Laser flash photolysis study of azides derived from Cr(III) and Mn(III) salen complexes

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Laser flash photolysis of (salen)Cr(III) and (salen)Mn(III) azides has shown that photodenitrogenation occurs through the intermediacy of triplet metal nitrenes. A minor competing pathway consisting in the formation of tetra-coordinated Mn(II) and Cr(II) fragments has also been observed. Both reaction paths are explained through two sorts of photocleavages centered on the azido apical ligand: (a) rupture of the N–N_2 bond to form the coordinated triplet nitrene and (b) homolytic dissociation of the metal–N_3 bond.

Chiral salen azido Mn(III) and Cr(III) complexes as well as the corresponding nitrido Mn(V) and Cr(V) complexes are important transition metal complexes in asymmetric catalysis for the enantioselective ring opening of meso epoxides and for nitrogen atom insertion into alkenes, respectively.[1,2]

Metal nitride complexes are conveniently generated under mild conditions by photochemical denitrogenation of the azides.[3,4] This reaction requires a two-electron oxidation of the metal accompanied by N_2 loss with the presumable formation of a metal nitrene as reaction intermediate. In fact, nitrene intermediates have been proposed in the photodenitrogenation of azide ions and in a large number of organic azides.[4] In this regard, irradiation of several transition metal azide complexes has evidenced a variety of decomposition modes depending on the metal.[5–10] Thus, azido heavy metal complexes belonging to the second and third row series undergo an efficient photodenitrogenation generating coordinated nitrene intermediates whereas analogous transition metal complexes of the first row decompose through alternative photoredox modes or a combination of both redox and nitrene pathways.[5–10] Up to now, no direct detection of a transient metal nitrene has been reported.

More recently, the photochemistry of penta-coordinated manganese salen complexes has been studied by laser flash photolysis.[11] It was found that these metal salen complexes undergo variable proportions of homolytic and heterolytic photocleavage of the apical metal–ligand bond depending on the nature of the ligand and solvent. Hence, in view of the importance of (salen) metal nitrido complexes and that they can be obtained photochemically, we carried out a laser flash photolysis study of these complexes with the aim to determine which are the preferred pathways in the photochemistry of catalytically important penta-coordinated azides derived from Cr(III) and Mn(III) salen complexes. Our results confirm the prevalence of a nitrene pathway accompanied by the occurrence of metal photoreductionl. Both processes take place exclusively through two sorts of cleavages localized on the apical azide ligand. Contrary to other related penta-coordinated manganese(III) salen complexes, spectroscopic evidence in favor of a heterolytic photocleavage of the apical metal–ligand bond yielding azide anion could not be obtained.

Finally, the information obtained from emission spectroscopy and photoreactivity determined by laser flash photolysis have been combined to get a more detailed description of the photochemistry of (salen) metal azido complexes.

Results and discussion

Complexes Cr(III)(salchd)N_3 (**1**) [salchd = 1,2-bis(salicylidenimino)cyclohexane] and Mn(III)(salchd)N_3 (**2**) were synthesized by replacing the chloride ligand in the starting complexes Cr(III)(salchd)Cl (**3**) and Mn(III)(salchd)Cl (**4**) by the N_3^- ligand following the general procedure reported by Larrow and Jacobsen for highly substituted salen derivatives (Scheme 1; see also Experimental).[12]

The complexes were isolated in high yields, recrystallized and characterized by analytical and spectroscopic techniques. Hence, the infrared spectra of complexes **1** and **2** showed intense absorptions around 1620 and 1540 cm^{-1} assigned to C=N and M–O stretching vibrations, respectively, and a sharp absorption at 2037 cm^{-1} typical of the coordinated azide group.[13] On the other hand, the nitrides **5** and **6** that were obtained by hypochlorite oxidation of **3** and **4** in the presence of ammonia, respectively (Scheme 1; see also Experimental), exhibited two intense vibrations at 1620 and 1540 cm^{-1} and a significant vibration in the region of 1000–1100 cm^{-1} characteristic of metal–nitrogen triple bonds.[12]

The electronic spectra of the complexes **1**, **2**, **5** and **6** were recorded in acetonitrile solution. The UV-Vis spectra of complex **1** exhibited an intense absorption at 230 nm with a shoulder at 248 nm and a second absorption band at 380 nm. Similarly, the UV spectrum of complex **2** consisted of an intense absorption at 230 nm with shoulders at 250, 280 and 310 nm and a second band at 425 nm. In striking contrast, the nitrido complexes **5** and **6** exhibited two prominent absorption bands at approximately 370 and 540 nm.

