

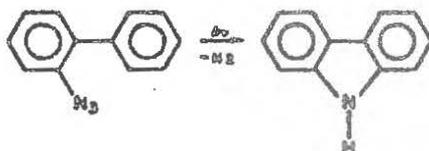
Ligand Photofragmentation of Metal Complexes

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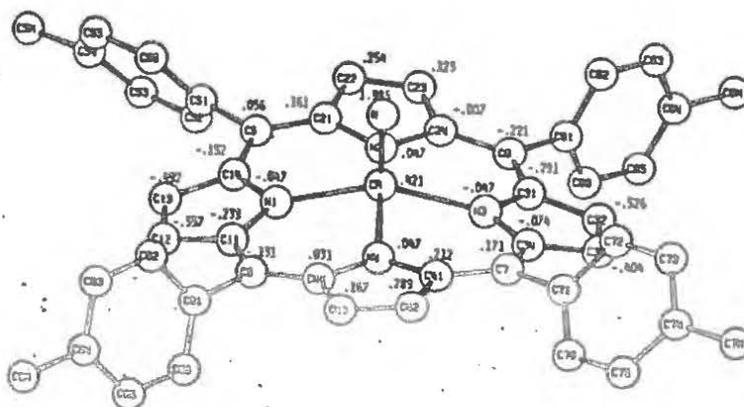
Photofragmentation or photoelimination reactions have been a valuable means of generating reactive intermediates in organic chemistry for many years. These photoreactions are initiated by the cleavage of a sigma bond and result in net rearrangement, fragmentation, or elimination of a small molecule (e.g. N_2 , CO, CO_2 , etc.)



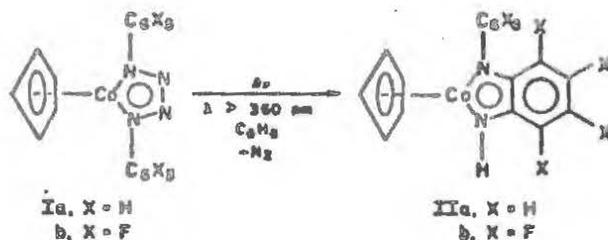
The application of this general type of photoreaction to transition metal coordination compounds has been found to give interesting results.

Ultraviolet irradiation of transition metal oxalate complexes leads to irreversible fragmentation of the oxalate ligand into two molecules of carbon dioxide concomitant with two electron reduction of the metal [1]. In 1969 Nyman [2] suggested that photolysis of $M(PPh_3)_2(C_2O_4)$ ($M=Pt(II), Pd(II)$) might produce the 14 electron $M(PPh_3)_2$ ($M=Pt(0), Pd(0)$) fragment as the reactive intermediate in the absence of competing ligands. Indeed, he found that $Pt(0), Pd(0)$ complexes could be isolated from the photochemical reactions [3]. Later, Trogler et al. working with $Pt(PEt_3)_2(C_2O_4)$ found that $Pt(PEt_3)_2$ could be generated in situ upon UV irradiation [4]. The existence of the $Pt(PEt_3)_2$ fragment was supported by the following experimental facts: (1) irradiation of solutions of $Pt(PEt_3)_2(C_2O_4)$ in the presence of donor and acceptor ligands L, lead to formation of $Pt(PEt_3)_2L_n$ (2) the compounds $Pt(PEt_3)_2XY$ can be formed if the platinum(II) oxalate species is irradiated in the presence of oxidative addition substrates XY (3) two equivalents of carbon dioxide per equivalent of starting material are evolved and (4) each product contains the $Pt(PEt_3)_2$ moiety.

The coordinated azide ligand has been the subject of many photochemical investigations. The azide ligand has been observed to decompose via three routes. The azidopentacyano complexes of Rh(III) and Ir(III) have been found to eliminate the N_3^- anion upon photoaquation. Alternatively, the azido complexes of Pt(II), Au(III), and $Co(NH_3)_5N_3^{2+}$ produced azide radicals from photoredox chemistry. And thirdly, the azidopentaamines of Rh(III) and Ir(III) were found to form coordinated nitrenes [5]. The differences in photoreactivity of these azido ligands were attributed to: ligand back-bonding interactions in the CTM excited state, metal to ligand charge transfer [6], and efficiencies of internal conversion processes. Later work with other transition metals showed that photolysis of $Cr(NH_3)_5N_3^{2+}$ also proceeded via the nitrene pathway [7] and that redox and nitrene modes of reaction occurred in competition. Recently, nitrido-(porphyrinato) $M(V)$ ($M=Cr, Mn$) complexes have been synthesized using this technique [8].



Paralleling azido photochemistry, the diaryltetraazadiene ligand in cyclopentadienylcobalt 1,4-diaryltetraazadiene was found to also extrude N_2 upon photolysis [9]. The final product was believed to form through the insertion of



one coordinated nitrene into the ortho C-H bond of its partner followed by a subsequent [1,3] (N,Co,N) suprafacial hydrogen shift.

Both the azido and diaryltetraazadiene ligands were found to extrude dinitrogen upon photolysis and result in coordinated nitrene products and their derivatives whereas the photolysis of the oxalato-bis(phosphine) Pt complexes resulted in a reactive coordinatively unsaturated bisphosphine Pt(0) intermediate. All three are examples of the use of photochemistry to produce new molecules through reactive metal-centered intermediates. Further directions of research could include the adaptation of these ligands to other metal centers or possibly the use of this idea on as yet untried ligands such as coordinated azo compounds.

