Available online at www.sciencedirect.com

Inorganic Chemistry Communications 8 (2005) 1185–1186

INORGANIC CHEMISTRY COMMUNICATIONS

www.elsevier.com/locate/inoche

Photochemistry of trichloro(phenylazo)bis(triphenylphosphine)ruthenium(II) induced by Ru to phenyldiazonium MLCT excitation

Horst Kunkely, Arnd Vogler *

Institut für Anorganische Chemie, Universität Regensburg, D-93040 Regensburg, Germany

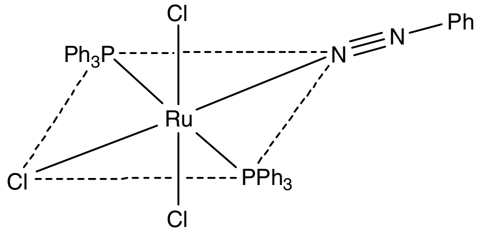
Received 23 June 2005; accepted 6 October 2005

Abstract

The complex trichloro(phenylazo)bis(triphenylphosphine)ruthenium(II) shows a longest-wavelength absorption at $\lambda_{max} = 520$ nm which is assigned to a Ru(II) → phenyldiazonium$^+$ MLCT transition. MLCT excitation leads to the oxidation of the metal and reduction of the diazonium cation which decays to nitrogen and phenyl radical.

Keywords: Electronic spectra; MLCT; Photochemistry; Ruthenium; Phenyldiazonium

Generally, transition metal complexes in MLCT excited states are less reactive than in other excited states although various complexes have been shown to be exceptions from this rule [1,2]. Properties of MLCT excited states have been examined for almost any type of π-acceptor ligand. Recently, metal to NO$^+$ MLCT states have attracted much attention since the photolysis of such nitrosyl complexes frequently leads to the release of NO [3,4] which plays an important role in medicine. Aryldiazonium cations are isoelectronic with NO$^+$ and are also oxidants of considerable strength [5,6]. Accordingly, MLCT transitions to aryl-N_2^+ ligands and the photoreactivity originating from these MLCT states should be quite interesting. So it is rather surprising that this subject has apparently been completely neglected. We explored this possibility and selected the complex trichloro(phenylazo)bis(triphenylphosphine)-ruthenium(II) [7] ($RuCl_3(N_2Ph)(PPh_3)_2$) for the present study.



This compound can be easily prepared and contains Ru(II) as a well-known CT donor.

The electronic spectrum of $RuCl_3(N_2Ph)(PPh_3)_2$ in CH_3CN (Fig. 1) shows absorptions at $\lambda_{max} = 520$ (*sh*, $\varepsilon = 120\ M^{-1}\ cm^{-1}$), 420 (*sh*, 600), 310 (12,000) and 230 (*sh*, 18,300) nm. These solutions are light sensitive. Upon irradiation with visible light a photolysis takes place as indicated by the concomitant spectral changes (Fig. 2). The final spectrum shows a new maximum at 395 nm and a shoulder near 460 nm. This indicates the formation of $RuCl_3(CH_3CN)(PPh_3)_2$ with $\lambda_{max} = 395$ nm ($\varepsilon = 3300$) and 464 nm (*sh*, 1300). An authentical sample of this compound was prepared by the reaction of $RuCl_3$ with a stoichiometric amount of PPh_3 in CH_3CN [8]. The photolysis of $RuCl_3(N_2Ph)(PPh_3)_2$ is also accompanied by evolution

---

* Corresponding author. Tel.: +49 941 943 4716; fax: +49 941 943 4488.
E-mail address: arnd.vogler@chemie.uni-regensburg.de (A. Vogler).

1387-7003/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.inoche.2005.10.002

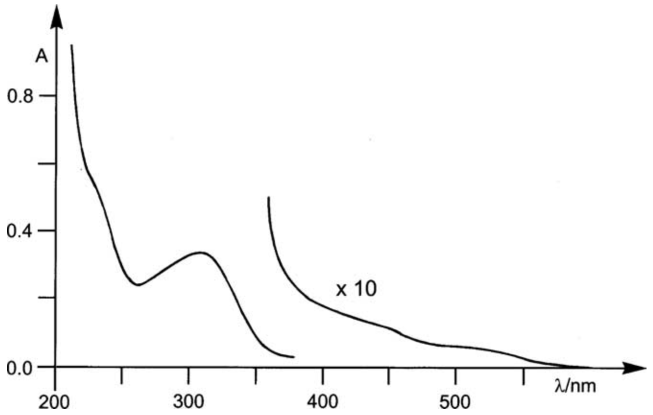


Fig. 1. Electronic absorption spectrum of 2.79×10^{-5} M $RuCl_3(N_2Ph)(PPh_3)_2$ in CH_3CN under argon at room temperature, 1-cm cell.