Laser flash excitation of a nitrogen-purged acetonitrile solution of **1** (*ca.* 10^{-5} M) using the 308 nm output of a pulsed excimer laser (8 ns pulse width, energy per pulse $\approx$ 30 mJ) resulted in the appearance of two transient absorption bands with maxima at 420 and 470 nm (Fig. 1). Both bands decayed in

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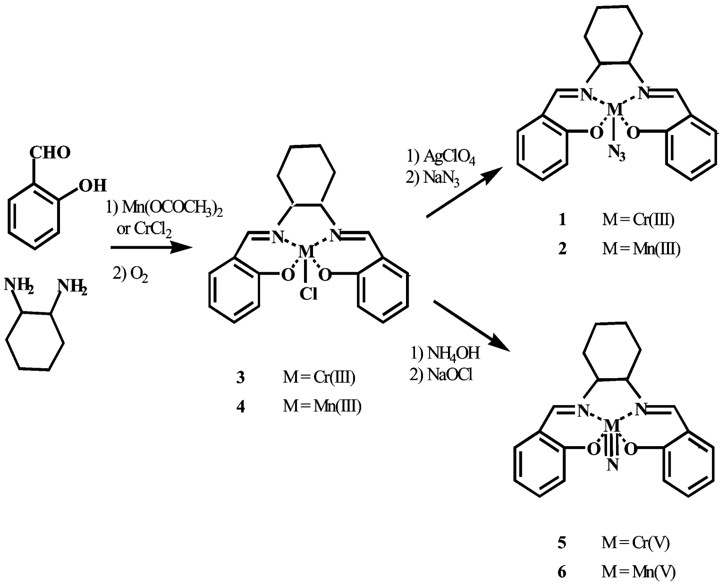


Scheme 1 Synthesis of azides derived from Mn(III) and Cr(III) salen and their respective nitrido manganese(V) and chromium(V) salen complexes.

the microsecond time scale with different first-order kinetics and lifetimes of 7.1 and 19.6 μs, respectively (Fig. 1). In the presence of oxygen, the 420 nm band exhibited a much more rapid decay with a shorter lifetime (< 0.2 μs) giving an approximate quenching constant of $k_q > 5 \times 10^9$ M^{-1} s^{-1} (Fig. 2). In addition to this, the absence of any effect due to the presence of amines indicates that the transient lacks a positive charge and does not exhibit electron pair acceptor character. Finally, the quenching with alkenes like styrene ($k_q = 1 \times 10^3$ M^{-1} s^{-1}), 1-hexene ($k_q = 2.6 \times 10^6$ M^{-1} s^{-1}) and cyclohexene ($k_q = 8.2 \times 10^4$ M^{-1} s^{-1}) strongly support the assignment of the transient responsible for the 420 nm band to triplet nitrene. In fact, as a biradical the triplet nitrene should be relatively unreactive toward Lewis bases (amines) but strongly effective at alkene and oxygen trapping. The observation of a triplet nitrene intermediate is also compatible with preparative studies in which complex **1** afforded upon irradiation the corresponding nitrido chromium(V) salen complex **5** with good material balance.[3a,13]

On the other hand, the decay of the second transient characterized by the 470 nm band was also accelerated by oxygen. In fact, in the presence of oxygen, the 470 nm transient decays faster (Fig. 2). The identity of this species was assigned to a Cr(II) salen complex, partly by its reactivity against oxygen [Cr(II) complexes are rapidly reoxidized to higher oxidation states in the presence of oxygen], partly based on the photochemical behavior of the analogous Mn complex **2**. Formation of the Cr(II) salen complex is compatible with homolytic cleavage of the Cr–N_3 bond to afford an azide radical and simultaneous reduction of the metal to Cr(II). Such homolytic cleavage of a coordinative metal–ligand bond has also been observed for other penta-coordinated metal (salen) complexes. While nitrogen loss to form triplet nitrene seems to be metal independent, homolytic photodetachment of the azido radical clearly depends on the nature of the metal and the strength of the metal–N_3 bond. Thus, the branching ratio between nitrogen loss and $N_3^{\bullet}$ photodetachment should be strongly dependent on the transition metal.

