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Chemistry of the Cyclopentadienylmetal Carbonyls. VIII.[1] The Reaction of a Cationic Cyclopentadienylnickel Compound with Pentafluorophenyllithium

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Several reactions leading to formation of the cationic complex $C_5H_5Ni[(C_6H_5)_3P]_2^+$ *are described. This complex, as the tetraphenylborate salt, undergoes thermal decomposition in tetrahydrofuran solution under reflux conditions giving* $C_5H_5Ni[(C_6H_5)_3P]C_6H_5$*. Reaction of the cationic complex* $C_5H_5Ni[(C_6H_5)_3P]_2^+$ *and* C_6F_5Li *proceeds with nucleophilic displacement of a triphenylphosphine ligand by* C_6F_5*, to give* $C_5H_5Ni[(C_6H_5)_3P]C_6F_5$*, in a reaction analogous to others reported recently.*

Introduction

We have recently described synthesis of cationic cyclopentadienyl-iron,[2] and cyclopentadienyl-molybdenum and -tungsten,[3] carbonyl complexes. These substances are susceptible to attack by nucleophilic reagents such as pentafluorophenyllithium[1,4] leading in some cases to uncharged pentafluorophenyl-metal derivatives. In this paper we describe related studies involving reactions of the cation $C_5H_5Ni[(C_6H_5)_3P]_2^+$.[5]

Experimental Section

Our studies on the synthesis of the cationic complex $C_5H_5Ni[(C_6H_5)_3P]_2^+$ varied somewhat from those of McArdle and Manning,[5] and so we have summarized this work below. The precursor for this synthesis, $C_5H_5Ni[(C_6H_5)_3P]Cl$, was prepared from $[(C_6H_5)_3P]_2NiCl_2$ and nickelocene.[6] Pentafluorophenyllithium was prepared in tetrahydrofuran by the literature method.[7] All reactions were carried out under nitrogen.

The infrared spectra were recorded on a Beckman IR-10 spectrophotometer, and the proton n.m.r. spectra on a Varian A-60. Microanalyses were performed by the Bernhardt Laboratories, Max Planck Institut für Kohlenforschung, Mulheim, Germany and by the Schwartzkopf Microanalytical Laboratory, Woodside, N. Y.

Preparation of $C_5H_5Ni[(C_6H_5)_3P]_2^+ClO_4^-$*, using* $AgClO_4$ *as a Halide Acceptor.* A solution containing 2.0 g $C_5H_5Ni[(C_6H_5)_3P]Cl$ (4.6 mmoles) and 1.22 g triphenylphosphine (4.6 mmole) in 100 ml benzene was prepared. At room temperature, the dropwise addition of a saturated solution of $AgClO_4$ in benzene caused immediate formation of a precipitate. The $AgClO_4$ solution was added until no additional formation of precipitate was observed. The precipitate was collected on a filter. It was then dissolved through the filter with acetone, and the addition of ether to this acetone solution caused immediate precipitation of pale green $C_5H_5Ni[(C_6H_5)_3P]_2^+ClO_4^-$ (2.6 g., 75.7% yield), m.p. = 197°C (d).

Anal. Calcd. for $C_{41}H_{35}NiP_2O_4Cl$: C, 65.85; H, 4.72; Ni, 7.85; Cl, 4.71. Found: C, 65.68; H, 4.95; Ni, 7.74; Cl, 4.36.

The infrared spectrum (nujol mull, KBr plates) shows peaks at: 1310 (w), 1185 (w), 1090 (vs, b), 1000 (w), 840 (m), 820 (m), 750 (s), 700 (s), 625 (m), 540 (m), 528 (s), 515 (m), 500 (m) cm^{-1}.

The n.m.r. spectrum (acetone) showed absorptions at τ 4.55 (singlet, C_5H_5) and τ 2.52 (multiplet, C_6H_5), of appropriate intensities.

This compound was also formed in 97% yield directly from $C_5H_5Ni[(C_6H_5)_3P]Cl$ and $AgClO_4$ in benzene at room temperature. (The yield based on the reaction $2C_5H_5Ni[(C_6H_5)_3P]Cl \rightarrow 1C_5H_5Ni[(C_6H_5)_3P]_2^+ClO_4^-$.) The only other product obtained from this reaction from workup in aqueous solution, was $Ni(H_2O)_6(ClO_4)_2$ (62%).

