

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

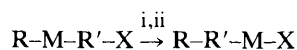
Masanori Wada,* Koichi Nishiwaki, and Makoto Kumazoe

Department of Applied Chemistry, Osaka University, Suita, Osaka 565, Japan

Thermolysis of *trans*-[Ni(CCl=CCl₂)(C₆H₄Y)(PMe₃)₂] (Y = NMe₂-4, Me-4, Me-3, or Cl-4) resulted in the formation of the isomeric mono-organonickel(II) complexes, *trans*-[Ni{C₂Cl₂(C₆H₄Y)}Cl(PMe₃)₂], the products expected from reductive elimination followed by oxidative addition.

Both oxidative addition and reductive elimination are well-established processes in forming or degrading organometallic complexes, and a combination of these reactions often occurs in organic synthesis catalysed by transition metal complexes.¹ If reductive elimination from a diorganometal complex, R-M-R'-X, gives products which can oxidatively add, this could provide a useful method for preparing mono-organometal complexes (Scheme 1). We report here a successful application of this procedure in aryl(trichlorovinyl)nickel(II) complexes.

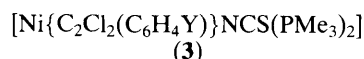
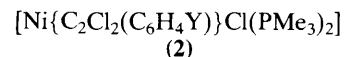
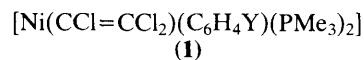
The aryl(trichlorovinyl)nickel(II) complex, *trans*-[Ni(CCl=CCl₂)(C₆H₄Me-4)(PMe₃)₂] (**1a**), was prepared from *trans*-[Ni(CCl=CCl₂)Cl(PMe₃)₂] and 4-tolyl-lithium (-60 °C to room temp., under argon, 65% yield), m.p. 134–136 °C (decomp., sealed capillary), ¹H n.m.r. (C₆H₆, 100 MHz) δ 2.22 (s, 4-Me) and 0.79 (t, *J* 8 Hz, PMe₃).[†] When the air-sensitive, yellow solution of (**1a**) in benzene was heated in an evacuated glass tube at 81 °C for 15 h, a reddish brown solution was formed with a small amount of a dark precipitate. From the filtrate, brown crystals of an air and thermally stable complex,



Scheme 1. i, Reductive elimination; ii, oxidative addition.

[†] Further ¹H n.m.r. data for (**1a**), (**2a**), and (**3a**) in CH₂Cl₂ (δ, *J* in Hz): (**1a**) 7.15 (d, 2 H, 2,6-H, *J* 7.5), 6.79 (d, 2 H, 3,5-H, *J* 7.5). (**2a**) 7.81 (d, 2 H, 2,6-H, *J* 8), 7.14 (d, 2 H, 3,5-H, *J* 8). (**3a**) 7.70 (d, 2 H, 2,6-H, *J* 8.5), 7.17 (d, 2 H, 3,5-H, *J* 8.5).

trans-[Ni{C₂Cl₂(C₆H₄Me-4)}Cl(PMe₃)₂] (**2a**), were isolated in 56% yield, m.p. 140–141 °C, ¹H n.m.r. (C₆H₆) δ 2.11 (s, 4-Me) and 1.03 (t, *J* 8 Hz, PMe₃).[†] Complex (**2a**) was found to be an isomer of (**1a**) by elemental analyses (% C, H, and Cl) and to have a *trans* square-planar configuration by observation of the triplet n.m.r. signal for the PMe₃ protons. Treatment of (**2a**) with NaNCS resulted in substitution of one of the chlorine atoms to give [62% yield from (**1a**)] *trans*-[Ni{C₂Cl₂(C₆H₄Me-4)}NCS(PMe₃)₂] (**3a**),[†] m.p. 139–140 °C (decomp.), ν_{NCS} (Nujol) 2098 cm⁻¹ (s), the formation of which confirmed the presence of a Ni-Cl bond in (**2a**). Thermolysis of (**1a**) was monitored by ¹H n.m.r. spectroscopy, and (**2a**) was the sole product detected in solution. We did not determine the detailed configuration for (**2a**), for which there are three possibilities depending on the reaction sites (C-Cl bonds) of the intermediate CCl₂=CCl(C₆H₄Me-4).