Complex **2** was also submitted to laser flash photolysis ($\lambda = 355$ nm) in a nitrogen-purged acetonitrile solution (*ca.* 10^{-5} M). The transient spectrum recorded after the initial 3 μs exhibited the presence of two absorption bands with maxima at 300 and 430 nm. (Fig. 3). The different time profile monitored at the two λ_{max} indicates again that two different transients have been formed. The influence of oxygen on both transients is qualitatively analogous to that described above

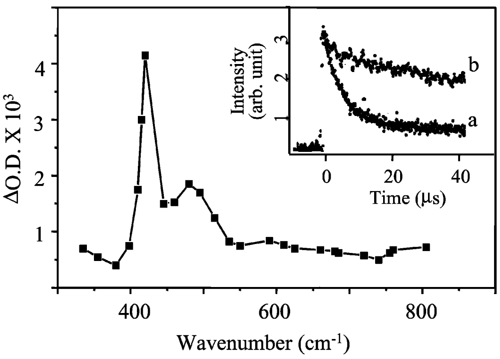


Fig. 1 Transient spectrum recorded 0.5 μs after 308 nm excitation of complex **1** (10^{-5} M) in nitrogen-purged acetonitrile. The inset shows the corresponding decay traces monitored at (a) 420 and (b) 470 nm under nitrogen.

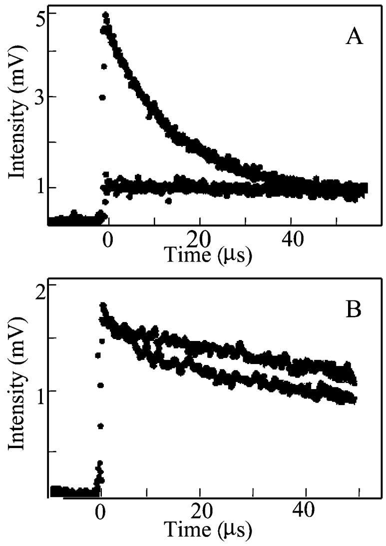


Fig. 2 Decay kinetics of the (A) 420 and (B) 470 nm bands, measured after 308 nm excitation of complex **1** in acetonitrile solution at room temperature under nitrogen purging (signal with higher intensity) or under air equilibrated conditions.

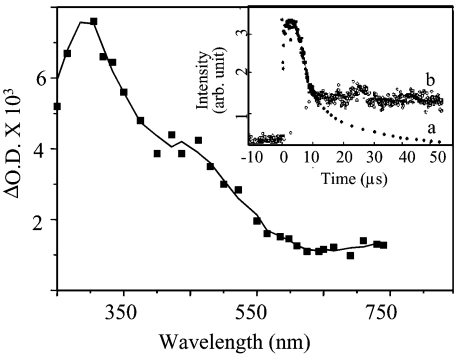
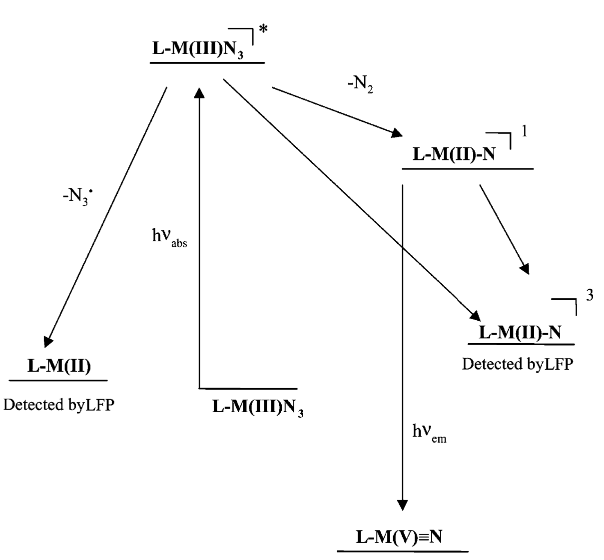


Fig. 3 Transient spectrum recorded 3 μs after 355 nm excitation of complex **2** ([**2**] = 10^{-5} M) in nitrogen-purged acetonitrile solution. The inset shows the decays of the (a) 300 and (b) 430 nm bands measured at room temperature in nitrogen-purged acetonitrile.



