

Preliminary communication

REACTIONS OF SOME DIORGANONICKEL(II) COMPLEXES WITH *N*-BROMOSUCCINIMIDE

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Summary

The reactions of some diorganonickel(II) complexes with *N*-bromosuccinimide (NBS) resulted in facile bromine for hydrogen substitution in aromatic, alkynyl or alkenyl substituents, or in the addition of NBS to $C\equiv C$ bonds.

Diorganonickel(III) complexes appear to be intermediates in the reductive elimination process of diorganonickel(II) complexes [1—3]. Since *N*-bromosuccinimide (NBS) reacted with some monoorganonickel(II) complexes to give paramagnetic, pentacoordinated monoorganonickel(III) complexes of the type $RNi(PR'_3)_2Br_2$ [4], we intended to extend the reaction to several diorganonickel(II) complexes. Unexpectedly, the reaction resulted in the facile formation of a variety of novel bromoorganonickel(II) complexes. Some typical results are reported here.

The reactions were performed in acetone at room temperature without any catalyst, the diorganonickel(II) complexes reacting, in general, in less than a few minutes.

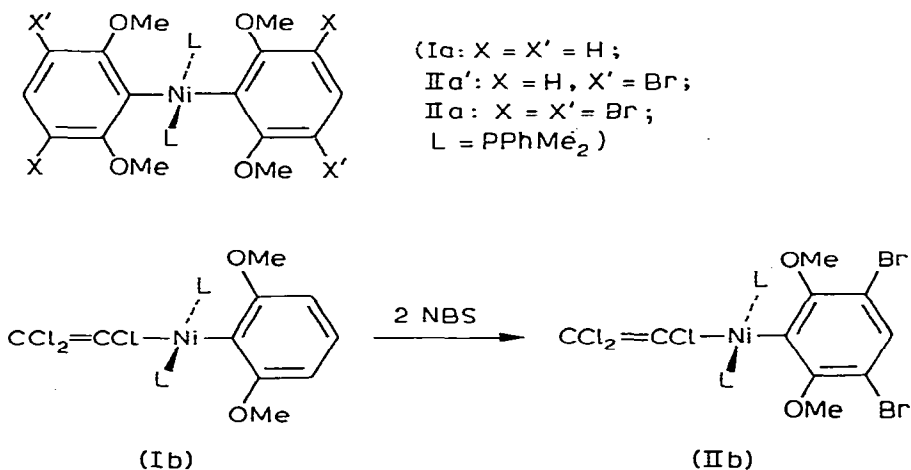


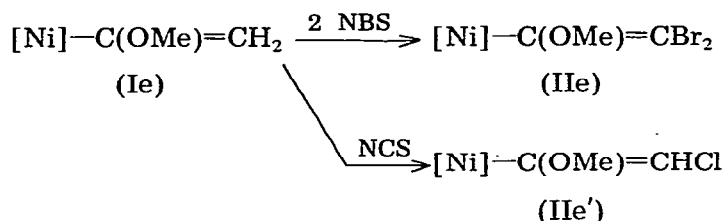
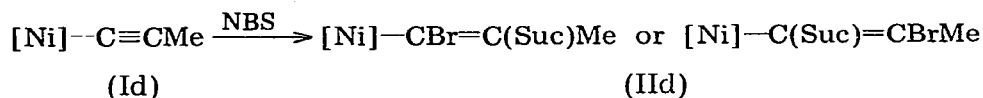
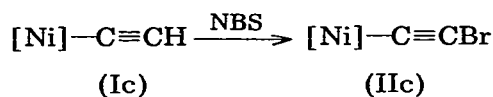
TABLE I

ANALYTICAL AND SPECTRAL DATA FOR *trans*-R(R')Ni(PPhMe₂)₂^a

| Complexes | M.p. (°C) | Analyses (found (calcd.)) (%) | | | IR Data (Nujol) (cm ⁻¹) | ¹ H NMR Data (CDCl ₃) (δ (ppm) [J (Hz)]) |
|-----------|------------------|-------------------------------|----------------|------------------|---|---|
| | | C | H | N | | |
| Ia | 153 ^b | 63.26 (63.06) | 6.88 (6.62) | | 1225vs, 1100vs (ν(COC)) | 1.07t [7] 12H (PMe); 3.63s 12H (OMe); 6.07d [8] 4H (m-H); 6.7-7.1m 12H (p-H and PPh) |
| Ib | 124-125 | 51.59 (51.83) | 5.24 (5.19) | | 1225vs, 1100vs (ν(COC)) | 1.37t [7,5] 12H (PMe); 3.25s 3H and 3.35s 3H (OMe); 5.91d [8] 2H (m-H); 6.75m 1H (p-H); 7.15s and 7.17s 10 H (PPh) |
| IIa' | 161 ^b | 50.27 (50.10) | 4.90 (4.99) | 20.82 (20.83) | 1220vs, 1080vs (ν(COC)) | 1.02t [7] 6H and 1.25t [7] 6H (PMe); 3.42s 6H and 4.20s (OMe); 5.91d [8] 2H (m-H); 7.02d-t [1.3] 2 (p-H); 6.6-7.2m 12H ^d (PPh) |
| IIa | 181 ^b | 41.40 (41.56) | 3.71 (3.92) | 34.60 (34.56) | 1205vs, 1060s (ν(COC)) | 1.23t [7] 12H (PMe); 3.68s 12H (OMe); 7.35t [1.3] 2 H (p-H); 6.6-7.2m 10H (PPh) |
| IIb | 110-111 | 40.97 (41.07) | 3.74 (3.84) | 34.81 (35.01) | 1205vs, 1060s (ν(COC)) | 1.40t [7,5] 6H and 1.55t [7,5] 6H (PMe); 4.06s 3H and 4.35s 3H (OMe); 7.2-7.3m 11H (p-H and PPh) |
| IIc | 110 ^b | 41.60 (41.88) | 3.08 (3.22) | 37.58 (37.37) | 2050w (ν(C≡C)) | 1.64t [8] 12H (PMe); 7.2-7.6m 10H (PPh) |
| IIc | 202 ^b | 43.20 (43.47) | 3.47 (3.65) | 1.62 (1.75) | 1715vs (ν(C=O)) | 1.63t [8] 6H and 1.76t [8] 6H (PMe); 1.98t [2.5] 3H (CMe); 2.73s 4H (CH ₂ CH ₂); 7.1-7.3m 10H (PPh) |
| IIe | 161 ^b | 37.48 (37.57) | 3.19 (3.15) | 42.49 (42.18) | 1515m (ν(C=C)) ^f 1115s (ν(COC)) | 1.53t [7,5] 6H and 1.65t [7,5] 6H (PMe); 3.93s 3H (OMe); 7.0-7.3m 10H (PPh) |
| IIe' | 127 ^b | 44.26 (44.43) | 3.82 (3.88) | | 1520w (ν(C=C)) ^f 1095s (ν(COC)) | 1.49t [8], 1.64t [8] and 1.35-1.7m-broad total 12H (PMe); 3.10s 1.9H and 3.59s 1.1H (OMe); 4.26t [3.0] 3 0.35H and 5.47t [4.0] 3 0.65H (CH); 7.1-7.4m 10H (PPh) |