- a; Y = Me-4
- b; Y = NMe₂-4
- c; Y = Cl-4
- d; Y = Me-3
- e; Y = Me-2

The analogous aryl(trichlorovinyl)nickel(II) complexes, *trans*-[Ni(CCl=CCl₂)(C₆H₄Y)(PMe₃)₂] [Y = NMe₂-4 (**1b**), Cl-4 (**1c**), Me-3 (**1d**), Me-2 (**1e**)^{2,3}],^{‡§} were treated similarly, and the corresponding mono-organonickel(II) complexes, *trans*-[Ni{C₂Cl₂(C₆H₄Y)X(PMe₃)₂] (X = Cl or NCS) [(**2b**),

[‡] Melting points and yields: complex (**1b**), m.p. 95–100 °C (decomp.), 64% yield; (**1c**), 133–134 °C (decomp.), 47%; (**1d**), 119–120 °C (decomp.), 52%; (**2b**), 130–135 °C (decomp.), 27%; (**2c**), not isolated; (**2d**), 144–145 °C, 52%; (**3b**), 125–126 °C (decomp.); (**3c**), 139–140 °C, 63% from (**1c**).

[§] 100 MHz ¹H N.m.r. spectral data (δ, J in Hz) for the organonickel(II) complexes (**1b–d**), (**2b–d**), and (**3b,c**): (**1b**) (CH₂Cl₂) 7.02 (d, 2 H, 2,6-H, J 7.5), 6.53 (d, 2 H, 3,5-H, J 7.5); (C₆H₆) 2.62 (s, 6 H, NMe₂), 0.83 (t, 18 H, PMe₃, J 8). (**1c**) (CH₂Cl₂) 7.22 (d, 2 H, 2,6-H, J 8), 6.91 (d, 2 H, 3,5-H, J 8); (C₆H₆) 0.68 (t, 18 H, PMe₃, J 8). (**1d**) (CH₂Cl₂) 7.10 (s, 1 H, 2-H), 7.05 (d, 1 H, 6-H, J 8), 6.80 (t, 1 H, 5-H, J 8), 6.56 (d, 1 H, 4-H, J 8); (C₆H₆) 2.23 (s, 3 H, 3-Me), 0.78 (t, 18 H, PMe₃, J 7.5). (**2b**) (CH₂Cl₂) 7.89 (d, 2 H, 2,6-H, J 9), 6.65 (d, 2 H, 3,5-H, J 9); (C₆H₆) 2.53 (s, 6 H, NMe₂), 1.07 (t, 18 H, PMe₃, J 7.5). (**2c**) (CH₂Cl₂) 7.93 (d, 2 H, 2,6-H, J 8), 7.33 (d, 2 H, 3,5-H, J 8); (C₆H₆) 0.95 (t, 18 H, PMe₃, J 8). (**2d**) (CH₂Cl₂) 7.69 (s, 1 H, 2-H), 7.66 (d, 1 H, 6-H, J 8), 7.22 (t, 1 H, 5-H, J 8), 7.04 (d, 1 H, 4-H, J 8); (C₆H₆) 2.20 (s, 3 H, 3-Me), 1.10 (t, 18 H, PMe₃, J 8). (**3b**) (CH₂Cl₂) 7.80 (d, 2 H, 2,6-H, J 9), 6.67 (d, 2 H, 3,5-H, J 9), 2.94 (s, 6 H, NMe₂), 1.21 (t, 18 H, PMe₃, J 8). (**3c**) (CH₂Cl₂) 7.81 (d, 2 H, 2,6-H, J 9), 7.35 (d, 2 H, 3,5-H, J 9), 1.24 (t, 18 H, PMe₃, J 7.5).

(**3c**), and (**2d**), respectively], were isolated except for (**1e**) where much slower decomposition occurred to give insoluble material. The relative reactivities of (**1a–e**) were compared by heating a solution of each in benzene in sealed n.m.r. tubes at 81 °C for 3 h, and the ratio of the conversions decrease in the order (**1b**) (ca. 100%) > (**1a**) (63%) > (**1d**) (52%) > (**1c**) (36%) > (**1e**).

We had difficulty in preparing PMe₂Ph complexes of type (**1**) probably owing to their lower thermal stability compared with the PMe₃ complexes. Aryl(pentachlorophenyl)nickel(II) complexes, *trans*-[Ni(C₆Cl₅)(C₆H₄NMe₂-4)L₂] (L = PMe₃ or PMe₂Ph⁴), were much more stable in benzene at 81 °C.

Received, 16th April 1984; Com. 547

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