*-bischlorodiazirine **1**[6] (Scheme 1) in an Ar matrix doped with H_2 (2%) produced the characteristic IR spectrum of diradical **2** (Figure 1).[10] Warming the matrix to 32 K caused the disappearance of the bands of **2** and the concurrent appearance of IR bands of monocarbene **4** (confirmed by independent generation from diazirine **5**, Figure 1).[11,12] Chlorocarbene **4**, whether generated from **2** or from **5**, could not be induced to react with H_2 at temperatures up to the degradation point of the matrix (ca. 35 K). Similarly, neither phenylchlorocarbene (**7**)[13] nor a singlet alkylchlorocarbene, **8**, would react on annealing in an H_2-doped Ar matrix.[14] Moreover, the bisfluorocarbene **6** was unreactive to H_2.

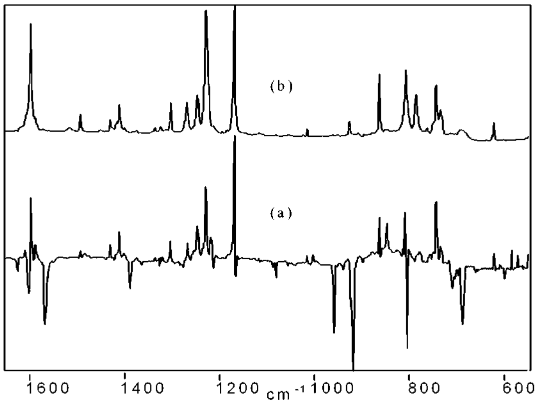
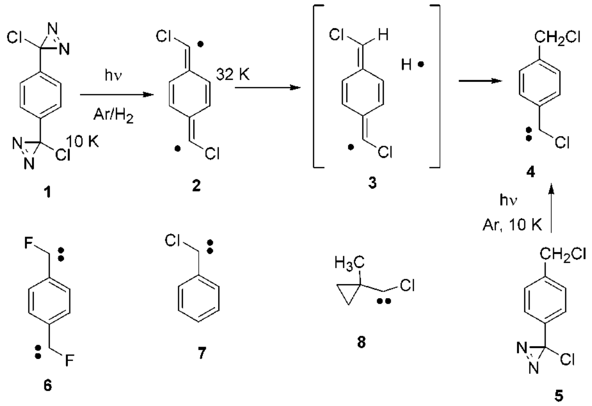
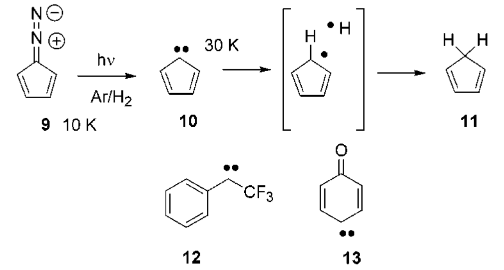


Figure 1. (a) Difference IR spectrum showing conversion of diradical **2** ("down bands", from 366 nm irradiation of **1**) to carbene **4** ("up bands") on warming to 32 K for 10 m in 2% H_2 in Ar. (b) IR of **4** in Ar/H_2 from irradiation of diazirine **5** at 366 nm for 1 h at 25 K.

Scheme 1



Scheme 2



Recognizing that diradical **2** might bear more electronic similarity to an open-shell triplet carbene than a closed-shell singlet, we explored the possibility of triplet carbene H_2 additions. Thus, 366 nm irradiation of diazocyclopentadiene (**9**) in 2% H_2/Ar at 10 K produced the well-known IR bands of triplet cyclopentadienylidene (**10**, Scheme 2).[15] On warming the resulting matrix to 30 K, the spectrum of **10** smoothly transformed into that of cyclopentadiene (**11**, accompanied by carbene dimer).[16] Similarly, we found that triplet phenyltrifluoromethylcarbene (**12**)[17] and triplet 4-oxocyclohexadienylidene (**13**)[18] reacted readily

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(1) See, e.g.: (a) Battin-Leclerc, F.; Smith, A. P.; Hayman, G. D.; Murrells, T. P. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 3305. (b) Braun, W.; Bass, A. M.; Pilling, M. *J. Chem. Phys.* **1970**, *52*, 5131.

