

New findings in the arene chemistry of the 3d transition metals

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Abstract - This article surveys some new organometallic chemistry with the bicyclic aromatic hydrocarbon naphthalene. Aspects to be covered include the synthesis and properties of mononuclear complexes having η^2 -, η^4 - or η^6 -bonded naphthalene ligands. Examples of complexes of the latter type are $\text{CpM}(\eta^6\text{-C}_{10}\text{H}_8)$ ($\text{M} = \text{Cr}, \text{V}$), which because of the lability of the arene ligands (naphthalene ligand effect) are valuable sources of CpM fragments. Also reported are the synthesis and structures of a series of homo- and heterodinuclear complexes in which the bicyclic arene functions as a bridging ligand. Finally, the two-step preparation of $\text{CpFe}(\eta^5\text{-C}_{10}\text{H}_8\text{-H})$ and $\text{CpFe}(\eta^5\text{-C}_{10}\text{H}_8\text{-D})$ starting from ferrocene is presented. These compounds, which can be regarded as a naphthalene molecule hydro- or deuterometallated by CpFe-H or CpFe-D fragments, undergo the *retro*-hydro(deutero)metallation very easily when reacted with suitable substrates, liberating naphthalene. Thus, unlike the parent compound $\text{CpFe}(\eta^5\text{-C}_6\text{H}_6\text{-H})$, these two benzocyclohexadienyl iron(II) complexes are ready sources of CpFe fragments with metal-H or metal-D bonds.

INTRODUCTION

In the past couple of years our research work on the arene chemistry of the 3d transition metals has concentrated mainly on systems involving mononuclear arenes such as benzene and alkylbenzenes^{1a,c}. The results can be summarized under the following aspects:

1. The first concerns the modes of coordination of monocyclic arenes in homo- and heterodinuclear complexes. We have found that arene bridges having all six ring carbon atoms metal-coordinated are capable of bonding two metal centres in at least four different ways. Two examples with benzene as the bridging ligand are shown in Fig. 1.

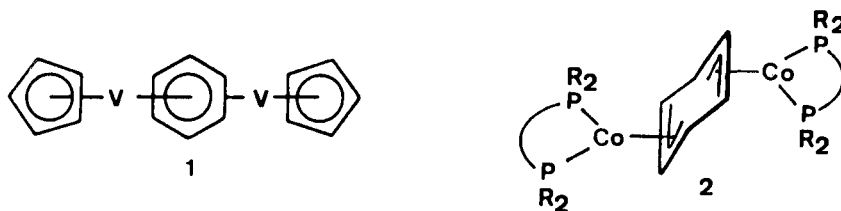
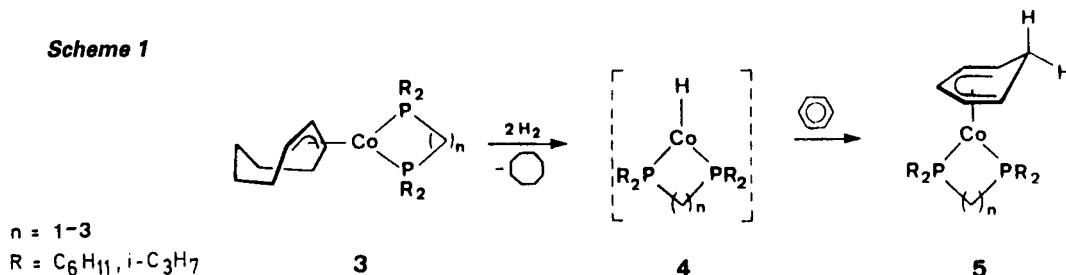


Fig. 1. Benzene as a bridging ligand in the triple-decker sandwich complex 1 and in the dicobalt complex 2.