Reactions of $C_5H_5Ni[(C_6H_5)_3P]Cl$ and $AgClO_4$ in the presence of other donors (CO, CH_3CN) led to mixtures of $C_5H_5Ni[(C_6H_5)_3P]_2^+ClO_4^-$ and $C_5H_5Ni[(C_6H_5)_3P]L^+ClO_4^-$ (L = CO, CH_3CN) in which the former was always in much larger quantity. The compounds $C_5H_5Ni[(C_6H_5)_3P]L^+ClO_4^-$ decomposed rapidly and could not be isolated pure.

Preparation of $C_5H_5Ni[(C_6H_5)_3P]_2^+$ *using* $AlCl_3$ *as a Halogen Acceptor.* When 1.0 g (2.32 mmoles) $C_5H_5Ni[(C_6H_5)_3P]Cl$, 0.61 g (2.32 mmoles) triphenylphosphine, and 0.60 g (4.5 mmoles) aluminum chloride were refluxed for two hours in benzene a green

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(1) Previous paper: R. L. Shubkin and P. M. Treichel, *Inorg. Chem.*, 6, 1328 (1967).
(2)P. M. Treichel, R. L. Shubkin, K. W. Barnett, D. Reichard, *Inorg. Chem.*, 5, 1177 (1966).
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(4) R. L. Shubkin and P. M. Treichel, *J. Organometal. Chem.*, 5, 488 (1966).
(5) P. A. McArdle and A. R. Manning, *Chem. Comm.*, 417 (1967).
(6) U. S. Patent 3,054,815 (1962); *C. A.*, *58*, 1494 (1963).
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oil settled out. The benzene was decanted, and the oil dissolved in methanol, and then this solution was added dropwise to a saturated solution of $NaB(C_6H_5)_4$ in 1:1 ethanol-water. The yellow solid, $C_5H_5Ni[(C_6H_5)_3P]_2^+B(C_6H_5)_4^-$ was recrystallized from acetone-water, m.p. 139° (2.0 g, 90% yield).

Anal. Calcd. for $C_{65}H_{55}NiP_2B$: C, 83.37; H, 5.93; Ni, 6.28; B, 1.16. Found: C, 82.12; H, 5.49; Ni, 5.75; B, 1.04.

The infrared spectrum (nujol mull, KBr plates) shows peaks at: 1310 (w), 1185 (w), 1090 (m), 1030 (w), 1000 (w), 835 (m), 810 m), 740 (s), 730 (s), 700 (s), 690 (m), 540 (m), 528 (s), 515 (m), 500 (m) cm^{-1}.

Preparation of $C_5H_5Ni[(C_6H_5)_3P]_2^+B(C_6H_5)_4^-$ using $NaB(C_6H_5)_4$ as a Halogen Acceptor. Wiliknson, *et al.* report the use of $NaB(C_6H_5)_4$ as a halogen acceptor in synthesis of cationic iron complexes.[8] We attempted syntheses using this reagent and observed two alternate products to be formed, the choice being determined by temperature and solvent. When 1.35 g of $C_5H_5Ni[(C_6H_5)_3P]Cl$ (3.13 mmoles) in benzene: ethanol was treated with excess $NaB(C_6H_5)_4$ at room temperature, yellow-green $C_5H_5Ni[(C_6H_5)_3P]_2^+B(C_6H_5)_4^-$ (0.8 g, 55% yield) precipitated.

Concentration of the benzene filtrate and chromatography of the residue on silica gel with benzene as eluent gave 0.1 g $C_5H_5Ni[(C_6H_5)_3P]C_6H_5$ (6.9% yield), m.p. 136°C (lit.,[9] 137-139°C).

Anal. Calcd. for $C_{29}H_{25}NiP$: C, 75.19; H, 5.44; P, 6.69. Found: C, 75.13; H, 5.30; P, 6.56.

In contrast, when the same mixture of reagents was refluxed in tetrahydrofuran for 2 hr only $C_5H_5Ni[(C_6H_5)_3P]C_6H_5$ was found (86% yield). When $C_5H_5Ni[(C_6H_5)_3P]_2^+B(C_6H_5)_4^-$ was refluxed in tetrahydrofuran, the same covalent product was obtained (74%).