Scheme 2 Approximate representation of the energy *vs.* reaction coordinate during the photodenitrogenation and photoreduction of azido chromium(III) and manganese(III) salen complexes in liquid phase at room temperature.

for the oxygen quenching experiments with complex **1**. That is, the 300 nm band was strongly affected by oxygen, decaying rapidly with an approximate quenching constant of $kq > 5 \times 10^9$ M^{-1} s^{-1} and a lifetime shorter than 0.2 μs. As in the previous case, this transient was assigned to triplet nitrene. In this regard, the intermediacy of triplet nitrene was again compatible with the product distribution of the steady-state photolysis since the main reaction product isolable from the irradiation of azido complex **2** was the nitridomanganese(V) salen complex **6**.

On the other hand, the long persistence of the 430 nm band under aerated conditions (lifetime longer than 50 μs) allows the temporal resolution of the spectrum. Thus, Fig. 4 shows the transient spectrum recorded 25 μs after laser flash excitation of complex **2**. This transient spectrum coincides with that recorded by us for the (salen)Mn(II) complex inside zeolite supercages and, therefore, can be safely assigned to this complex. As for complex **1**, formation of the Mn(II) salen complex is compatible with apical ligand photodetachment, affording an azide radical and concurrent reduction of the metal to labile Mn(II).

It is worth to remark that despite the fact that heterolytic photocleavage of the metal–apical ligand bond can be the predominant photodecomposition process for related pentacoordinate Mn(III) salen complexes, no spectroscopic evidence supporting the formation of cationic Cr(III) or Mn(III) salen complexes that could have been generated under our experimental conditions was obtained.[9] Clearly, the dramatic difference in the photochemical behavior of azido complexes compared to other related (salen) metal complexes must be dictated by the photolability of the azido group giving N_2, a factor not found in the analogous complexes bearing photostable axial ligands. In fact, it is difficult to associate the fission of the nitrogen–nitrogen bond necessary for formation of a nitrene intermediate with a reaction coming from a metal-centered ligand field excited state. Rather, it is more feasible that the reaction or at least part of the photochemistry derives from a localized internal azide ligand excited state.[14] The formation of metal nitrene would be satisfactorily explained if, after irradiation of the charge transfer bands, the initial excited state would undergo efficient internal conversion to a ligand-centered state. If this reactive azide state lies energetically below a charge transfer or a ligand field state, nitrene formation would occur predominantly over other metal–ligand decomposition processes and this could be the case for azido metal complexes[15] (Scheme 2). Finally, although another possible nitrene reaction is dimerization to afford azo compounds, this product has not been reported in the irradiation of azido salen complexes or detected after laser pulse excitation in the highly diluted solutions required by the laser flash technique.[4c]

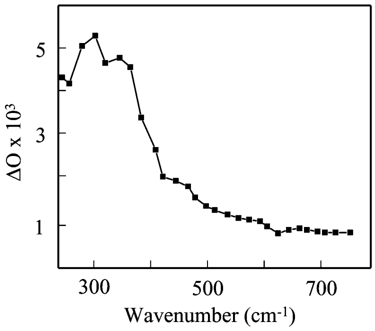


Fig. 4 Transient spectrum registered 25 μs after laser flash excitation of complex **2** in acetonitrile solution under nitrogen.

Besides our present laser flash photolysis study in solution, previous investigations have shown that pure azides **1** and **2** do not emit in solution.[3b] However in low temperature solids, the thermalized Cr(III) quartet and doublet excited states can both be emissive.[10] The failure to observe emission from Cr(III) complexes in room temperature solutions has been attributed to the extremely short lifetime of both excited states, consistent with their extreme reactivity on the subnanosecond time scale. Although a similar reasoning can be surely applied to Mn(III) complexes, up to now no extensive study on emission properties of these complexes has appeared in the literature.

Surprisingly, when the same azido metal complexes are incorporated within the cavities of zeolite Y, a characteristic emission dominated by weak and broad bands around 575 and 600 nm are recorded for complexes **1** and **2**, respectively. This emission, not observed in solution, has been explained through an adiabatic crossing from the energy potential surface of the excited metal azide to that of the excited metal nitride complex.[3b] According to this mechanism, the absorbing species is the azide but the emitting one should be the nitride. In fact, emission spectra of nitrides **5** and **6** in solution show coincident broad and unstructured emissions centered at 575 and 600 nm, respectively.[3b]

The fact that identical emission bands are obtained for nitrides **5** and **6** and when the azides **1** and **2** are embedded into a zeolite suggests that the emitting states of **1** and **2** are clearly implicated in the photochemical pathway towards the formation of the nitrides **5** and **6**. That is, the denitrogenation reaction occurs from or *via* these emitting states.

