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The Potential of π-Bonded Organometallic Polymers in Catalyst Design

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ABSTRACT

Reductive substitution, the process whereby a hydrocarbon ligand, usually a cyclopentadienyl group, in a transition metal complex is replaced by another unsaturated hydrocarbon with concomitant metal reduction has been utilized to prepare novel complexes of Cr^{o}, Cr^{I}, Mn^{I}, Co^{I} and Ni^{o}. Similarly, ligand substitution, defined more generally as replacement of ligand(s) of a metal complex by an unsaturated hydrocarbon but with no change in the oxidation state of the metal, has resulted in the synthesis of a series of tetraphenylborate and substituted tetraphenylborate complexes of Fe^{II}, Mo^{I}, Cr^{I}, W^{I}, and Co^{I}. These procedures and the complexes derived therefrom are considered models for polymers incorporating a variety of novel features.

INTRODUCTION

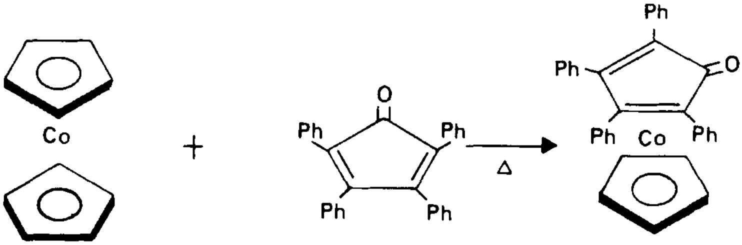
Reductive substitution and ligand substitution of metallocenes and related compounds has been successful in the synthesis of a wide variety of new and unusual π-complexes. Reductive substitution is defined as the process whereby a hydrocarbon ligand, usually a cyclopentadienyl group, in a transition metal complex is replaced by a new hydrocarbon ligand containing an appropriately different number of π-electrons so as to bring the new complex into conformity with the EAN rule; an additional feature is that formal reduction of the metal atom in the new complex is effected. Ligand substitution is a related process: one hydrocarbon ligand replaces another hydrocarbon ligand or even non hydrocarbon ligand such as CO, halide, etc., but with no accompanying reduction of the metal. As the reducing or displacing ligand a neutral unsaturated species, its corresponding radical anion or other suitably structured anion may be used.

The procedures for the syntheses of these complexes can serve as prototypes for the π-complexation of diene and arene polymers by transition metals. It is anticipated that these polymers will avoid certain drawbacks of the more conventional method of attachment of transition metal catalysts to polymers, i.e., phosphine ligation. Phosphine liganding polymers are notorious for their tendency to "leak" their complexed metals. These new polymers will be multiply-bonded to the metal atom, usually by an η^4 or η^6 ligation; said multiple-bonding should significantly decrease the tendency for the metal atoms to "leak". It is also anticipated, based on the model compounds studied, that reductive substitution and ligand substitution will afford several new types of organometallic polymers.

As models for these polymers, a number of high molecular weight dienes and arenes have been used. These include terphenyl and related polyaromatic systems, the tetraphenylborate anion and substituted tetraphenylborate anions, fluorene, carbazole and tetracyclones (tetraphenylcyclopentadienones).

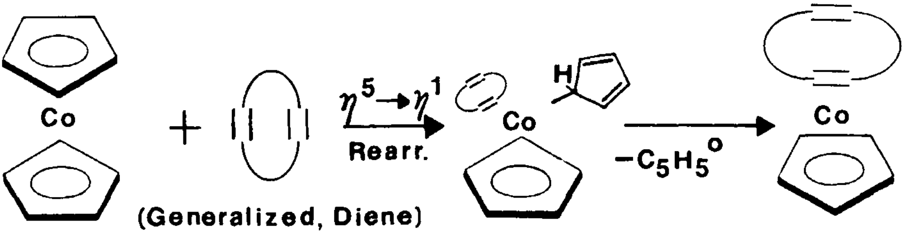
REDUCTIVE SUBSTITUTION

Reductive substitution of cobaltocene with the tetracyclone ligand and substituted tetracyclone ligands has afforded a series of $C_5H_5Co^I(\eta^4\text{-diene})$ complexes (equation 1). This reaction is envisioned



(1)

as proceeding via an $\eta^5 \to \eta^1$ rearrangement prior to complete dissociation and reductive displacement of the cyclopentadienyl ligand (equation 2). Our thinking is



(2)

that all the reductive substitutions described in this section proceed via this or a related mechanism. Substituted complexes of this class that have been prepared are bis-substituted at the p-positions of the 3- and 4- position phenyl groups (Table I).

