Facile Lithiation of Co-ordinated t-Methylphosphines in Bis-(2,6-dimethoxyphenyl)nickel(II) Complexes

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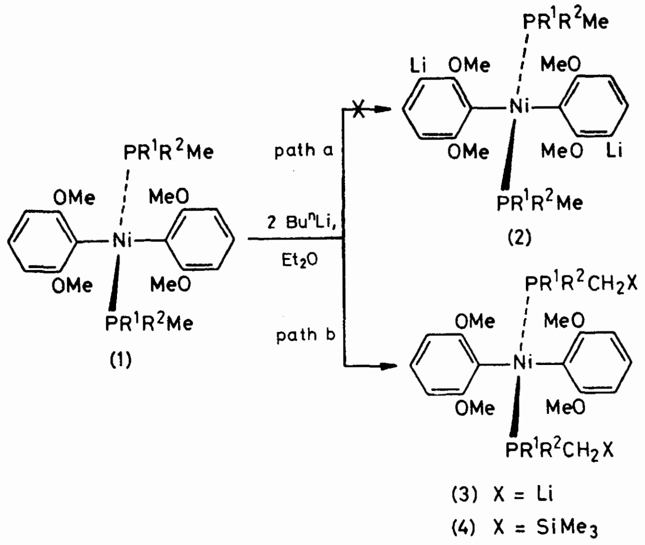
Summary Reactions of n-butyl-lithium with the bis-(2,6-dimethoxyphenyl)nickel(II) complexes, *trans*-[Ni{C_6H_3(OMe)$_2$-2,6}$_2$(PR$_3$)$_2$] (PR$_3$ = PMe$_3$ and PMe$_2$Ph), in diethyl ether resulted in the facile lithiation at the methyl carbon in the PR$_3$ ligands.

The bis-(2,6-dimethoxyphenyl)nickel(II) complexes, *trans*-[Ni{C_6H_3(OMe)$_2$-2,6}$_2$(PR$_3$)$_2$] [PR$_3$ = PMe$_3$ (**1a**) and PMe$_2$Ph (**1b**)], are easily obtainable, highly crystalline, and air-stable.[1] Since methoxyphenyl derivatives are well known to be lithiated by n-butyl-lithium *ortho* to the methoxy-group,[2] we attempted the reaction for complexes (**1a**) and (**1b**) in order to obtain the 3-lithiated intermediates (**2**) (path a, Scheme). We report herein the unexpected result that a methyl proton in the PR$_3$ ligands was substituted easily by lithium (**3**) (path b, Scheme). No report of unambiguous proton abstraction from a co-ordinated t-phosphine has yet appeared,[3] although proton abstractions from free t-phosphines[4] and co-ordinated diphosphines[5] have been discussed.

Treatment of compound (**1a**) with an excess of n-butyl-lithium in dry diethyl ether at 0 °C under nitrogen gave, in less than a few minutes, a light yellow precipitate. This was stirred at room temperature for 2 h and then quenched with D_2O. The ^{1}H n.m.r. spectrum ($CDCl_3$) of deuteriated (**1a**) was essentially identical with that of (**1a**), but showed a decrease in the intensity of the PMe$_3$ proton resonances by *ca.* two protons. When the lithiated intermediate was treated with Me$_3$SiCl, an air-stable orange-yellow crystalline complex, *trans*-[Ni{C_6H_3(OMe)$_2$-2,6}$_2$(PMe$_2$CH$_2$SiMe$_3$)$_2$] (**4a**), m.p. 87—88 °C (45—55% yield), was obtained [^{1}H n.m.r. ($CDCl_3$) δ −0·07 (s, 18 H, SiMe), 0·67 (t, 4 H, J_P 10 Hz, PCH$_2$Si), 0·79 (t, 12 H, J_P 7·5 Hz, PMe), 3·86 (s, 12 H, OMe), 6·29 (d, 4 H, J_H 7·5 Hz, *m*-H), and 6·91 (br t, 2 H, J_H 7·5 Hz, *p*-H)]. These observations suggest that a proton was abstracted by n-butyl-lithium from PMe$_3$ ligands rather than from the 2,6-dimethoxyphenyl groups. Compound (**4a**) was treated with carbon monoxide (1 atmosphere) in the presence of MeI and decomposed, in less than 2 h at room temperature, to give [C_6H_3(OMe)$_2$-2,6]$_2$CO and the [Me$_3$PCH$_2$SiMe$_3$]$^+$ salt.



a; R^1 = R^2 = Me
b; R^1 = Me, R^2 = Ph

Scheme

Reaction of compound (**1b**) with n-butyl-lithium followed by treatment with Me_3SiCl gave an analogous complex, *trans*-$[Ni\{C_6H_3(OMe)_2\text{-}2,6\}_2(PMePhCH_2SiMe_3)_2]$ (**4b**) (70—80%), but as a mixture of the *racemo*- and *meso*-isomers with respect to the two asymmetric phosphine ligands [^{1}H n.m.r. ($CDCl_3$) δ −0·30 (s, SiMe), 0·96 (overlapped t, J_P 11 Hz, PCH_2Si), 1·04 (overlapped t, J_P 7 Hz, PMe), 3·47 (s, OMe, *meso*), 3·58 (s, OMe, *racemo*), 3·69 (s, OMe, *meso*), 6·03 (d, J_H 8, *m*-H, *meso*), 6·08 (d, J_H 8, *m*-H, *racemo*), 6·14 (d, J_H 8, *m*-H, *meso*), and 6·7—7·2 (m, ArH)]. The relative *meso*:*racemo* ratio was 62:38 for the initial product and varied in the recrystallized fractions.

Two other complexes, *trans*-$[Ni\{C_6H_3(OMe)_2\text{-}2,6\}(C_6H_2Me_3\text{-}2,4,6)(PMe_3)_2]$ and *trans*-$[Ni(C_6H_2Me_3\text{-}2,4,6)(C_6H_4Me\text{-}2)(PMe_3)_2]$, reacted slowly with n-butyl-lithium even in the presence of tetramethylethylenediamine (15—22 h), and gave, on treatment with Me_3SiCl, *trans*-$[Ni\{C_6H_3(OMe)_2\text{-}2,6\}(C_6H_2Me_3\text{-}2,4,6)(PMe_3)(PMe_2CH_2SiMe_3)]$ (70%) and *trans*-$[Ni(C_6H_2Me_3\text{-}2,4,6)(C_6H_4Me\text{-}2)(PMe_2CH_2SiMe_3)_2]$ (30%), respectively.

These results clearly indicate that proton abstraction by n-butyl-lithium from t-methylphosphine co-ordinated to a transition metal has occurred. The high reactivity of bis(2,6-dimethoxyphenyl)nickel(II) complexes is probably due to the presence of four methoxy-groups, which increase the reactivity of n-butyl-lithium by co-ordination and/or which stabilize the lithiated intermediate by forming bicyclic rings with the *COO*-chelated lithium ion, both above and below the nickel(II) co-ordination plane. The difficult double-lithiation of *trans*-$[Ni\{C_6H_3(OMe)_2\text{-}2,6\}(C_6H_2Me_3\text{-}2,4,6)(PMe_3)_2]$ is tentatively attributed to steric interference by the two bulky aryl groups.

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