However, the decay kinetics of emission in fluid solution ($\tau < 1$ μs for complexes **5** and **6**) do not coincide with those of the transients detected here by us under laser flash conditions; thereby confirming their different chemical identity. Indeed, from previous work, the observed luminescence has been proposed to arise from a spin-allowed $a'(x_2 - y_2) \leftarrow d\pi^*$ transition.[3b,16] This transition, which has been associated with the promotion of an antibonding electron ($d\pi^*$) to a non-bonding ($x_2 - y_2$) orbital, is partly ligand localized (surely centered at the M≡N core) and may not necessarily involve a change in the formal valence of the metal center (Mn^{5+} or Cr^{5+}). A possible diagram showing the different excited states detected in the photochemistry of complexes **1** and **2** is shown in Scheme 2.

Conclusions

The photochemistry of azido manganese(III) and chromium(III) salen complexes after charge transfer excitation are cleavage of the azide N–N_2 bond to give a triplet nitrene intermediate and homolytic apical ligand photodetachment occurring in competition. The failure to observe heterolytic photocleavage of the metal apical bond for these complexes contrasts sharply with the photochemical behavior of related penta-coordinated Mn(III) complexes. This has be attributed to a more efficient internal conversion process populating ligand-centered states and to the lability of the azido group. The localized azide excited state formed would then lead to almost exclusively a nitrene reaction pathway.

Finally, a careful study on the photochemistry and photophysics of these azido coordination compounds confirms that neither the triplet nitrene nor the photoreduced Mn(II) or Cr(II) systems are the emissive species responsible for the luminescence previously observed for these complexes within a rigid zeolite structure.

Experimental

Synthesis of complexes 1 and 2[10,11]

A 50 ml round bottom flask fitted with a dropping funnel was charged with 0.269 g (1.3 mmol) of $AgClO_4$ and 5 ml of dry CH_3CN. The dropping funnel was charged with a solution of 0.5 g of Mn(III)(salchd)Cl (**4**) (1.219 mmol) or Cr(III)(salchd)Cl (**3**) (1.3 mmol) in 5 ml of dry CH_3CN. Complexes **3** and **4** were prepared in turn as reported in the literature.[10,11] The solutions of complexes **3** or **4** were added dropwise into the flask of $AgClO_4$. A precipitate formed almost immediately. The suspensions were stirred for 24 h and then they were filtered through celite with 3 portions of 10 ml of CH_3CN. The filtrates were concentrated to a volume of 10 ml and 1.219 mmol of NaN_3 was added in each case. The solutions were stirred for 24 h and a solid was formed. The solids were filtered, washed with CH_3CN and dried.

Complex 1. IR(KBr): 1620, 1540, 2037 cm^{-1}; UV-Vis (CH_3CN): 230, 248 and 380 nm; MS (FAB) *m/z*: 828 (2 M^+), 372, 320.

Complex 2. IR(KBr): 1620, 1540, 2037 cm^{-1}; UV-Vis (CH_3CN): 230, 250, 2.80, 310 and 425 nm; MS (FAB) *m/z*: 834 (2 M^+), 372, 320.

Synthesis of complexes 5 and 6[12]

In a typical preparation, 0.15 g of Mn(III)(salchd)Cl (3.4×10^{-4} mmol) or 0.138 g Cr(III)(salchd)Cl (3.4×10^{-4} mmol) were added to 25 ml of a degassed dichloromethane solution containing 4 ml of NH_4OH. To this solution 8 ml of hypochlorite(4%) and 3 ml of NH_4OH were added dropwise over a period of 10 min. After additional 3 h stirring under inert atmosphere a solid precipitated. The green solid was filtered, washed exhaustively with dichloromethane, n-pentane and dried.

Complex 5. IR(KBr): 1622, 1545, 1045 cm^{-1}; UV-Vis (CH_3CN): 370 and 535 nm; MS (FAB) *m/z*: 396 ($M^{+\bullet}$), 372, 320.

Complex 6. IR(KBr): 1618, 1547, 1050 cm^{-1}; UV-Vis (CH_3CN): 365 and 533 nm; MS (FAB) *m/z*: 399 ($M^{+\bullet}$), 375, 320.

FT-IR and UV-Vis spectroscopy

FT-IR spectra were recorded at room temperature in KBr disks using a Nicolet 710 FT spectrophotometer. Room temperature transmission UV-Vis spectra of acetonitrile solutions were recorded in a Shimadzu UV-Vis scanning spectrophotometer.