Reaction of $C_5H_5Ni[(C_6H_5)_3P]_2^+ClO_4^-$ and Pentafluorophenyllithium. To a tetrahydrofuran solution of pentafluorophenyllithium (2.7 mmoles) was added 2.0 g of $C_5H_5Ni[(C_6H_5)_3P]_2^+ClO_4^-$. The mixture was stirred at 0°C for 1 hr and then at room temperature for 3.5 hr. The solvent was removed and the resulting residue dissolved in benzene. Addition of octane to the benzene solution gave 1.7 g of green precipitate which was mostly starting material. The filtrate was evaporated to dryness, leaving 0.2 g (90% yield based on starting material used) $C_5H_5Ni[(C_6H_5)_3P]C_6F_5$.[10]

Anal. Calcd. for $C_{29}H_{20}NiPF_5$: C, 62.97; H, 3.64; P, 5.60; F, 17.17. Found: C, 63.04; H, 3.71; P, 5.48; F, 17.38.

The n.m.r. spectrum ($CDCl_3$) consists of a multiplet at τ 2.68 and a singlet at τ 4.75 (ratio 3:1). The infrared (nujol, KBr plates) has peaks at 1498 (s), 1435 (m), 1095 (m), 1055 (m), 850 (s), 835 (w), 790 (m), 782 (m), 750 (m), 740 (w), 690 (m), 535 (s), 510 (m), and 487 (w) cm^{-1}.

Results and Discussion

The green to yellow crystalline compounds $C_5H_5Ni[(C_6H_5)_3P]_2^+X^-$ ($X^- = ClO_4^-$, $B(C_6H_5)_4^-$) are air and water stable and possess a relatively high degree of thermal stability. The cationic complexes arise from reactions of $C_5H_5Ni[(C_6H_5)_3P]Cl$ and triphenylphosphine in the presence of halogen acceptors; this is the most general method of preparation of cationic complexes.[2,3] Any of several halogen acceptors may be used in this reaction with apparently equal facility. It is interesting that the cationic complex is also formed rapidly and in high yield even if the triphenylphosphine is omitted in these reactions. Since in our earlier studies using silver perchlorate as a halogen acceptor[11] we observed evidence of an unstable σ-bonded metal perchlorate, one might postulate a similar intermediate, $C_5H_5Ni[(C_6H_5)_3P]OClO_3$, here. This intermediate would then be required to undergo some sort of valence disproportionation to give the observed product.

Our observations using sodium tetraphenylborate were particularly interesting because the products of the reaction were dependent on the reaction temperature and solvent. At room temperature the primary product of the reaction of $C_5H_5Ni[(C_6H_5)_3P]Cl$ and $NaB(C_6H_5)_4$ in benzene-ethanol was the cationic $C_5H_5Ni[(C_6H_5)_3P]_2^+B(C_6H_5)_4^-$ which precipitated from the reaction with only a small amount of covalent $C_5H_5Ni[(C_6H_5)_3P]C_6H_5$ [9] being formed. If the same reaction was run in solution in refluxing tetrahydrofuran, only the latter product was obtained. We subsequently confirmed that the former product could be converted to the latter on simple heating in solution. The preparation of a phenyl-metal compound by this route may well have utility in other situations. The standard route, involving a metal carbonyl anion and benzoyl chloride followed by decarbonylation, is often inconvenient or impossible because of accessibility of a suitable anion.

The reaction of $C_5H_5Ni[(C_6H_5)_3P]_2^+$ with pentafluorophenyllithium could logically have afforded any of three products if one can draw analogies with other systems.[1] Displacement of triphenylphosphine by the group $C_6F_5^-$ to form $C_5H_5Ni[(C_6H_5)_3P]C_6F_5$ seemed the most likely alternative, and in fact was observed to be the only reaction to occur. The products expected from attack at the C_5H_5-ring, and from reduction, were not observed. A high percent conversion into the known compound,[10] $C_5H_5Ni[(C_6H_5)_3P]C_6F_5$, (90%) was indicated in our experiments. This observed reaction, which involves displacement of triphenylphosphine from the metal, has some precedent; in the reaction of $C_5H_5Fe(CO)_2[(C_6H_5)_3P]^+$ with phenyllithium a very small quantity of $C_5H_5Fe(CO)_2C_6H_5$ was observed, although the primary product was *exo*-1-C_6H_5-$C_5H_5Fe(CO)_2[(C_6H_5)_3P]$.[1] Displacement of pyridine and acetonitrile in similar reactions were observed to occur also.[1]

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