BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (11), 3451—3452 (1979)

Photoisomerization of Bis(*t*-butyl isocyanide)dichlorobis(triphenylphosphine)ruthenium(II)

Tamotsu Tsuihiji, Takeo Akiyama, and Akira Sugimori*

Department of Chemistry, Faculty of Science and Technology,
Sophia University, Kioi-cho 7, Chiyoda-ku, Tokyo 102

(Received March 24, 1979)

Synopsis. UV-irradiation of bis(*t*-butyl isocyanide)dichlorobis(triphenylphosphine)ruthenium(II) brings about isomerization. The composition of the photo-stationary state is wavelength-dependent. A mechanism *via* the photoelimination of triphenylphosphine is proposed.

Photochemical redox and ligand substitution reactions of ruthenium complexes have been extensively investigated.[1,2] However, only a few studies have been done on the photoisomerization. Jeffery and Mawby observed the isomerization of dicarbonyldiiodobis(triphenylphosphine)ruthenium(II) by sunlight.[3] We report here the photochemical mutual conversion of bis(*t*-butyl isocyanide)dichlorobis(triphenylphosphine)ruthenium(II) isomers with light from 254 to 436 nm.

Experimental

Materials. *af*-Bis(*t*-butyl isocyanide)-*bd*-dichloro-*ce*-bis(triphenylphosphine)ruthenium(II) (**1**) was prepared by the reaction of dichlorotris(triphenylphosphine)ruthenium(II) with *t*-butyl isocyanide. *ad*-Bis(*t*-butyl isocyanide)-*bf*-dichloro-*ce*-bis(triphenylphosphine)ruthenium(II) (**2**) was prepared by refluxing **1** in benzene for 2 days according to the preparation of corresponding ethyl isocyanide complex.[4] Elemental analyses: **1**, Found: C, 63.85; H, 5.65; N, 3.34%. **2**, Found: C, 63.75; H, 5.50; N, 3.00%. Calcd for $C_{46}H_{48}Cl_2N_2P_2Ru$: C, 64.03; H, 5.61; N, 3.25%. The structures of **1** and **2** were established from the comparison of their IR spectra and color with those of dichlorobis(ethyl isocyanide)bis(triphenylphospine)ruthenium(II).[4] **1**, Yellow; IR: 2110 (ν_{NC}) and 320 cm^{-1} (ν_{RuCl}). **2**, Colorless; IR: 2135 and 2090 cm^{-1} (ν_{NC}); no absorption of ν_{RuCl} was observed above 300 cm^{-1}. Ruthenium(II) complexes in which two chlorine atoms are situated in *trans*-position have an IR band above 300 cm^{-1} and those in which two chlorine atoms are in *cis*-position have two IR absorption bands below 300 cm^{-1}.[4,5]

Photoreaction. The photoreaction was followed by the change of NMR spectra. Solutions containing 5.8—8.5 mmol dm^{-3} of **1** or **2** in CD_2Cl_2 in quartz NMR sample tubes were irradiated with UV-light. For the irradiation with 254 nm, a low pressure mercury lamp was employed. For the irradiation with 313, 365, and 436 nm, the light from a high pressure mercury lamp was filtered with interference filters M-313, M-365, and M-436 of Karl Zeiss Co., respectively.

After the irradiation, five proton NMR peaks were observed. The peak at δ=7.75—8.06 (multiplet) is assigned to the *o*-proton of coordinated triphenylphosphine (PPh_3), and the peak at δ=7.29—7.57 (multiplet) to *m*- and *p*-protons of coordinated and *o*-, *m*-, and *p*-protons of free PPh_3. The peaks at δ=0.76 (singlet) and 1.04 (singlet) are due to *t*-butyl of **2** and **1**, respectively. The peak at δ=1.34 is ascribed to *t*-butyl of an unidentified product (**X**).