TABLE I

(η^5-Cyclopentadienyl)(η^4-tetracyclone)cobalt Compounds Prepared by the Reductive Substitution of Cobaltocene[a,b]

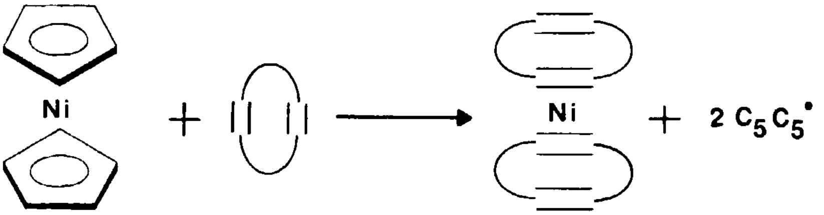
Para 3- and 4-position substituent	% Yield	m.p. (°C)
-H	37	325-327
$-OCH_3$	22.9	238-239
$-CH_3$	11.5	241-242
-Cl	30.5	299-300

[a] Reactions run in refluxing diethylbenzene or reactants simply melted together with no solvent present.

[b] All compounds are red crystals from CH_2Cl_2/petroleum ether.

Studies of the electronic influence of these remote substituents on the metal atom using ^{13}C nmr(1) and mass spectroscopy are in progress, but preliminary indications are that these remote substituents do not have much of an effect.

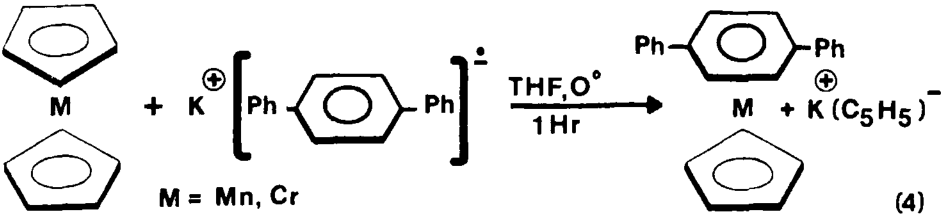
Direductive bis-substitution of nickelocene (equation 3) with tetracyclone has afforded bis-tetracyclone nickel, an extremely intractable material. A second model derivative that has been prepared by this technique is bis-duroquinone nickel, but at present the yield is extremely low. Attempts to prepare a mixed complex of these two ligands have failed.



(3)

Diene = Tetracyclone or Duroquinone

Manganocene and chromocene upon reductive substitution have afforded a series of polyphenyl derivatives of Mn^{I}, Cr^{I}, and Cr^{0}. This process is illustrated with terphenyl radical anion functioning as the reducing ligand (equation 4).



(4)

Terphenylcyclopentadienylmanganese is an air-stable, high melting solid whereas the analogous chromium derivative, being only a 17-electron system, is not air stable. Ir and nmr evidence indicate that complexation has taken place at the central ring of the terphenyl moiety. Other arenecyclopentadienylmanganese complexes that have been prepared are listed in Table II, although

TABLE II

$(\eta^5\text{-}C_5H_5)Mn(\eta^6\text{-}ArH)$ Derivatives

Prepared by Reductive Substitution of Manganocene

Arene	m.p.(°C dec)	% Yield	Color
$C_6H_5\text{-}C_6H_5$	116	30	orange
$C_6H_4\text{-}1,2\text{-}(C_6H_5)_2$	oil	30	red
$C_6H_4\text{-}1,3\text{-}(C_6H_5)_2$	106	35	red
$C_6H_4\text{-}1,4\text{-}(C_6H_5)_2$	113	61	orange
$C_6H_3\text{-}1,3,5\text{-}(C_6H_5)_3$	147	20	red
$C_6H_1\text{-}1,2,3,4,5\text{-}(C_6H_5)_5$	158-162	25	red
$C_6H_5C(C_6H_5)_6{=}C(C_6H_5)_2$	76	20	dk. red