References

1. Balzani, V.; Carassit, V., "Photochemistry of Coordination Compounds," Academic Press: New York, 1970.
2. Blake, D. M.; Nyman, C. J., "New Precursors for Platinum(0) and Palladium(0) Complexes: Photochemical Decomposition of Oxalatobis(triphenylphosphine)platinum(II) and Related Complexes," J. Chem. Soc., Chem. Commun. **1969**, 483.

3. (a) Blake, D. M.; Nyman, C. J., "Photochemical Reactions of Oxalatobis-(triphenylphosphine)platinum(II) and Related Complexes," J. Am. Chem. Soc. **1970**, 92, 5339.
(b) Blake, D. M.; Leung, L. M., "Reactions of Carbonato and Oxalato Complexes of Platinum(II). Formation of Cationic Clusters of Platinum," Inorg. Chem. **1972**, 11, 2879.
4. (a) Paonessa, R. S.; Trogler, W. C., "Photochemical Generation of Bis(triethylphosphine)platinum(0) and Synthesis of Ethylenebis(triethylphosphine)platinum(0)," Organometallics **1982**, 1, 768.
(b) Paonessa, R. S.; Prignano, A. L.; Trogler, W. C., "Photochemical Generation of Bis(phosphine)palladium and Bis(phosphine) platinum Equivalents," Organometallics **1985**, 4, 647.
5. (a) Reed, J. L.; Wang, F.; Basolo, F., "Coordinated Nitrene Formation by the Photolysis of Azido Pentaamine Complexes of Rhodium(III) and Iridium(III)," J. Am. Chem. Soc. **1972**, 94, 7173.
(b) Ferraudi, G.; Endicott, J. F., "Charge-Transfer Photochemistry of Azido Complexes of Cobalt(III) and Rhodium(III). Observations on the Chemistry of Flash Photolytically Generated Nitrenes," Inorg. Chem. **1973**, 12, 2389.
(c) Gafney, H. D.; Reed, J. L.; Basolo, F., "Photochemical Reaction of the Azidopentaamineiridium(III) Ion. Coordinated Nitrene Intermediate," J. Am. Chem. Soc. **1973**, 95, 7998.
(d) Reed, J. L.; Gafney, H. D.; Basolo, F., "Photochemical Reactions of the Azidopentaammineiridium(III) Ion. Nitrene and Redox Reaction Paths," J. Am. Chem. Soc. **1974**, 96, 1363.
(e) Inoue, T.; Endicott, J. F.; Ferraudi, G. J., "Photoredox Energetics of Transition Metal Complexes. A Critical Probing of the Proposed Redox and Nitrene Pathways in Azidopentaammineiridium(III)," Inorg. Chem. **1976**, 15, 3098.
6. (a) Zink, J. I., "Molecular Orbital Approach to Photochemical Assignments of Excited States. Photoreactions of Coordinated Azide," Inorg. Chem. **1975**, 14, 446.
(b) Dahlgren, R. Marc, Zink, J. I., "Photochemistry of Azidopentacarbonyltungstate(0)," Inorg. Chem. **1979**, 18, 597.
7. (a) Sriram, R.; Endicott, J. F., "Photoredox Energetics of Transition Metals. Redox and Nitrene Pathways in Azidopentaamminechromium(III)," Inorg. Chem. **1977**, 16, 2766.
(b) Katz, M.; Gafney, H. D., "Photochemical Reactions of Azidopentaaminechromium(III). Evidence for a First Transition Series Coordinated Nitrene Intermediate," Inorg. Chem. **1978**, 17, 93.
8. (a) Groves, J. T.; Takahashi, T., "Activation and Transfer of Nitrogen from a Nitridomanganese(V) Porphyrin Complex. The Aza Analogue of Epoxidation," J. Am. Chem. Soc. **1983**, 105, 2073.
(b) Groves, J. T.; Takahashi, T.; Butler, W. M., "Synthesis and Molecular Structure of a Nitrido(porphyrinato)chromium(V) Complex," Inorg. Chem. **1983**, 22, 884.

- (c) Buchler, J. W.; Dreher, C., "Metal Complexes with Tetrapyrrole Ligands XXXIII. Preparation of Azidochromium(III); Azidomanganese(III); and Azidoiron(III) Porphyrins and their Photolysis to Terminal or Bridged Nitridometal Porphyrins," Z. Naturforsch. **1984**, 39b, 222.
9. (a) Gross, M. E.; Trogler, W. C., "Photochemical Loss of Dinitrogen from Cyclopentadienylcobalt 1,4-Diaryltetraazadienes," J. Organomet. Chem. **1981**, 209, 407.
- (b) Gross, M. E.; Trogler, W. C.; Ibers, J. A., "Delocalized π Bonding in Tetraazadiene Metallocycles," J. Am. Chem. Soc. **1981**, 103, 192.
- (c) Gross, M. E.; Trogler, W. C.; Ibers, J. A., "Cyclopentadienylcobalt 1,4-Diaryltetraazadienes. A Structural, Spectroscopic, and Theoretical Study," Organometallics **1982**, 1, 732.
- (d) Gross, M. E.; Ibers, J. A.; Trogler, W. C., "Structural and Spectroscopic Study of Cyclopentadienylcobalt N-Phenyl-o-benzoquinone Diimines. A Case for Delocalized π Bonding," Organometallics **1982**, 1, 530.
- (e) Gross, M. E.; Johnson, C. E.; Maroney, M. J.; Trogler, W. C., "Photochemistry of Cyclopentadienylcobalt 1,4-Diaryltetraazadienes. Examples of C-H, C-F, and C-C Bond Breaking," Inorg. Chem. **1984**, 23, 2968.