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COMMUNICATIONS

Published on Web 05/17/2006

Photochemical Isomerization of N-Heterocyclic Carbene Ruthenium Hydride Complexes: In situ Photolysis, Parahydrogen, and Computational Studies

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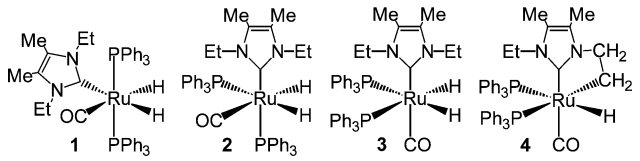
Over the past decade, N-heterocyclic carbenes (NHCs) have become an important class of ligands as alternatives to phosphines in inorganic chemistry.[1] Their strong σ-donor properties have been used to successfully manipulate the stability and reactivity of catalytically important metal fragments.[2] It seems remarkable, however, that their effect on the chemistry of photochemically formed coordinatively unsaturated metal species has yet to be studied. In this communication, we describe how UV irradiation of the NHC-containing dihydride complex $Ru(IEt_2Me_2)(PPh_3)_2(CO)H_2$ (**1**, IEt_2Me_2 = 1,3-bis(ethyl)-4,5-dimethylimidazol-2-ylidene)[3] results in a very facile isomerization reaction involving loss of either H_2 or phosphine. This contrasts the reported photochemistry of the all-phosphine species $Ru(PPh_3)_3(CO)H_2$, which loses only H_2 on the way to postulated dimeric products.[4] We describe the use of a unique combination of in situ photolysis with NMR detection, parahydrogen, and DFT calculations to map both intermediates and photoproducts in the reactions of **1**.



Irradiation of a d_8-toluene sample of **1** at <223 K (Hg arc, 125 W, 6 h), followed by rapid transfer into the NMR spectrometer for observation at 223 K, revealed the partial isomerization of **1** into **2**, which displays hydride resonances in the low-temperature ^1H NMR spectrum at δ −5.6 and −7.3 (each with ddd multiplicity) and two mutually coupled doublets in the $^{31}P\{^1H\}$ NMR spectrum. Upon warming, **2** cleanly reforms **1**. To elucidate the pathway for photoisomerization in more detail, a second sample of **1** was subjected to in situ photolysis (325 nm HeCd laser, 38 mW) within the NMR probe at 223 K. After 120 s of irradiation, 7% of **1** converts into a 1:1 mixture of **2** and a new isomer **3**. The $^1H\{^{31}P\}$ NMR spectrum displays the expected two hydride doublets for **2** and a singlet for **3** (δ −7.0; couples to a single ^{31}P resonance at δ 43.9). Upon further photolysis, the ratio of **2**:**3** changes to favor **2**, and signals for the C−H activated species **4** were also observed to grow in (^1H: δ −7.1, dd, J_{HP} = 102.6, J_{HP} = 25.8 Hz; $^{31}P\{^1H\}$: δ 56.9, d, 36.6 d, J_{PP} = 18.0 Hz).[5]

The time course plot showing the experimentally observed variation in proportions of **1**, **2**, **3**, and **4** with photolysis time is shown in Figure 1. The trace was simulated for a series of first-order interconversion processes to yield an empirical understanding

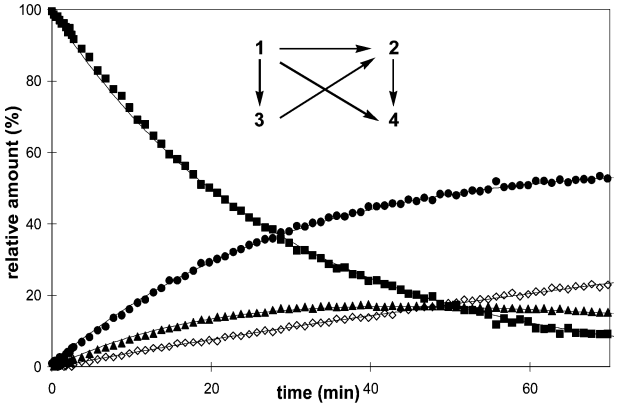


Figure 1. Time profile for conversion of **1** (■) into **2** (●), **3** (▲), and **4** (◇) over 70 min upon photolysis at 223 K (observed points and fitted lines with the dominant pathways indicated).

of the available pathways. This procedure revealed that (i) **1** converts readily into both **2** (rate constants reported relative to k_{12} = 1.00 (reciprocal time)) and **3** (k_{13} = 0.57), (ii) **4** forms from both **1** and **2** ($k_{14} \approx k_{24}$ = 0.23), (iii) **2** and **3** have lower photochemical activity than **1**, (iv) **3** converts to **2** photochemically, and (v) **4** is stable under photolysis at 223 K.