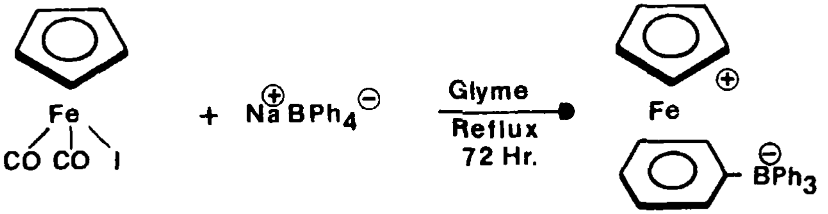
the evidence is not as strong that the indicated arene ring is the one π-bonded to the metal atom.

An 18-electron bis-terphenylchromium derivative has resulted from direductive bis-substitution of chromocene where the ratio of radical anion to metallocene was 2:1. This result coupled with the results of direductive bis-substitution in the nickel series (equation 3) suggests that this process may prove useful in cross-linking of certain types of polymers.

LIGAND SUBSTITUTION

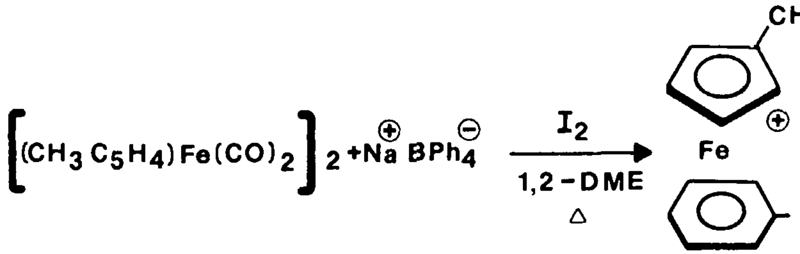
Ligand substitution is a process whereby a hydrocarbon ligand or σ-type ligands such as CO or halogen are displaced by a new hydrocarbon ligand but without accompanying reduction of the metal atom of the complex. Several notable sequences incorporating this process have been carried out.

Cyclopentadienylirondicarbonyl iodide upon treatment with the bulky, negatively charged tetraphenylborate anion produced a novel zwitterionic organometallic complex (equation 5). In like manner a series of phenyl-substituted tetraphenylborates have been used to synthesize a series of correspondingly substituted zwitterionic complexes (Table III).



(5)

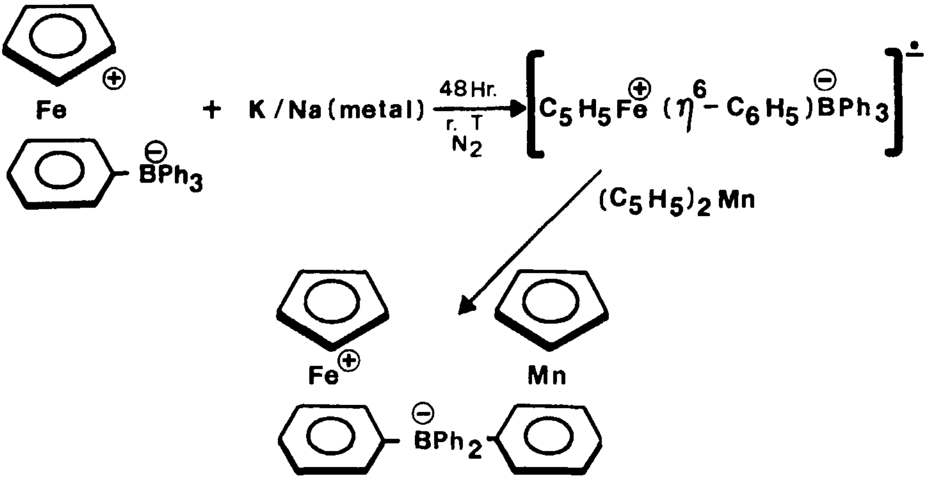
Modification of this route has allowed preparation of not only the parent complex but also the methylcyclopentadienyl derivative (equation 6).



(6)

Ir, mass spectral, ^1H and ^{13}C nmr data support the assignment of the unusual zwitterionic structure in these complexes.

