

### Preliminary communication

## PHOTOCHEMISTRY OF METAL-METAL BONDED COMPLEXES.

### IV \*. BREAKING OF THE METAL-METAL BOND AND DECOUPLING OF THE TWO 1,4-DIAZA-1,3-BUTADIENE (= R-DAB) FRAGMENTS OF BIS(1-t-BUTYLIMINO-2-t-BUTYLAMINOETHANE) (= t-Bu-IAE) DURING THE PHOTOCHEMICAL CONVERSION OF $\text{Mo}_2(\text{CO})_6(\text{t-Bu-IAE})$ INTO $\text{Mo}_2(\text{CO})_6(\text{t-Bu-DAB})_2$

RONALD R. ANDRÉA, HERO E. DE JAGER, DERK J. STUFKENS \*\* and AD OSKAM.

*Anorganisch Chemisch Laboratorium, University of Amsterdam, J.H. van 't Hoff Instituut,  
 Nieuwe Achtergracht 166, 1018 WV Amsterdam (The Netherlands)*

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#### Summary

The complex  $\text{Mo}_2(\text{CO})_6(\text{t-Bu-IAE})$  (I) (bis(1-t-butylimino-2-t-butylaminoethane) which contains a Mo-Mo bond and a tetradentate 10e donor ligand t-Bu-IAE, consisting of two C-C coupled t-Bu-DAB (t-BuN=CHCH=NBu-t) ligands has been irradiated into its  $\sigma \rightarrow \sigma^*$  transition. The photolysis yields  $\text{Mo}_2(\text{CO})_6(\text{t-Bu-DAB})_2$  (II), a complex in which the Mo-Mo bond is broken and the uncoupled t-Bu-DAB ligands act as 6e ( $\sigma\text{-N}, \mu^2\text{-N}', \eta^2\text{-CN}'$ ) donors.

In contrast to 2,2'-bipyridine and 1,10-phenanthroline, the simple substituted  $\alpha$ -diimine 1,4-diaza-1,3-butadiene (= R-DAB; RN=CH-CH=NR) not only acts as a 2e ( $\sigma\text{-N}$ ) or 4e ( $\sigma\text{-N}, \sigma\text{-N}'$ ) donor ligand, but also shows 4e ( $\eta^2\text{-CN}, \eta^2\text{-CN}'$ ) [1], 2e,2e ( $\sigma\text{-N}, \sigma\text{-N}'$ ) [2], 6e ( $\sigma\text{-N}, \mu^2\text{-N}', \eta^2\text{-CN}'$ ) [3] and 8e ( $\sigma\text{-N}, \sigma\text{-N}', \eta^2\text{-CN}, \eta^2\text{-CN}'$ ) [4] coordination behaviour. Of these bonding modes, the latter three are only observed for bi- and poly-nuclear metal complexes. The bonding of the R-DAB ligand is often accompanied by an activation of the  $\alpha$ -diimine skeleton, which may lead to C-C coupling reactions. Such a C-C bond can, for example, be formed between two R-DAB ligands, giving rise to the so-called R-IAE ligand (R-IAE = bis(1-R-imino-2-R-aminoethane)). Up to now these R-IAE ligands, which are tetradentate and act as 10e donors, have been found in complexes of Mo, Mn, Ru and Zn [5-8]. The structure of one of them, viz.  $\text{Mo}_2(\text{CO})_6(\text{R-IAE})$ , is shown in Fig. 1 (complex I).

\* For part III see ref. 13.

\*\* To whom correspondence should be addressed.

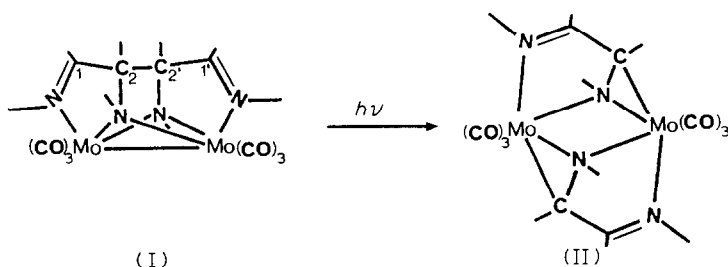


Fig. 1. Reaction of  $\text{Mo}_2(\text{CO})_6(\text{t-Bu-IAE})$  (I) to  $\text{Mo}_2(\text{CO})_6(\text{t-Bu-DAB})_2$  (II) upon irradiation with  $\lambda$  457.9 nm.

