

Cationic η^3 allylic complexes. III⁶

The reaction of S-allyl iso tetramethyl thioüronium salts with nickel tetracarbonyl^{*}

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Recently we have described the preparation of air stable η^3 allylbis(triphenylphosphine) nickel(II) salts of the type 3 by reaction of allyloxytris(dimethylamino)phosphonium salts 1^{1,2} and nickel tetracarbonyl in acetonitrile (AN) followed by the addition of triphenylphosphine to the solution of the intermediate complex 4.

This reaction showed that cationic η^3 allylic complexes³ can be prepared directly from a suitable allylic cationic salt bearing a neutral leaving group (hexamethyl phosphoric triamide).

We show here that this type of reaction can be observed from S-allyl isotetramethyl thioüronium salts, where the tetramethylthioürea (TTU), is the neutral leaving group, trapped at once as a ligand by the metal.

- The S-methallyl tetramethylisothioüronium hexafluorophosphate 2⁴ reacts with nickel tetracarbonyl in acetonitrile solution and in the presence of one equivalent of TTU to give 5 (quantitative yield). The reaction is therefore slower than with 1 and the presence of TTU is necessary.

- η^3 methallyl bis(tetramethylthioürea) nickel(II) hexafluorophosphate 5

Air sensitive orange red solid MP (dec) : 135°C

Analysis : $C_{14}H_{31}F_6N_4NiPS_2$; MW : 523,23 g ; Found (calc.) : C : 32,18 (32,14) ; H : 6,00 (5,97) ; N : 10,65 (10,71) ; Ni : 11,54 (11,22)

¹H NMR (D_3CCN) : 2,13 δ , s, (3 H), CH_3 ; 2,22 δ , s, (2 H), anti protons ; 2,95 δ , s, (2 H), syn protons ; 3,13 δ , s (24 H), $N-CH_3$

¹³C NMR (H_3CCN) : 20,3 δ , CH_3 ; 41,3 δ , $N-CH_3$; 56,3 δ , CH_2 ; 120,6 δ , $C-CH_3$; 187,2 δ , $S=C$

This method allows a wide generalization of the available structures of the type 5 ; indeed we had observed that only the less substituted salts of the type 1 are stable.

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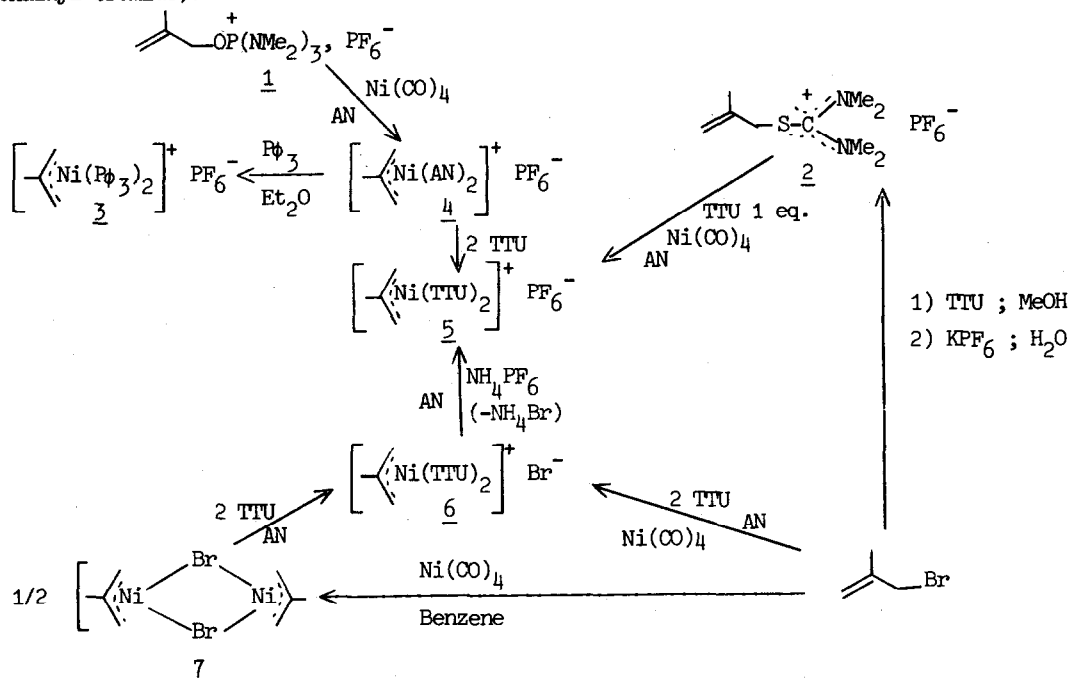
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A number of analogs of 5 will be described in a full paper.

The structure of 5 is confirmed by its synthesis by three other methods. The treatment of 4 by TTU gives rise to the complex 5 precipitated from acetonitrile by diethyloxide and quantitatively isolated by filtration.

- The bis η^3 methallyl di μ bromonickel(II) 7⁵ reacts readily with TTU to give 6 (not isolated) whose solution treated by NH_4PF_6 in acetonitrile gives 5 by precipitation of NH_4Br (yield : 67 % based on methallyl bromide).

- Finally a one pot preparation is possible starting from the mixture of methallyl bromide, TTU and $\text{Ni}(\text{CO})_4$ in acetonitrile followed by treatment with NH_4PF_6 (yield : 65 % based on methallyl bromide).



These methods provide the more ready access to the less known η allylic cationic complexes of nickel(II), whose catalytic properties are under investigation.

Bibliography

- (1) B. Castro and D. Neibecker, *J. Organometal. Chem.* **85**, C 39, 1975
- (2) D. Neibecker and B. Castro, *ibid*, accepted for publication
- (3) C.A. Tolman, *J. Amer. Chem. Soc.* **92**, (1970) 6777
- (4) This salt is prepared by reacting methallyl bromide and TTU in methanol solution and treatment of the resulting mixture by aqueous KPF_6 . Extraction with CH_2Cl_2 gives, after evaporation under reduce pressure, the white solid 2 which can be recrystallized in ethyl acetate (MP : 67°C ; quantitative yield).
- (5) M.F. Semmelhack and P.M. Helquist, *Organic Syntheses* (Ed. H.O. House) J. Wiley, New York **52**, 115, 1972
- (6) Part II, B. Castro and D. Neibecker, *J. Organomet. Chem.* in press