Reductive substitution of the parent iron zwitterionic complex with manganocene gave a bimetallic compound, illustrating the fact that two contiguous rings can be complexed (equation 7). This result also suggests



(7)

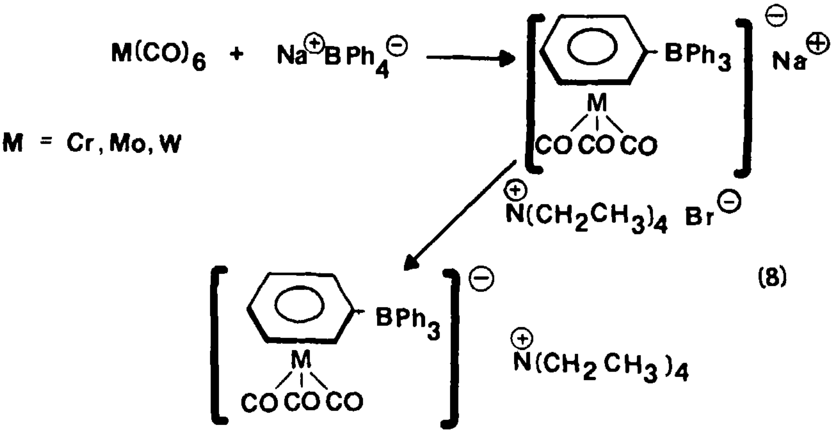
that more than one transition metal may be incorporated into a suitable polymer with this technique.

Group VI hexacarbonyls have been found to be susceptible to displacement by the bulky, negatively charged tetraphenylborate ion. Equation 8 illustrates the synthesis of a series of arene metal tricarbonyls.

TABLE III

(η^5-Cyclopentadienyl)(η^6-tetraarylborate)iron Complexes Prepared by Ligand Substitution of Cyclopentadienylirondicarbonyl iodide

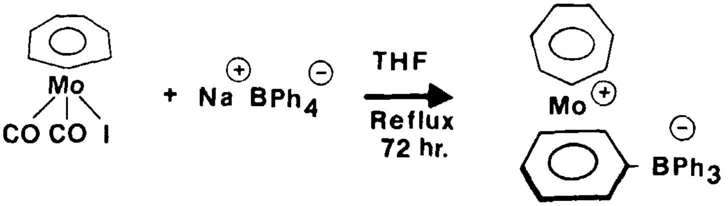
Aryl substituent	% Yield	m.p.(°C dec)
C_6H_5-	65	275-278
p-$CH_3C_6H_4$-	60	241-242
m-$CH_3C_6H_4$-	56	190-192
p-$CH_3OC_6H_4$-	18	198-200



(8)

These molecules were isolated and characterized as their tetraethylammonium salts. In addition to the usual ir and nmr characterization of these compounds, an x-ray structure of the molybdenum member of the series has been completed(2).

It was desirable to demonstrate that at least one of these model compounds could function as a homogeneous catalyst. To this end the most soluble of the zwitterionic complexes was examined. This was prepared by a method analogous to the synthesis of the iron compound (equation 5), i.e., cycloheptatrienyl molybdenumdicarbonyl iodide was treated with sodium tetraphenylborate (equation 9). In addition

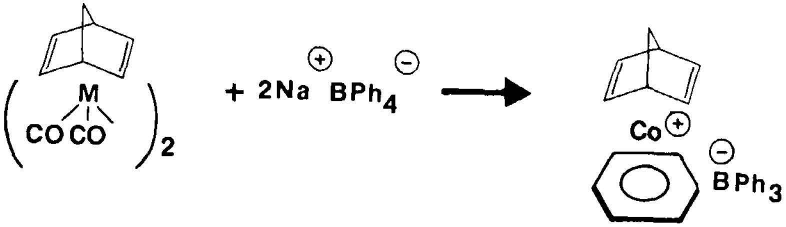


(9)

to ir, ^{1}H and ^{13}C nmr data for this complex, and x-ray structural analysis has been obtained(2). Its visible spectrum was consistent with a significant amount of low-lying electron density on the metal atom while the x-ray diffraction study revealed that the molybdenum atom might well possess additional coordination sites. The anticipated result of these observations, namely, that this complex would promote reduction of olefins under mild conditions, has now been realized(3).