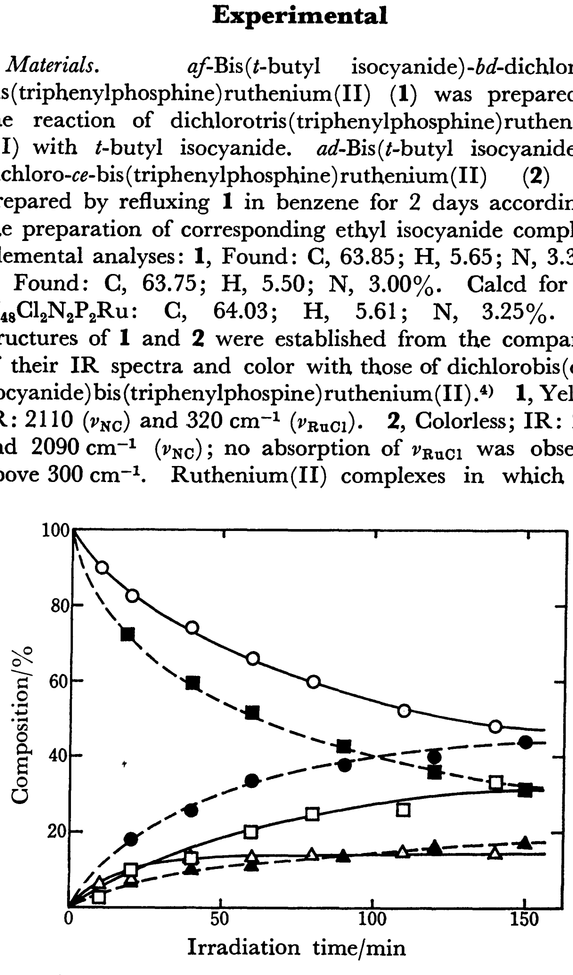


Fig. 1. Dependence of the composition of products on irradiation time (Irradiated with 254 nm).
Products in the irradiation of **1** —○—, **1**; —□—, **2**; —△—, **X**. Products in the irradiation of **2** —●—, **1**; —■—, **2**, —▲—, **X**.

Results and Discussion

UV-irradiation of bis(*t*-butyl isocyanide)dichlorobis(triphenylphosphine)ruthenium(II) isomers brings about the mutual isomerization and the formation of a complex **X**. No reaction occurs in the dark at room temperature. Over the wide range of the wavelength of the irradiating light (254—436 nm), almost no other photoproducts are formed.

Complex **X** which has an NMR peak at δ=1.34 can be assigned to a dimer of the five-coordinate complex **3** or **4**, which is formed by the photochemical elimination of a molecule of PPh_3 from **1** or **2**. The area of the NMR absorption ascribed to *t*-butyl of **X** corresponds well with the increase in the area ascribed to the free PPh_3. The shift of the *t*-butyl peak to lower field can be explained by the increase in the positive charge of the central metal caused by the elimination of a PPh_3 molecule.

The change in the composition of the products with the irradiation time is shown in Fig. 1, as exemplified by the 254 nm irradiation. The prolonged irradiation gives photo-stationary mixtures, the composition of which depends on the wavelength of the irradiating light. Results are summarized in Table 1.

Photochemical conversion of **X** to **1** and **2** is suggested, because the quantity of **X** showed a maximum or saturation at the earlier stage of the photoreaction. The mechanism shown in Scheme 1 is proposed. The intermediacy of the five-coordinate complexes (**3** and **4**) is supported by the suppression of the formation of **X** by the addition of excess PPh_3. Similar five-coordinate complexes have been postulated in the

Table 1. Photoreactions of bis(t-butyl isocyanide)dichlorobis(triphenylphosphine)ruthenium(II)

Wavelength nm	$\frac{\varepsilon_2}{\varepsilon_1}$	Starting complex	Additive	Composition at photo-stationary state $\frac{[\mathbf{1}]_s}{[\mathbf{2}]_s}$	$\frac{[\mathbf{X}]_s}{[\mathbf{1}]_s+[\mathbf{2}]_s+[\mathbf{X}]_s}$
254	1.3	**1**		1.3	0.17
		2		1.5	0.22
		1	PPh_3[a]	1.5	0.07
313	0.85	**1**		0.11	0.04
		2		0.05	0.03
365	6.7	**1**		5.4	0.11
		2		3.0	0.06
436	0.01	**1**		0.05	0.02
		2		≈0	≈0

a) $[PPh_3]/[\mathbf{1}]=10$.