To examine the individual steps involved in these transformations, **1** was irradiated (223 K) in d_8-toluene under 3 atm of p-H_2. Enhanced hydride resonances for both **2** and **3** were immediately apparent in the corresponding ^1H NMR spectrum (Figure 2a); with ^{31}P decoupling (Figure 2b), the two hydride resonances observed for **1** match expectations for unenhanced doublets superimposed on weak antiphase doublets. This observation indicates that the hydride ligands of **1** are partially exchanged for those of p-H_2. One of the pathways for the isomerization of **1** to **2** and **3**, therefore, must involve the photochemical loss of H_2 to give the 16e fragment $Ru(IEt_2Me_2)(PPh_3)_2(CO)$. DFT calculations[6] on the full species **1**, **2**, and **3** predict the relative stabilities **1** ≈ **2** > **3** (Figure 3), so in conjunction with the fact that **2** reforms **1** thermally, we conclude that the photolysis reaction is under kinetic control. These calculations located two forms of $Ru(IEt_2Me_2)(PPh_3)_2(CO)$, **A** and **B**. Their reaction with H_2 leads directly to **3** and **2**, respectively, but **4** could only be formed from intermediate **A**. The selectivity for H_2 addition to **A** and **B** can be estimated from the p-H_2 data, which show a 1:3.7 ratio for the p-H_2 enhanced hydride signals for **1** and **2**.[7]

The roles of different quenching agents on the isomer distribution formed upon in situ photolysis conditions have also been assessed. $^1H\{^{31}P\}$ NMR spectra obtained after 50% conversion in the presence or absence of H_2 showed no difference in the relative amounts of **1**, **2**, and **3**, indicating that H_2 does not reduce the rate of isomerization of **1** into **2** and **3**.[8] Evidence for a photochemical

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10.1021/ja0622397 CCC: $33.50

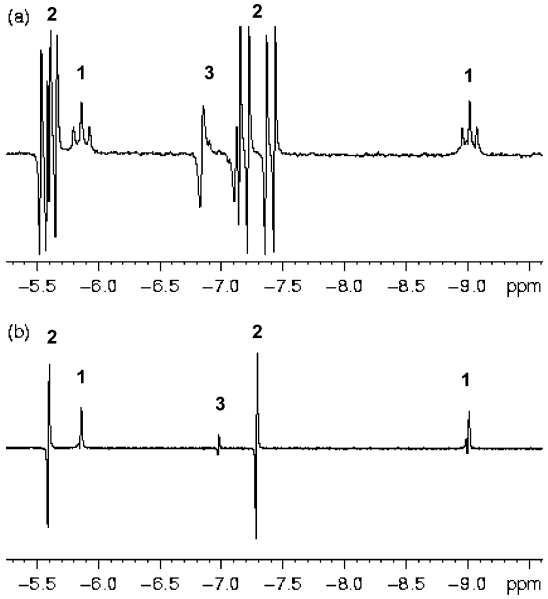

Figure 2. ^{1}H NMR spectra showing the hydride region only of d_8-toluene solutions of **1** under UV photolysis with *p*-H_2 at 223 K. (a) Fully coupled spectrum, with enhanced resonances for **2** and **3** indicated. (b) $^1H\{^{31}P\}$ spectrum showing weak signal enhancement for **1**.

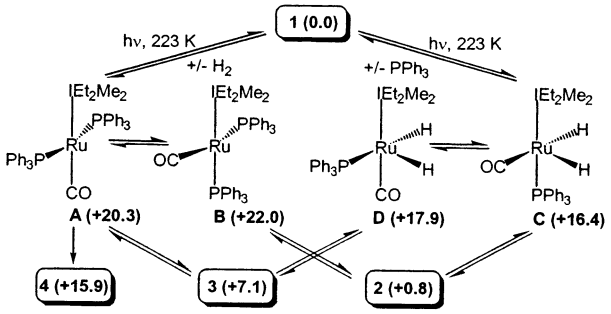

Figure 3. Computed reaction profile (kcal/mol) for the interconversions of **1**, **2**, **3**, and **4** via H_2 and PPh_3 loss pathways.

process involving PPh_3 loss[9] was obtained at extended irradiation times under H_2 at 223 K. This gave rise to two very broad hydride resonances (δ −5.4 and −4.9), with measured T_1 values of ca. 15 and 22 ms, respectively, that are consistent with an η^2-H_2 complex.[10] These signals disappeared very quickly upon warming to 233 K; when the photolysis of **1** was performed in the presence of both PPh_3 and H_2, the formation of this species was suppressed. We therefore conclude that this species is the phosphine loss product $Ru(IEt_2Me_2)(PPh_3)(CO)(\eta^2\text{-}H_2)H_2$, **6**.[11] Confirmation of a phosphine loss pathway was obtained by in situ irradiation of **1** in d_8-toluene in the presence of an 8.6-fold excess of pyridine. This led to the immediate formation of a new monophosphine dihydride species, which we assign as $Ru(IEt_2Me_2)(PPh_3)(C_5H_5N)(CO)H_2$, **7** (^{1}H NMR: δ −3.3, dd, J_{HH} = −9.0 Hz, J_{HP} = 31.5 Hz; δ −14.2, dd, J_{HH} = −9.0, J_{HP} = 21.0 Hz), with hydride ligands *trans* to CO and pyridine, respectively, by comparison to the NMR of the related species $Ru(PR_3)(C_5H_5N)(CO)_2H_2$.[12] In spectra recorded at early reaction times, the formation of both **2** and **3** was essentially quenched. This suggests that **1** undergoes photochemical phosphine loss as the dominant reaction pathway, leading to **7** via trapping of the same 16e intermediate that leads to **2**.