Because of the interesting and potentially significant properties of this molybdenum complex, a series of analogues have been synthesized utilizing substituted tetraphenylborates. The fully characterized members of this series are recorded in Table IV.

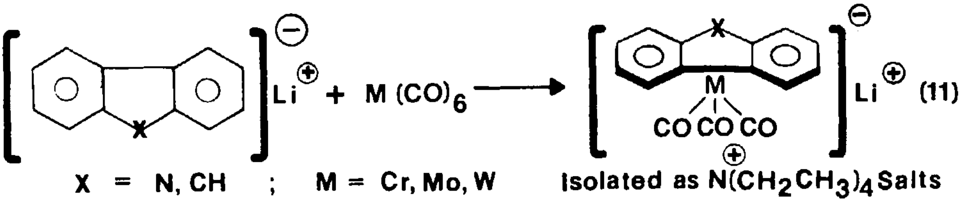
A tetraphenylborate derivative of cobalt had recently been prepared. Bis-(norbornadienecobalt dicarbonyl) was prepared by heating dicobaltoctacarbonyl with two equivalents of norbornadiene. This intermediate was treated with sodium tetraphenylborate (equation 10)



(10)

thereby producing a 45% yield of the zwitterionic cobalt complex. This compound is the least soluble of the tetraphenylborate complexes; as such UV-visible and nmr spectra could not be obtained.

Lastly, an intriguing series of complexes containing polynuclear aromatic rings has been discovered(4). These are the group VI complexes of carbazole and fluorene. Preparation of the tricarbonyl and tetraphenylborate members of these two series are illustrated in equations 11 and 12, respectively.



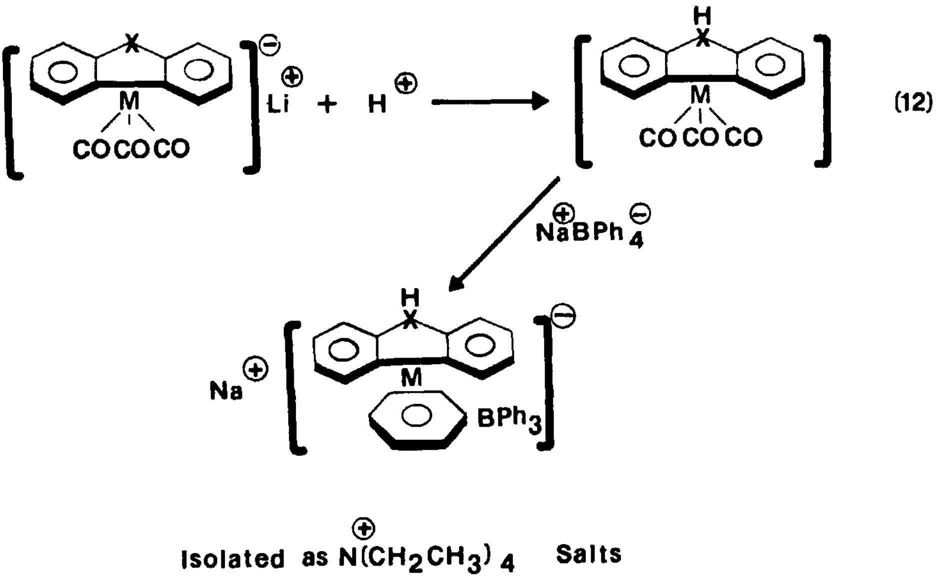


TABLE IV

(η^7-Cycloheptatrienyl)(η^6-tetraphenylborate)M^{VI} Complexes

Metal (M)	Aryl Substituent	Yield (%)	m.p.(°C dec)
Mo	H	83	318-320
Mo	p-CH_3	11	267
Mo	m-CH_3	51	283-284
Cr	H	--	221-224
W	H	--	180

Thus complexes containing Ni^o, Co^I, Fe^{II}, Mn^I, Cr^o, Cr^I, Mo^o and W^o have been prepared. Most of these materials possess high thermal and air stability. One of these complexes has been demonstrated to function as a homogeneous catalyst for the reduction of olefins. All of these results are encouraging in our efforts to incorporate these same ideas into the manufacture of transition metal complexed polymers.

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