(2) Ignatyev, I. S.; Schaefer, H. F. *J. Am. Chem. Soc.* **1997**, *119*, 12306 and references therein.

(3) Bauschlicher, C. W.; Bender, C. F.; Schaefer, H. F. *J. Am. Chem. Soc.* **1976**, *98*, 3072

(4) (a) Sander, W.; Kötting, C. *Chem. Eur. J.* **1999**, *5*, 24. (b) Kötting, C.; Sander, W. *J. Am. Chem. Soc.* **1999**, *121*, 8891.

(5) (a) Sander, W.; Hübert, R.; Kraka, E.; Gräfenstein, J.; Cremer, D. *Chem. Eur. J.* **2000**, *6*, 4567. (b) Sander, W.; Kötting, C.; Hübert, R. *J. Phys. Org. Chem.* **2000**, *13*, 561. The addition of H_2 to the tetrafluoro analogue of **13** was noted, but possible reaction of **13** itself was not addressed.

(6) Zuev, P.; Sheridan, R. S. *J. Am. Chem. Soc.* **1993**, *115*, 3788.

(7) See also: (a) Tomioka, H.; Komatsu, K.; Nakayama, T.; Shimizu, M. *Chem. Lett.* **1993**, 1291. (b) Nicolaides, A.; Enyo, T.; Miura, D.; Tomioka, H. *J. Am. Chem. Soc.* **2001**, *123*, 2628.

(8) Zuev, P. S.; Sheridan, R. S. *J. Am. Chem. Soc.* **1994**, *116*, 9381.

(9) (a) Trindle, C.; Datta, S. N.; Mallik, B. *J. Am. Chem. Soc.* **1997**, *119*, 12947. (b) Jean, Y. *Theochem-J. Mol. Struct.* **1998**, *424*, 29. (c) Flock, M.; Pierloot, K.; Nguyen, M. T. *J. Phys. Chem. A* **2000**, *104*, 4022. (d) Subhan, W.; Rempala, P.; Sheridan, R. S. *J. Am. Chem. Soc.* **1998**, *120*, 11528.

(10) For a description of the matrix isolation instrumentation and techniques, see: Rempala, P.; Sheridan, R. S. *J. Chem. Soc., Perkin Trans. 2* **1999**, 2257.

(11) Major IR bands of **4** (H_2/Ar, 7 K): 1598(s), 1225(s), 1169(s), 864(m), 809(m), 787(m) cm^{-1}.

(12) See the Supporting Information for synthetic details.

(13) Ganzer, G. A.; Sheridan, R. S.; Liu, M. T. H. *J. Am. Chem. Soc.* **1986**, *108*, 1517.

(14) The diazirine precursor for **8** was made in analogous fashion to cyclopropylchlorodiazirine as described in: Ho, G.-J.; Krogh-Jespersen, K.; Moss, R. A.; Shen, S.; Sheridan, R. S.; Subramanian, R. *J. Am. Chem. Soc.* **1989**, *111*, 6875.

(15) Baird, M. S.; Dunkin, I. R.; Hacker, N.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 5190.

(16) H_2 trapping experiments for **10**, **12**, and **13** are shown in the Supporting Information

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with H_2 on annealing in Ar to give the corresponding adducts.[16,19] In contrast, the carbenes were completely unreactive with D_2 under comparable conditions.

These results suggest the potential mechanisms shown in Schemes 1 and 2, where the triplet carbenes and diradical/biscarbene react through H-abstraction followed by recombination of the resultant radical pair to give the observed products. The closed shell carbenes and biscarbene, requiring concerted addition, do not react under our cryogenic conditions.

Previous theoretical investigations have predicted that although both reactions are highly exothermic, concerted insertion of singlet CH_2 into H−H has a negligible energy barrier,[2] but abstraction of H from H_2 by triplet CH_2 may have a barrier as high as ca. 10 kcal/mol.[3] However, our admittedly limited survey implies that at low temperatures, triplet carbenes can find a mechanism for reaction with H_2, whereas singlet halocarbenes cannot. We thus carried out B3LYP/6-31G** calculations of several of the relevant reactions and potential intermediates.[20] Although this level of theory may be inaccurate for these reactions, we expect that approximate comparisons are valid.[21,22] For simplicity, we utilized the triplet state of diradical **2**, which is expected to be nearly degenerate with a singlet open shell ground state.[9,23−24] The results are summarized in Table 1.

