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Photo-induced Conversion of Aryl(trichlorovinyl)nickel(II) Complexes into Two Isomeric Mono-organonickel(II) Complexes

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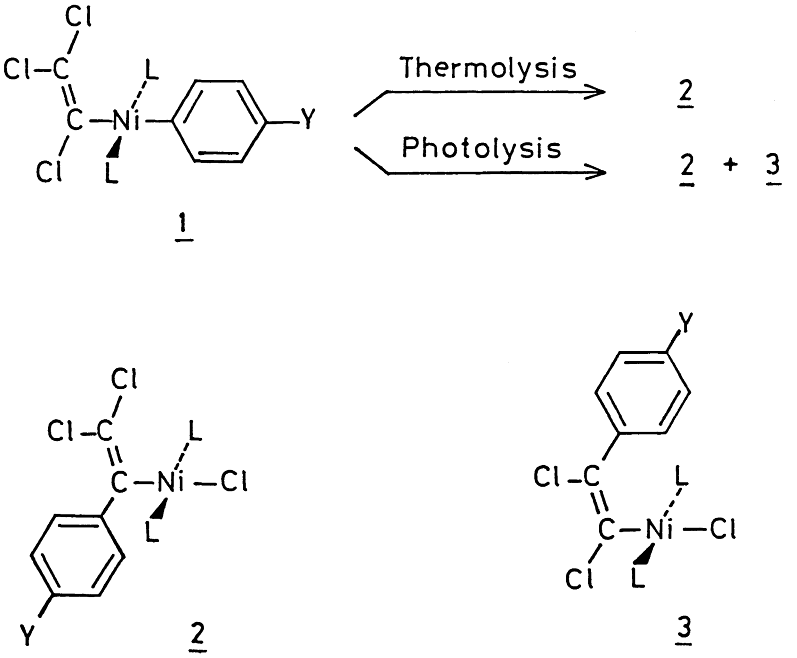
Photolysis (>330 nm) of trans-[Ni(CCl=CCl_2)(C_6H_4Y)(PMe_3)$_2$] (Y= Me-4, Cl-4) resulted in the formation of two isomeric mono-organonickel(II) complexes, trans-[Ni{CCl=CCl(C_6H_4Y)} Cl(PMe_3)$_2$] and trans-[Ni{C(C_6H_4Y)=CCl_2} Cl(PMe_3)$_2$], possibly by reductive elimination followed by oxidative addition.

Little is known about the photochemical properties of square-planar organonickel(II) complexes, trans-[NiRXL_2],$^{1)}$ while these are commonly coloured yellow to brown owing to the presence of the so-called 'd-d band' in their electronic spectrum.$^{2)}$ The trichlorovinylnickel(II) complexes, trans-[Ni(CCl=CCl_2)XL_2] { X= C_6H_4Me-4 (1a), C_6H_4Cl-4 (1b), C_6H_4Me-2 (1c), Cl (1d) } also exhibit such a band in the 320-430 nm region.$^{3)}$ Since the d-d excitation would transfer an electron in a non-bonding d orbital to the antibonding $d_{x^2-y^2}$ orbital, we thought that it would weaken the Ni-C, Ni-X, and/or Ni-L bonds.$^{4)}$ We have now studied the photolysis of 1a and 1b, since the thermolysis of these complexes has recently been reported to give isomeric mono-organonickel(II) complexes, trans-[Ni{C(C_6H_4Y)=CCl_2} Cl(PMe_3)$_2$], (2a) (Y= Me-4)$^{5,6)}$ and (2b) (Y= Cl-4).$^{5)}$

The air-sensitive yellow solution of 1a in benzene (0.1 M) [^{1}H NMR (100 MHz) δ 2.22 (s, 4-Me) and 0.79 ppm (t, J= 8 Hz, PMe)] was irradiated in an evacuated NMR tube at room temperature for 3 h using 500W Xe lamp. The ^{1}H NMR spectrum of resultant brown solution showed a formation (35% conversion) of two organonickel(II) complexes, 2a [δ 2.12s and 1.03t] and 3a [δ 2.11s and 0.94t], in almost same ratio. Complex 2a is identical to the thermolysis product of 1a.5) Irradiation of 1a in dichloromethane solution under the same conditions increased both the conversion ratio (50%) and the relative ratio of 3a [2a:3a = 11:39]. When 1a was irradiated in a larger scale (1 mmol in 10 cm^3 of dichloromethane) in an evacuated Pyrex test tube using 300 W high-pressured Hg lamp, the ^{1}H NMR spectrum showed the formation of NiCl$_2$(PMe$_3$)$_2$ (δ 1.36 broad) in considerable amount in addition to 2a and 3a. It was soon found that the formation of NiCl$_2$(PMe$_3$)$_2$ is depressed almost completely by using acetone (2 cm thickness) as the UV filter (< 330 nm), which is transparent in the d-d band region. Irradiation for 30 h, followed by concentration to dryness and extraction with hexane, resulted to give a mixture of 2a and 3a in 12 and 65% yields, respectively. Pure 3a could be obtained as yellow-brown crystals by recrystallization from hexane.7) Complex 3a is air-stable in solutions, and was found to be an isomer of 1a and 2a by elemental analysis, to be a mono-organonickel(II) complex from the position of d-d band, and to have a trans



L= PMe$_3$

Y= a:Me , b:Cl

Scheme 1.

square-planar configuration by observation of the triplet NMR signal for the PMe_3 protons. Treatment of 3a with NaNCS resulted in substitution of one of the chlorine atoms to give 4a, which confirmed the presence of a Ni-Cl bond in 3a. Complex 1b also reacted by irradiation in analogous manners giving two isomeric monoorganonickel(II) complexes, 2b and 3b. Complex 2b also was identical with the thermolysis product of 1b.