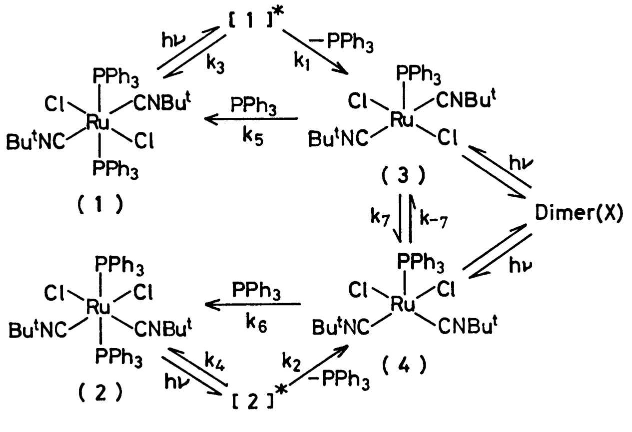
photoisomerization of tetracarbonylbis(triphenylphosphine)molybdenum(0).[6] The fact that the addition of PPh_3 does not retard the photoisomerization of the ruthenium complex indicates that the conversion between **3** and **4** occurs efficiently.

If the reaction giving the dimer is neglected, we can obtain an approximate equation for the composition at the photo-stationary state as

$$\frac{[\mathbf{1}]_s}{[\mathbf{2}]_s}=\frac{k_2k_5k_{-7}\,(k_3+k_1)}{k_1k_6k_7\,(k_4+k_2)}\,\frac{\varepsilon_2}{\varepsilon_1}$$

where suffix s represents the stationary state, the k's are rate constants of the specified reactions in Scheme 1, and ε_1 and ε_2 are the molar absorption coefficients of **1** and **2**, respectively. In the equation, $[\mathbf{1}]_s/[\mathbf{2}]_s$ is independent on the concentration of free PPh_3. The fact that the addition of PPh_3 does not change the value supports the mechanism in Scheme 1.

Complex **1** has three electronic absorption bands at 268 (ε=26900 dm^3 mol^{-1} cm^{-1}), 315 (ε=3200 dm^3 mol^{-1} cm^{-1}), and 439 nm (ε=165 dm^3 mol^{-1} cm^{-1}), which could be assigned to the excitations of coordinated PPh_3, CT, and d-d, respectively. For **2** the separation of CT and d-d bands is not enough, and **2** has no absorption in the visible region.



Scheme 1.

The value $[\mathbf{1}]_s/[\mathbf{2}]_s$ does not follow the ratio of molar absorption coefficients. Especially, in the irradiation with 313 nm, the isomerization from **1** to **2** occurs efficiently, whereas almost no reverse reaction occurs. This suggests that the irradiation with different wavelength produces different excited states, and each excited state has different efficiency of the elimination of PPh_3. For 254 nm irradiation, by which **1** and **2** are brought to excited states of a similar character (the excitation of coordinated PPh_3), $[\mathbf{1}]_s/[\mathbf{2}]_s$ is almost equal to $\varepsilon_2/\varepsilon_1$. This indicates that the overall efficiency from **1** to **2** is equal to that from **2** to **1** in the photoisomerization with 254 nm light.

References

1) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, London (1970), p. 307.

2) P. Ford, R. E. Hintze, and J. D. Petersen, "Photochemistry of Heavier Elements" in "Concepts in Inorganic Photochemistry," ed by A. W. Adamson and P. D. Fleischauer, John Wiley, N. Y. (1975), p. 203.

3) J. Jeffery and R. J. Mawby, *J. Organomet. Chem.*, **40**, C42 (1972).

4) B. E. Prater, *J. Organomet. Chem.*, **34**, 379 (1972).

5) J. D. Gilbert and G. Wilkinson, *J. Chem. Soc., A*, **1969**, 1749.

6) D. J. Darensbourg and M. A. Murphy, *J. Am. Chem. Soc.*, **100**, 463 (1978).