The formation of such R-IAE complexes can be accomplished by reduction of a mononuclear transition metal complex (e.g.  $\text{Mo}(\text{CO})_4(\text{t-Bu-DAB})$ ) [5,9] by electron transfer [6], or by photochemical excitation [10].

The  $\text{Ru}_2(\text{CO})_4(\text{R-IAE})$  compounds have been found to react thermally to a thermodynamically stable product  $\text{Ru}_2(\text{CO})_4(\text{R-DAB})_2$  where R is *i*-Pr or *c*-Hex [11]. During this reaction both the C–C bond between the R-DAB ligands and the metal–metal bond are broken. Although no such conversion of complex I into  $\text{Mo}_2(\text{CO})_6(\text{R-DAB})_2$  (II) takes place thermally, it seemed possible to be accomplished photochemically. We here present evidence for such a conversion, which represents a novel photochemical reaction of metal–metal bonded  $\alpha$ -diimine complexes.

Complex I possesses a weak MLCT (metal to R-IAE) band at 570 nm ( $\log \epsilon = 2.77$ ) and a strong band at 410 nm ( $\log \epsilon = 4.16$ ; THF 293 K). This latter band shows a strong intensity increase upon lowering of the temperature, an effect which has been observed before for  $\sigma \rightarrow \sigma^*$  transitions of metal–metal bonded complexes [12]. Further support for this assignment is provided by the resonance Raman spectra of I. These spectra show a large increase in intensity of the  $200 \text{ cm}^{-1}$  band, assigned to  $\nu(\text{Mo-Mo})$ , with respect to the  $284 \text{ cm}^{-1}$  band of  $\text{CH}_2\text{Cl}_2$  upon variation of the exciting laser line from 514.5 to 457.9 nm (Fig. 2). The observation of this resonance Raman effect for  $\nu(\text{Mo-Mo})$  upon approaching the 410 nm band with the laser line confirms the assignment of this band to the  $\sigma \rightarrow \sigma^*$  transition.

Irradiation of complex I with  $\lambda$  457.9 nm (argon ion laser,  $p \approx 200 \text{ mW}$ ) into the  $\sigma \rightarrow \sigma^*$  transition, causes the colour of the solution to change from green to purple. The changes in the IR (CO-stretching region) and UV/Visible spectra accompanying this reaction are shown in Figs. 3 and 4, respectively.

The  $\nu(\text{CO})$  IR pattern hardly changes, the main effect of the reaction being a shift of the bands to lower frequency (I: 1994s, 1942vs, 1871s,  $\text{br cm}^{-1}$ ; II: 1972s, 1915s, 1849s,  $\text{br cm}^{-1}$  in THF 293 K). This indicates that the photoproduct is probably also a binuclear complex containing two equivalent groups of three CO ligands, just like I. In the absorption spectrum the main change is the disappearance of the  $\sigma \rightarrow \sigma^*$  transition, which means that the Mo–Mo bond has been broken. This breaking of the metal–metal bond is also evident from the disappearance of the  $\nu(\text{Mo-Mo})$  band in the resonance Raman spectrum. At the same time the MLCT band slightly shifts to higher energy (546 nm,  $\log \epsilon = 3.54$ ) and increases in intensity, indicating a change of coordination of the R-IAE ligand. These spectral

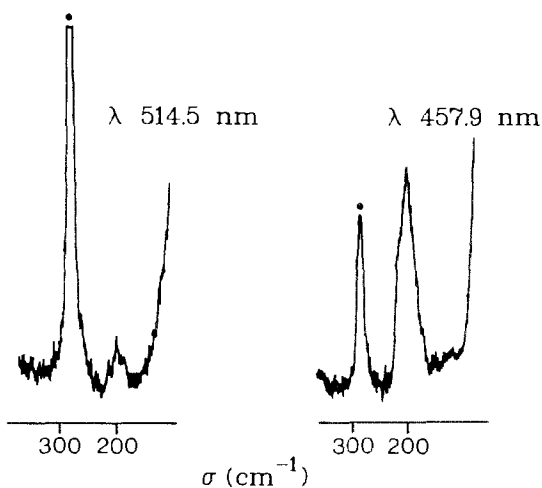


Fig. 2. Resonance Raman effect of  $\nu(\text{Mo-Mo})$  upon excitation of  $\text{Mo}_2(\text{CO})_6(\text{t-Bu-IAE})$  at two different wavelengths (● =  $\nu(\text{CH}_2\text{Cl}_2)$  at  $284 \text{ cm}^{-1}$ ).