Laser flash photolysis experiments

Laser flash photolysis experiments were performed at concentrations in the 10^{-5} M range using the 308 nm output of a pulsed excimer laser (8 ns, energy per pulse ≈ 30 mJ) or the third harmonic of a Nd-YAG laser (7 ns, ≈20 mJ per pulse). The signal was captured with a Tektronic TDS640A oscilloscope and transferred to a computer that controls the experiment. The solutions were placed in a reservoir previously purged with N_2 and flushed through Suprasil cuvettes to ensure excitation of fresh solution.

Steady-state irradiations

Steady-state irradiations of complexes **1** and **2** were carried out in 10^{-3} M acetonitrile solutions using a 250 W medium pressure mercury lamp through quartz for 4 h. After this time, the solvent was removed and the residue analyzed by different spectroscopic techniques.

References

1 (*a*) L. E. Martinez, J. L. Leighton and D. H. Carsten, *J. Am. Chem., Soc.*, 1995, **117**, 5897–5898; (*b*) E. N. Jacobsen, *Acc. Chem. Res.*, 2000, **33**, 421–431.

2 (*a*) J. Du Bois, C. S. Tomooka, J. H. Hong and E. M. Carreira, *Acc. Chem. Res.*, 1997, **30**, 364–370; (*b*) J. Du Bois, J. Hong, E. M. Carreira and M. W. Day, *J. Am. Chem. Soc.*, 1996, **18**, 915–916; (*c*) J. Du Bois, C. S. Tomooka, J. Hong and E. M. Carreira, *J. Am. Chem. Soc.*, 1997, **119**, 3179–3180.

3 (*a*) Von S. I. Arshankow and A. L. Poznjak, *Z. Anorg. Allg. Chem.*, 1981, **481**, 201–206; (*b*) P. Formentín, J. V. Folgado, V. Fornés, H. García, F. Márquez and M. J. Sabater, *J. Phys. Chem. B*, 2000, **104**, 8361–8365.

4 (*a*) A. Albini, G. Bettinetti and G. Minoli, *J. Am. Chem. Soc.*, 1997, **119**, 7308; (*b*) A. Albini, G. Bettinetti and G. Minoli, *J. Chem. Soc., Perkin Trans. 2*, 1999, 2803; (*c*) A. Albini, G. Bettinetti and G. Minoli, *J. Am. Chem. Soc.*, 1999, **121**, 3104; (*d*) E. Leyva and R. Sagredo, *Tetrahedron*, 1998, **54**, 7367.

5 R. Sriram and J. F. Endicott, *Inorg. Chem.*, 1977, **16**, 2766.

6 G. Ferraudi and J. F. Endicott, *Inorg. Chem.*, 1973, **12**, 2389.

7 J. L. Reed, H. D. Gafney and F. Basolo, *J. Am. Chem. Soc.*, 1972, **94**, 7173–7179.

8 J. L. Reed, H. D. Gafney and F. Basolo, *J. Am. Chem. Soc.*, 1974, **96**, 1363–1369.

9 R. Ngay, Y-H. L. Wang and J. L. Reed, *Inorg. Chem.*, 1985, **24**, 3802–3807.

10 A. D. Kirk, *Chem. Rev.*, 1999, **99**, 1607–1640.

11 M. J. Sabater, M. Álvaro, H. García, E. Palomares and J. C. Scaiano, *J. Am. Chem. Soc.*, 2001, **123**, 7074–7080.

12 J. F. Larrow and E. N. Jacobsen, *J. Org. Chem.*, 1994, **59**, 1939–1942.

13 M. A. S. Goher, M. A. M. Abu-Youssef and F. A Mautner, *Z. Naturforsch. B*, 1992, **47**, 139.

14 C. L. Hill and F. J. Hollander, *J. Am. Chem. Soc.*, 1982, **104**, 7318–7319.

15 Monitoring this reaction *via* IR spectroscopy revealed that the photoreaction occurred *via* the destruction of the coordinated azide group (2037 cm^{-1}) with a concomitant increase of a new absorption in the 1000–1100 cm^{-1} region, characteristic of a metal–nitrogen triple bond.

16 K. Srinivasan, P. Michaud and J. K. Kochi, *J. Am. Chem. Soc.*, 1986, **108**, 2309–2320.