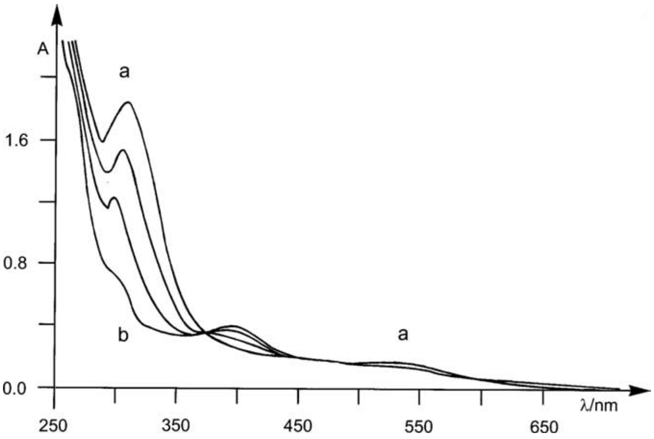


Fig. 2. Spectral changes during the photolysis of 1.56×10^{-5} M $RuCl_3(N_2Ph)(PPh_3)_2$ in CH_3CN at room temperature after 0 min (a), 1, 2 and 6 min (b) irradiation times with $\lambda_{irr} > 420$ nm (Osram HBO 200 W/2 lamp; Schott cut off WG 435), 1-cm cell.

of nitrogen gas bubbles. While $RuCl_3(N_2Ph)(PPh_3)_2$ is not luminescent the photolyzed solution displays a blue emission at $\lambda_{max} = 305$ nm with a shoulder at 315 nm which indicates the formation of biphenyl [9]. The photolysis is monitored by following the decrease of the optical density at 310 nm. The complex disappears with $\phi = 0.007$ at $\lambda_{irr} = 520$ nm.

The compound $RuCl_3(N_2Ph)(PPh_3)_2$ is a typical octahedral d^6 complex. LF absorptions are expected to appear at wavelength not longer then 400 nm [10]. It follows that the longest-wavelength band at $\lambda_{max} = 520$ nm can be only assigned to a $Ru(II) \rightarrow Ph-N_2^+$ MLCT transition. $Ru(II) \rightarrow NO^+$ transitions occur at comparable energies [11]. MLCT excitation of $RuCl_3(N_2Ph)(PPh_3)_2$ in CH_3CN proceeds according to the simple scheme:

$$Ru^{II}Cl_3(N_2Ph)(PPh_3)_2 \rightarrow Ru^{III}Cl_3(CH_3CN)(PPh_3)_2 + PhN_2 \tag{1}$$

$$PhN_2 \rightarrow N_2 + Ph \tag{2}$$

$$2Ph \rightarrow \text{biphenyl} \tag{3}$$

The photolysis is certainly facilitated by the lability of the phenyl diazonium radical as the primary photoproduct which undergoes an irreversible decay.

In summary, we have shown that the aryldiazonium cation is a strong CT acceptor which is photooxidized to phenyl radicals upon MLCT excitation. Various applications including initiation of radical polymerization are conceivable.

References

[1] A. Vogler, H. Kunkely, Coord. Chem. Rev. 177 (1998) 81.
[2] A. Vogler, H. Kunkely, Coord. Chem. Rev. 208 (2000) 321.
[3] P.C. Ford, J. Bourassa, K. Miranda, B. Lee, I. Lorkovic, S. Buggs, S. Kudo, L. Laverman, Coord. Chem. Rev. 171 (1998) 185.
[4] K. Szacilowski, W. Macyk, G. Stochel, Z. Stasicka, S. Sostero, O. Traverso, Coord. Chem. Rev. 208 (2000) 277.
[5] N. Farrell, D. Sutton, Can. J. Chem. 55 (1977) 360.
[6] N. Farrell, M.N. de Olivera Bastos, A.A. Neves, Polyhedron 2 (1983) 1243.
[7] K.R. Laing, S.D. Robinson, M.F. Uttley, J. Chem. Soc., Dalton (1973) 2713.
[8] T.A. Stephenson, G. Wilkinson, J. Inorg. Nucl. Chem. 28 (1966) 945.
[9] I.B. Berlman, Handbook of Fluorescence Spectra of Aromatic Molecules, Academic Press, New York and London, 1971, p. 176.
[10] A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, 1984.
[11] S.I. Gorelsky, A.B.P. Lever, Int. J. Quantum Chem. 80 (2000) 636 (and references cited therein).