Characteristic of the ^1H NMR spectra for 3a and 3b is the observation of 2,6-H resonance at such a lower magnetic field region [δ 8.77 3a and 8.94 3b] than those for 1a (δ 7.15), 2a (δ 7.81), 1b (δ 7.22), or 2b (δ 7.89). A proton situated directly over and close to the nickel coordination plane is well-known to exhibit its resonance at considerably lower magnetic field.[8)] Therefore, we believe that the structure of 3a and 3b is trans-$[Ni\{CCl{=}CCl(C_6H_4Y)\text{-cis}\}Cl(PMe_3)_2]$, as shown in Scheme.

There are at least two possible mechanisms considered for the formation of 2 and 3 from 1, respectively: (i) a reductive elimination of $CCl_2{=}CClC_6H_4Y$ (5) from 1 to form Ni(0) species, followed by oxidative addition of 5 to Ni(0) to give 2 or 3, and (ii) an α-chlorine elimination to give $[Ni(C{=}CCl_2)Cl(C_6H_4Y)(PMe_3)_n]$ intermediate, followed by migration of the phenyl group to give 2, or (ii') a β-chlorine elimination to give $[Ni(ClC{\equiv}CCl)Cl(C_6H_4Y)(PMe_3)_n]$ intermediate, followed by migration of the phenyl group to give 3. In order to obtain informations about the mechanism, a tetrachloroethylene solution of 1a in NMR tube was irraditated for 3 h using Xe lamp, as above. The ^1H NMR spectrum showed a conversion (20%) less than those for benzene or dichloromethane solutions, an absence of 3a, and a formation of 2a, 5a, and 1d in 7:13:12 ratio. These results suggest that the mechanism (i) is working at least for the formation of 3a. A possibility of photo-isomerization of 2a to 3a was precluded by a separate experimental.

Thermolysis of 1a in tetrachloroethylene at 81 °C also gave mixtures of 1a, 2a, 5a, and 1d in 72:7:21:19 ratio after 3 h and in 11:44:40:39 after 15 h. These results also are suggestive of the mechanism (i) for thermolysis. The observation that the relative ratio of 2a among products increased after 15 h thermolysis is tentatively explained by assuming a higher reactivity of 5a than tetrachloroethylene to Ni(0) species. Further works are in progress in order to distinguish the detailed mechanisms at thermolysis and photolysis conditions.

It is worth noting here that, while complex 1c is thermally stable at 81 °C,[5,9] it is photo-sensitive to give at least three organonickel(II) complexes, although we had difficulties and have not yet succeeded in their pure isolations.

References

1) D. B. Pourreau and G. L. Geoffroy, Adv. Organomet. Chem., 24, 249 (1985).

2) R. G. Miller, R. D. Stauffer, D. R. Fahey, and D. R. Parnell, J. Am. Chem. Soc., 92, 1511 (1970); M. Wada and K. Oguro, Inorg. Chem., 15, 2346 (1976); M. Wada, S-I. Kanai, R. Maeda, M. Kinoshita, and K. Oguro, ibid., 18, 418 (1979).

3) 1a 345 nm (shoulder), 1b 339 nm (shoulder), 1c 343 nm (shoulder), and 1d 403 nm (ε 530) in CH_2ClCH_2Cl, C_6H_6, and/or $(CH_3)_2CO$.

4) M. Wada and M. Kumazoe, J. Chem. Soc., Chem. Commun., 1985, 1204.

5) M. Wada, K. Nishiwaki, and M. Kumazoe, J. Chem. Soc., Chem. Commun., 1984, 980.

6) The structure of 2a shown in Scheme has recently been established by X-ray crystallography; J. Chen, Y. Kai, and N. Kasai, to be reported.

7) All new complexes have been fully characterized by elemental (C, H, Cl, and/or N) analysis. 3a mp 124-125 °C, d-d band (CH_2ClCH_2Cl) 409 nm (ε 570), ^1H NMR (CH_2Cl_2) δ 8.77 (d, J= 8 Hz, 2,6-H), 7.27 (d, J= 8 Hz, 3,5-H), 2.38 (s, Me-4), and 1.18 (t, J= 8 Hz, PMe), ^{13}C NMR ($CDCl_3$) δ 145.2 (t, J= 40 Hz, α-C), 137.2 (s, 4-C), 135.8 (s, 1-C), 129.0 (s, 2,6-C), 126.0 (s, 3,5-C), 119.8 (t, J= 6 Hz, β-C), 21.0 (s, 4-Me), and 13.0 (t, J= 15 Hz, PMe); 2b mp 131-135 °C (decomposed), d-d band 427 nm (ε 663), ^1H NMR (CH_2Cl_2) δ 7.89 (d, J= 8 Hz, 2,6-H), 7.30 (d, J= 8 Hz, 3,5-H), and 1.23 (t, J= 8 Hz, PMe); 3b mp 134-135 °C (decomposed), d-d band 409 nm (ε 594), ^1H NMR (CH_2Cl_2) δ 8.94 (d, J= 9 Hz, 2,6-H), 7.40 (d, J= 9 Hz, 3,5-H), and 1.18 (t, J= 8 Hz, PMe); 4a mp 127-128 °C, ^1H NMR (CH_2Cl_2) δ 8.59 d, 7.28 d, 2.39 s, and 1.20 t; IR (Nujol) 2100 cm^{-1} (vs, ν_{NCS}).

8) D. R. Fahey, J. Organomet. Chem., 57, 385 (1973).

9) M. Wada and M. Kumazoe, J. Organomet. Chem., 259, 245 (1983).

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