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

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Thermolysis of *trans*-[Ni(CCl=CCl_2)(C_6H_4Y)(PMe_3)$_2$] (Y = NMe_2-4, Me-4, Me-3, or Cl-4) resulted in the formation of the isomeric mono-organonickel(II) complexes, *trans*-[Ni{C_2Cl_2(C_6H_4Y)}Cl(PMe_3)$_2$], 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=CCl_2)(C_6H_4Me-4)(PMe_3)$_2$] (**1a**), was prepared from *trans*-[Ni(CCl=CCl_2)Cl(PMe_3)$_2$] and 4-tolyl-lithium (−60 °C to room temp., under argon, 65% yield), m.p. 134—136 °C (decomp., sealed capillary), ^{1}H n.m.r. (C_6H_6, 100 MHz) δ2.22 (s, 4-Me) and 0.79 (t, *J* 8 Hz, PMe_3).† 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, *trans*-[Ni{C_2Cl_2(C_6H_4Me-4)}Cl(PMe_3)$_2$] (**2a**), were isolated in 56% yield, m.p. 140—141 °C, ^{1}H n.m.r. (C_6H_6) δ 2.11 (s, 4-Me) and 1.03 (t, *J* 8 Hz, PMe_3).† 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 PMe_3 protons. Treatment of (**2a**) with NaNCS resulted in substitution of one of the chlorine atoms to give [62% yield from (**1a**)] *trans*-[Ni{C_2Cl_2(C_6H_4Me-4)}NCS(PMe_3)$_2$] (**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 ^{1}H 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 CCl_2=CCl(C_6H_4Me-4).

$$\text{R–M–R}'\text{–X} \xrightarrow{\text{i,ii}} \text{R–R}'\text{–M–X}$$

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

[Ni(CCl=CCl_2)(C_6H_4Y)(PMe_3)$_2$]
(**1**)

[Ni{C_2Cl_2(C_6H_4Y)}Cl(PMe_3)$_2$]
(**2**)

[Ni{C_2Cl_2(C_6H_4Y)}NCS(PMe_3)$_2$]
(**3**)

a; Y = Me-4
b; Y = NMe_2-4
c; Y = Cl-4
d; Y = Me-3
e; Y = Me-2

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† Further ^{1}H n.m.r. data for (**1a**), (**2a**), and (**3a**) in CH_2Cl_2 (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).

The analogous aryl(trichlorovinyl)nickel(II) complexes, *trans*-[Ni(CCl=CCl$_2$)(C$_6$H$_4$Y)(PMe$_3$)$_2$] [Y = NMe$_2$-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{C$_2$Cl$_2$(C$_6$H$_4$Y)}X(PMe$_3$)$_2$] (X = Cl or NCS) [(**2b**), (**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 PMe$_2$Ph complexes of type (**1**) probably owing to their lower thermal stability compared with the PMe$_3$ complexes. Aryl(pentachlorophenyl)nickel(II) complexes, *trans*-[Ni(C$_6$Cl$_5$)(C$_6$H$_4$NMe$_2$-4)L$_2$] (L = PMe$_3$ or PMe$_2$Ph[4]), were much more stable in benzene at 81 °C.

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‡ 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 ^{1}H N.m.r. spectral data (δ, *J* in Hz) for the organonickel(II) complexes (**1b**—**d**), (**2b**—**d**), and (**3b,c**): (**1b**) (CH$_2$Cl$_2$) 7.02 (d, 2 H, 2,6-H, *J* 7.5), 6.53 (d, 2 H, 3,5-H, *J* 7.5); (C$_6$H$_6$) 2.62 (s, 6 H, NMe$_2$), 0.83 (t, 18 H, PMe$_3$, *J* 8). (**1c**) (CH$_2$Cl$_2$) 7.22 (d, 2 H, 2,6-H, *J* 8), 6.91 (d, 2 H, 3,5-H, *J* 8); (C$_6$H$_6$) 0.68 (t, 18 H, PMe$_3$, *J* 8). (**1d**) (CH$_2$Cl$_2$) 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); (C$_6$H$_6$) 2.23 (s, 3 H, 3-Me), 0.78 (t, 18 H, PMe$_3$, *J* 7.5). (**2b**) (CH$_2$Cl$_2$) 7.89 (d, 2 H, 2,6-H, *J* 9), 6.65 (d, 2 H, 3,5-H, *J* 9); (C$_6$H$_6$) 2.53 (s, 6 H, NMe$_2$), 1.07 (t, 18 H, PMe$_3$, *J* 7.5). (**2c**) (CH$_2$Cl$_2$) 7.93 (d, 2 H, 2,6-H, *J* 8), 7.33 (d, 2 H, 3,5-H, *J* 8); (C$_6$H$_6$) 0.95 (t, 18 H, PMe$_3$, *J* 8). (**2d**) (CH$_2$Cl$_2$) 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); (C$_6$H$_6$) 2.20 (s, 3 H, 3-Me), 1.10 (t, 18 H, PMe$_3$, *J* 8). (**3b**) (CH$_2$Cl$_2$) 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, NMe$_2$), 1.21 (t, 18 H, PMe$_3$, *J* 8). (**3c**) (CH$_2$Cl$_2$) 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, PMe$_3$, *J* 7.5).