Computed energies for likely intermediates on a phosphine loss pathway are included in Figure 3. The calculations show that PPh_3 loss from **1** is accompanied by spontaneous isomerization of the resultant five-coordinate species[13] to form isomer **C**. This isomer can then add PPh_3 directly to form **2** or isomerize to **D** with PPh_3 addition then yielding **3**. Once **C** is formed, there is therefore no direct low-energy pathway back to **1**. Experimental confirmation of this was seen upon photolysis of **1** in the presence of a 50-fold excess of PPh_3, which showed the production of **2** and **3** to be essentially unaffected. This is consistent with the formation of **2** and **3** upon photolysis being independent of phosphine concentration, assuming the **C**−**D** isomerization is rapid.

In summary, we have shown that incorporation of an N-heterocyclic carbene into $Ru(PPh_3)_3(CO)H_2$ has a dramatic effect on the overall photochemistry. The observed photoisomerization reaction involves loss of both H_2 and PPh_3, as revealed by a combination of in situ photolysis/*p*-H_2 studies allied with DFT calculations. This combination of approaches has also provided a unique insight into the role that key 16e intermediates play in these processes. In light of the high reactivity associated with photochemically generated M-PR_3 fragments in activating C−H bonds,[14] studies of their NHC analogues certainly warrant future investigations.

Acknowledgment. We thank the EPSRC for support.

Supporting Information Available: Kinetic and computational data. Complete ref 6. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Scott, N. M.; Nolan, S. P. *Eur. J. Inorg. Chem.* **2005**, *10*, 1815.
(2) Grubbs, R. H. *Tetrahedron* **2004**, *60*, 7117.
(3) Burling, S.; Mahon, M. F.; Paine, M. F.; Whittlesey, M. K.; Williams, J. M. J. *Organometallics* **2004**, *23*, 4537.
(4) (a) Geoffroy, G. L.; Bradley, M. G. *Inorg. Chem.* **1977**, *16*, 744. (b) Colombo, M.; George, M. W.; Moore, J. N.; Pattison, D. I.; Perutz, R. N.; Virrels, I. G.; Ye, T.-Q. *J. Chem. Soc., Dalton Trans.* **1997**, 2857.
(5) A different isomer of this C−H activated complex is reported in ref 3.
(6) Frisch, M.; et al.; *Gaussian 98*, revision A.11.4; Gaussian, Inc.: Pittsburgh, PA, 2001. Calculations used the BP86 functional. Ru and P were described with Stuttgart RECPs and associated basis sets. 6-31G** basis sets were used for all other atoms, with the exception of phosphine groups, where 6-31G was employed. Energies include corrections for zero-point energy. See Supporting Information for details.
(7) Since enhancement of the hydride signals in **3** results from their origin in a second-order spin system, its proportion cannot be estimated.
(8) The formation of **4**, however, was suppressed by H_2.
(9) (a) Bruno, J. W.; Huffman, J. C.; Green, M. A.; Zubkowski, J. D.; Hatfield, W. E.; Caulton, K. G. *Organometallics* **1990**, *9*, 2556. (b) Montiel-Palma, V.; Perutz, R. N.; George, M. W.; Jina, O. S.; Sabo-Etienne, S. *Chem. Commun.* **2000**, 1175.
(10) The broadness of the hydride and η^2-dihydrogen signals is consistent with exchange as seen in closely related complexes. See: Giunta, K. D.; Hölscher, M.; Lehmann, C. W.; Mynott, R.; Wirtz, C.; Leitner, W. *Adv. Synth. Catal.* **2003**, *345*, 1139.
(11) It is at the point where the detection of **6** is possible that the PHIP effect is no longer visible. This suggests that rapid exchange of the η^2-H_2 ligand with free *p*-H_2 leads to the destruction of *p*-H_2 enhancement.
(12) Dunne, J. P.; Blazina, D.; Aiken, S.; Carteret, H. A.; Duckett, S. B.; Jones, J. A.; Poli, R.; Whitwood, A. C. *Dalton Trans.* **2004**, 3616.
(13) The calculated energy of the $\{Ru(IEt_2Me_2)(PPh_3)(CO)H_2\}$ fragment formed upon PPh_3 loss from **1** is +34 kcal/mol.
(14) Baker, M. V.; Field, L. D. *J. Am. Chem. Soc.* **1987**, *109*, 2825.

JA0622397