changes are consistent all with a photochemical conversion of I into II. Definite proof for this reaction is provided by the changes in the  $^1\text{H}$  NMR spectrum upon irradiation of a solution of I ( $\text{CDCl}_3$ , 293 K,  $\delta$  relative to TMS; I: 8.66, 3.95, 1.49, 1.11 ppm; II: 9.3, 5.2, 1.62, 1.49 ppm). These data show a downfield shift for the imine protons at C(1) and C(1') from 8.66 to 9.3 ppm and for the amine protons at C(2) and C(2') from 3.95 to 5.2 ppm. Similar resonances have been found for  $\text{Ru}_2(\text{CO})_4(\text{R-DAB})_2$  [11] in which the R-DAB ligands act as  $6e$  ( $\sigma\text{-N}, \mu^2\text{-N}', \eta^2\text{-CN}'$ )

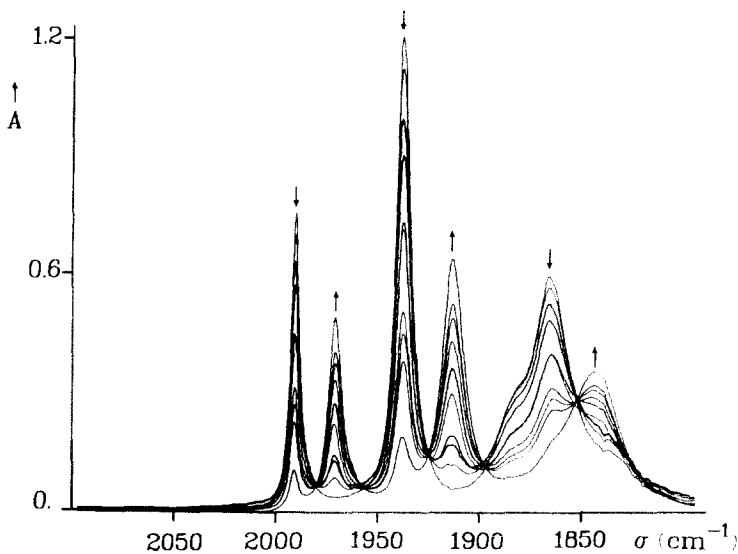


Fig. 3. IR spectral changes in the CO-stretching region upon photolysis of  $\text{Mo}_2(\text{CO})_6(\text{t-Bu-IAE})$  in THF at 293 K. ( $\lambda_{\text{irr}} 457.9 \text{ nm}$ ,  $p$  200 mW).

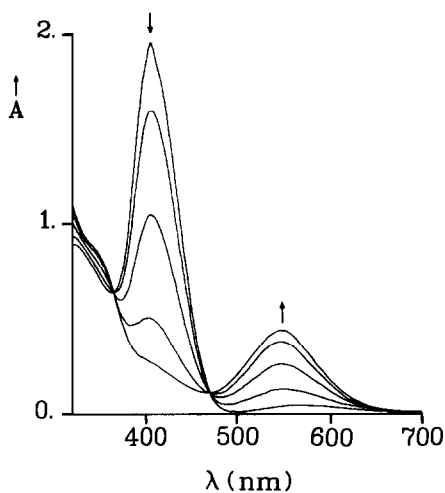


Fig. 4. UV/Vis spectral changes upon photolysis of  $\text{Mo}_2(\text{CO})_6(\text{t-Bu-IAE})$  in THF at 293 K.

donors, as in complex II. These  $^1\text{H}$  NMR results confirm our assumption that the photolysis of complex I leads to the formation of II. The quantum yield of the reaction is  $4.4 \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$ , a value much smaller than is normally found for photochemical reactions of metal-metal bonded species. This will partly be due to the presence of the lower-lying MLCT state and partly be the result of the extra energy needed for the breaking of the C-C bond between the R-DAB ligands. Unfortunately, complex II could not be isolated for an X-ray structure determination since it reverts to I on standing for a few hours. From the occurrence of this back reaction, which was also followed by  $^1\text{H}$  NMR spectroscopy, it can be concluded that I is the thermodynamically stable complex. This contrasts with the behaviour of the Ru complexes  $\text{Ru}_2(\text{CO})_4(\text{R-IAE})$ , which can be thermally converted into the stable end product  $\text{Ru}_2(\text{CO})_4(\text{R-DAB})_2$  [11].

### Experimental

All manipulations were performed under purified nitrogen and the solvents used were distilled from sodium wire. Complex I was made as described by Staal et al. [5].

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