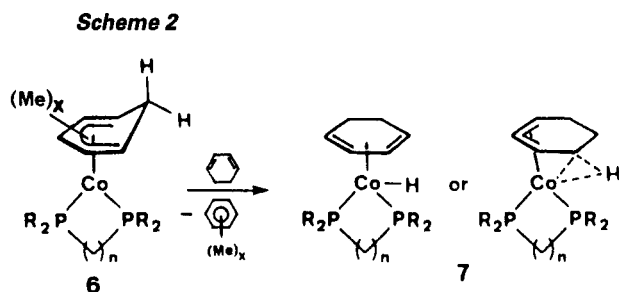
2. The second aspect relates to the addition of the metal-hydrogen bond to unsaturated hydrocarbons (hydrometallation), which was first established unambiguously for aromatic hydrocarbons when we demonstrated this type of reaction by the hydrocobaltation of benzene with diphosphenomonohydridocobalt fragments.

Scheme 1



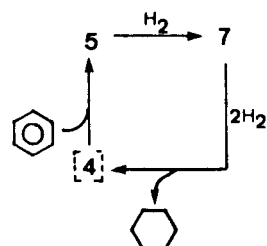
Generation of the 14e species 4 and its trapping by benzene to give hydrocobaltated benzene (5).

3. The cyclohexadienyl cobalt complexes **5** and the even more reactive methyl and dimethyl derivatives **6**, which are prepared analogously to **5** by hydrogenolysis of **3** in alkylbenzene, are labile compounds. On treatment with a wide range of substrates they readily undergo *retro*-hydrocobaltation, liberating benzene or alkylbenzene. This property makes **5** and **6** valuable transfer reagents for diphosphinemonohydridocobalt fragments (**4**), for example according to scheme 2.



Hydrocobaltated alkylbenzene **6** as a source of the 14e species **4**.

Scheme 3



Cobalt-catalyzed benzene hydrogenation.

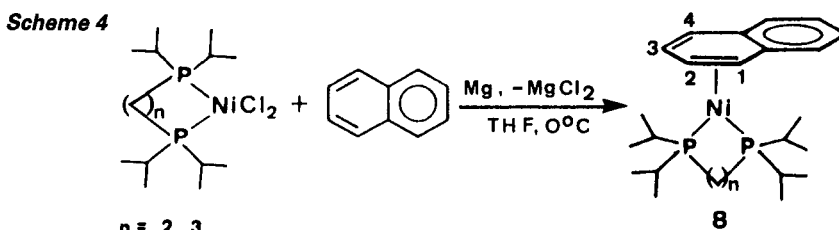
4. A second type of reaction of the cyclohexadienyl compounds **5** and **6** occurs when they are treated with hydrogen. For example, hydrocobaltated benzene **5** with $n = 3$ reacts with hydrogen to give **7**, which in turn reacts with two moles of hydrogen with release of the organic ligand as cyclohexane and regeneration of the 14e species **4** (Scheme 3). Thus **5** and **7** are compounds of a system that gives a detailed insight into the reaction course of a metal-catalyzed arene hydrogenation^{1a}.

Our most recent work has concentrated upon some new chemistry with the bicyclic molecule naphthalene.

I. MONONUCLEAR COMPLEXES HAVING η^2 -, η^4 - OR η^6 -BONDED NAPHTHALENE

η^2 -naphthalene complexes

In 1974 we reported the synthesis of $L_2Ni(\text{anthracene})$ [$L = (C_6H_{11})_3P]^{2a}$]; its structural characterization by X-ray crystallography as an η^2 -arene complex was carried out a couple of years later^{2b}). Recently we have focused our attention on this type of compound again and have now prepared the new nickel(0) complexes **8**. The X-ray structure analysis³) and the solid state NMR spectra show that the complexes **8** also have η^2 -coordinated arenes but the NMR studies in solid and solution reveal that the molecules are fluxional. The diphosphinenickel(0) moiety undergoes rapid exchange between the 1,2 and 3,4 positions in one ring and at higher temperature migrates from this ring to the other⁴).