All the H_2 additions in Table 1 are predicted to be very exothermic, including phenylchlorocarbene (**7**) which is in the upper range of the series. Thus, overall exothermicity does not appear to be the reason for the unreactivity of singlet **7**. Concerted addition of **7** to H_2 is calculated to have a barrier of 12.4 kcal/mol at this level of theory, prohibitively large at cryogenic temperatures. On the other hand, H-abstractions from H_2 by the triplet carbenes **10**, **12**, and **13**, as well as diradical **2**, are all predicted to be mildly exothermic with significantly lower energy barriers. However, the barriers would still be too large for classical reaction at 30 K. It is well established that radicals and carbenes can abstract hydrogen from hydrocarbons at extremely low temperatures via quantum mechanical tunneling (QMT).[25] We propose similarly that QMT facilitates stepwise reaction of **2** and the triplet carbenes with H_2. The direct insertion of singlet **7** (and the other singlet carbenes), in contrast, is less facile either because of the higher classical barrier or because of the lower probability of QMT involving two hydrogens simultaneously. Finally, the lack of D_2 reactivity is consistent with a tunneling mechanism.

Table 1. Energetics of Carbene + H_2 Reactions (kcal/mol) from (U)B3LYP/6-31G** Calculations[a]

carbene (or biscarbene)	intermediate $RH^\bullet + H^\bullet$	transition state[b,c]	product RH_2
2	−3.6	6.4	−74.2
7		12.4	−80.4
10	−6.1	4.4	−84.9
12	−3.5	5.7	−90.6
13	−3.5	5.4	−68.9

[a] Corrected for zero-point vibrational energies. [b] Calculated geometries are given in the Supporting Information. [c] Relative to H_2 + carbene, calculated for concerted addition for **7**, and H-abstraction for the other carbenes listed.

In sum, our results suggest that low-temperature addition of H_2 to triplet carbenes and diradicaloid biscarbenes may be a general reaction. The most likely pathway is single H-abstraction via tunneling to give a triplet radical pair, which then combines following intersystem crossing. We cannot rule out the possibility of ISC at an earlier point in the reaction sequence, however. In the case of reactions of diradical **2** and carbene **13**, possible products from alternate recombination regiochemistries from the intermediate radical pairs were not observed. The several singlet carbenes we probed did not react with H_2. However, much more reactive singlet carbenes, such as difluorovinylidine reported by Sander and co-workers,[4] appear to be able to surmount the restrictions on concerted additions even at very low temperatures.

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Supporting Information Available: Details of calculations, IR spectra of H_2 trapping of **10**, **12**, and **13**, geometries of carbene addition transition states, and synthetic details for **5** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Sander, W. W. *J. Org. Chem.* **1988**, *53*, 2091.

(19) The carbene−H_2 adducts were characterized by comparison to authentic sample (**2**, **10**, and **12**) or to calculated IR spectra (**13**).

(20) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.;Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998. UB3LYP was used for the doublet and triplet intermediates, and restricted methods were used for closed-shell singlets. Details of the calculations and transition state geometries are given in the Supporting Information.

(21) The B3LYP method has been shown to satisfactorily reproduce carbene geometries and thermodynamics, but may underestimate activation energies by several kilocalories/mole. See refs 2 and 22 for discussions and further references.

(22) Freeman, P. K.; Pugh, J. K. *J. Org. Chem.* **2001**, *66*, 5338.

(23) Theory predicts minimal coupling between the localized radical centers in **2**.[7b,9] Confirming this point, we found that broken spin symmetry UB3LYP calculations[22,24] on singlet **2** (or more correctly, mixed singlet/triplet) predicted ca. the same activation barrier for H-abstraction as for triplet. Interestingly, we found two different electronic configurations for radical **3**, a lower energy A′ σ radical, presumably formed by H-abstraction, and an A″ π radical/carbene, ca. 7 kcal/mol higher in energy.

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(25) Platz, M. S. In *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; Plenum: New York, 1990; pp 143−211.