^a Complexes Ie, Id and Ie have been reported elsewhere [5]. ^b Decomposition. ^c ⁶J_P value. ^d Total intensity of p-H and PPh proton signals. ^e ⁵J_P value.^f Tentative assignment. ^g ⁴J_P value.

Complex Ia was brominated stepwise and selectively at the *meta* positions of the $C_6H_3(OMe-o)_2$ groups to give either IIa' or IIa depending on the amount of NBS employed. Reaction of Ia or IIa with an excess of NBS gave a green solution, but we have found no evidence for nickel(III) complex formation at present [4]. Addition of alcohol or water to the green solution resulted in the recovery of IIa. Analogous bromination was observed with Ib, in which the nickel atom is sterically less hindered than that in Ia.



$[Ni] = trans-C_6Cl_5Ni(PPhMe_2)_2$, Suc = NC(O)CH₂CH₂CO.

The alkynyl proton in Ic and the alkenyl protons in Ie were substituted quite easily, giving IIc and IIe, respectively*. Although a monobromo(methoxy)vinyl complex could not be isolated from the reaction of Ie and NBS, a reaction with 1 equivalent of *N*-chlorosuccinimide gave an *E/Z* mixture of monochloro-substituted complexes (IIe'). Such examples of alkynyl- or alkenyl-hydrogen substitution by halogen are, to our knowledge, quite limited in the chemistry of these halogenating agents [6–8]. The reaction of Id, on the other hand, was rather slow, and a product (IID) containing a succinimido group was isolated. Although the structure or geometry of the bromo(succinimido)propenyl group in IID has not been determined, the product contained only a single isomer. The detailed mechanisms of these reactions are unknown at present, although the reactions can be readily explained in terms of a radical process [9], or an ionic process [10]. Another possibility is an autocatalyzed radical process, with the nickel(II) complex forming a pentacoordinated diorganonickel(III) bromide intermediate.

Experimental

Preparation of Ia, Ib, Ic, Id or Ie. An ethereal suspension (30 ml) of 2,6-dimethoxyphenyllithium [11] (22 mmol) was cooled (ice bath) under nitrogen, and Ni(PPhMe₂)₂Cl₂ (4.00 g, 10 mmol) was added with stirring. The mixture was stirred for 1 h at room temperature to give a yellow precipitate. Methanol (30 ml)

*Complex IIa reacted with perchloric acid to give a cationic carbene complex, $trans-[C_6Cl_5Ni(PPhMe_2)_2-\{C(OMe)CHBr_2\}]ClO_4$, an analogous reaction having been reported for Ie [5].

was added at 0°C, and the precipitate was filtered and recrystallized from acetone/methanol to give crystals of Ia (4.72 g, 79%).

Similar treatment of *trans*- $\text{CCl}_2=\text{CClNi}(\text{PPhMe}_2)_2\text{Cl}$ [4] with 2,6-dimethoxyphenyllithium in ether/benzene (1/1) gave Ib (60%). Complexes Ic, Id and Ie were prepared as described previously [5].

Reactions of Ia, Ib, Ic, Id or Ie with N-halosuccinimide. To a solution of Ia (0.608 g, 1 mmol) in 50 ml of acetone was added dropwise during about 5 min a solution of *N*-bromosuccinimide (0.358 g, 2 mmol) in 20 ml of acetone at room temperature. The solvent was removed under reduced pressure, and the residual solid was recrystallized from acetone/methanol to give IIa' (0.56 g, 74%). Use of 4 mmol of NBS dissolved in 40 ml of acetone in the above reaction afforded IIa (0.62 g, 67%).

Complex Ib, Ic or Ie reacted in an analogous manner with 2, 1 or 2 equivalents of NBS in acetone to give IIb (77%), IIc (69%) or IIe (75%), respectively.

Similar treatment of Ie with 1 equivalent of *N*-chlorosuccinimide at 0°C gave IIe' (65%).

A mixture of Id (0.312 g, 0.5 mmol) and NBS (0.089 g, 0.5 mmol) in 25 ml of acetone was kept at room temperature overnight. Similar work-up as above gave IIId (0.27 g, 67%).

The elemental analyses and spectral data are summarized in Table I.

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