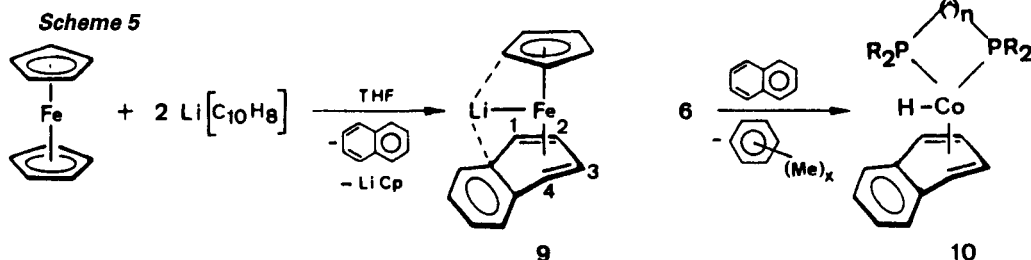


$n = 2, 3$

Synthesis of (η^2 -naphthalene)nickel(0) complexes.

η^4 -naphthalene complexes

There are still few examples of η^4 -arene complexes of which the structures have been elucidated by X-ray analysis⁵). Scheme 5 shows the syntheses and structures of new complexes containing η^4 -bonded naphthalene ligands.



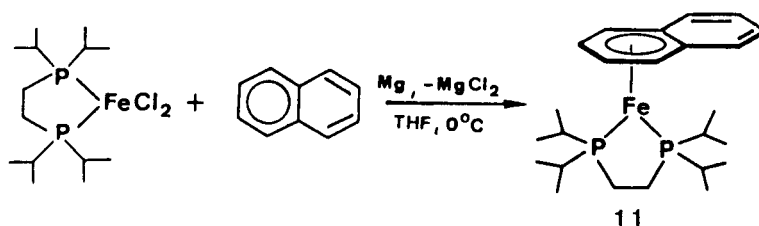
Simple routes to η^4 -naphthalene complexes of iron and cobalt.

The synthesis of the lithium iron compound **9** is a further example of the wide range of application of the reductive abstraction of five-membered ring ligands from metallocenes and related compounds, a method of high synthetic potential that has proved invaluable in numerous cases¹⁾ (see also the synthesis of **12** and **14** according to scheme 7). The main feature of crystalline **9** is the substantial folding of the naphthalene ligand along the C(1)-C(4) axis so that the plane of the carbon atoms not bonded to iron is bent away from the plane of the four coordinated atoms of the diene part by 40.2° ³⁾. This value is consistent with those found for the arene "hinges" in the other structurally characterized η^4 -arene complexes⁵⁾. The synthesis of the hydrido-cobalt complexes **10** is very closely related to that of the 18e complexes **7**. In all cases the hydrocobaltated alkylbenzene **6** functions as the source of the 14e diphosphinemonohydridocobalt fragment **4**. The addition of this species to cyclohexadiene or naphthalene is accompanied with the extrusion of alkylbenzene which is the driving force for all the transfer reactions according to scheme 2 and 5.

η^6 -naphthalene complexes

Having found that 14e diphosphenickel(0) moieties are η^2 -bonded to naphthalene to give 16e complexes and that the isoelectronic diphosphinemonohydridocobalt fragments **4** form 18e monohydridocobalt(η^4 -arene) complexes, we were interested to see how the 12e species diphosphineiron(0) behaves towards naphthalene. To examine this, diphosphineiron dichloride was reduced with magnesium in the presence of naphthalene analogously to the preparation of the nickel(0) complexes **8**.

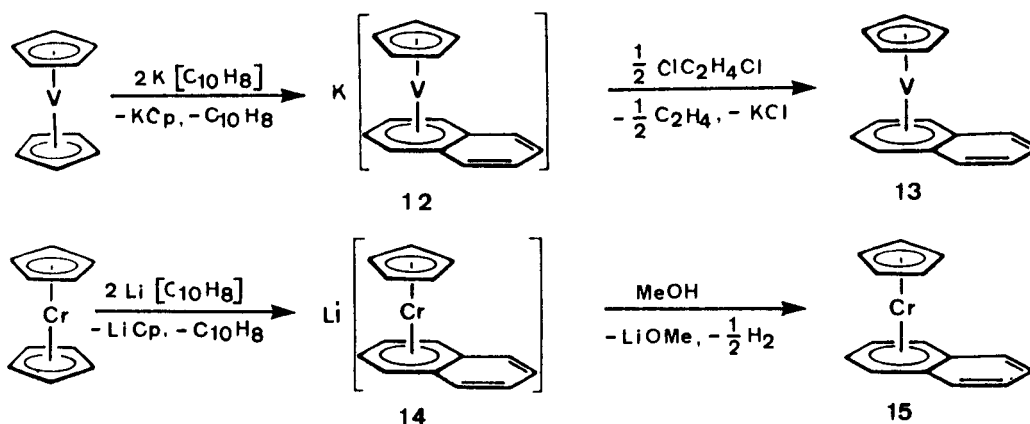
Scheme 6



Synthesis of the (η^6 -naphthalene)iron(0) complex **11**.

The naphthalene ligand in the 18e iron complex **11** is planar³⁾. Other complexes having this structural feature are (η^6 -C₁₀H₈)Cr(η^6 -C₆H₆)⁶⁾ and (η^6 -C₁₀H₈)Cr(CO)₃⁷⁾ and also very probably bis(η^6 -naphthalene)chromium(0)⁸⁾. The high lability of the naphthalene ligands in the latter two complexes, compared with the analogous benzene complexes (naphthalene ligand effect)⁶⁾, is of great synthetic value. We have found similarly striking differences in the reactivities of the pairs of compounds CpV(η^6 -naphthalene) (**13**)^{1b)}/ CpV(η^6 -benzene)^{1c)} and CpCr(η^6 -naphthalene) (**15**) / CpCr(η^6 -tetralin) (**16**).

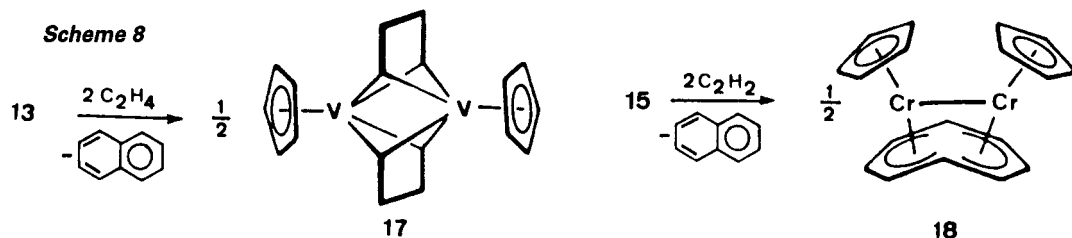
Scheme 7



Synthesis of the ate complexes **12** and **14** by reductive abstraction of cyclopentadienyl ligands and the transformation of **12** and **14** into the alkali metal-free sandwich complexes **13** and **15**.

For example, whereas CpV(η^6 -benzene) is inert towards ethylene the corresponding naphthalene complex **13**, which is readily accessible in two steps starting from vanadocene (see scheme 7), yields with ethylene **17**, the first dinuclear complex with fourfold alkyl-bridging. The bridging ligands are two butanediyl ligands both formed by coupling of two ethylene molecules^{1b)}.

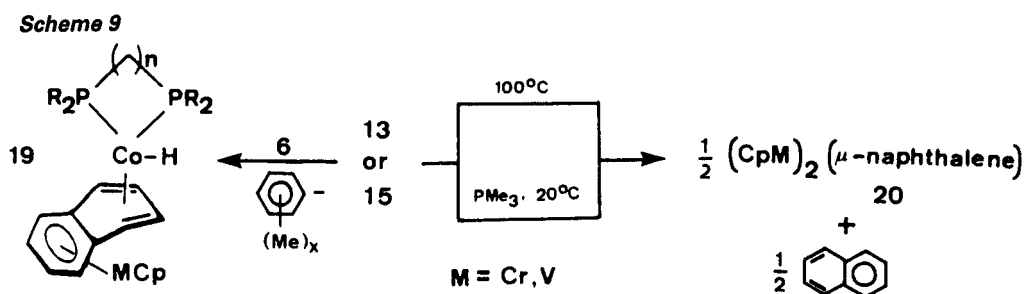
From 15 and the simplest alkyne, acetylene, one obtains in the presence of PMe_3 as a catalyst the dichromium complex 18, which has a bridging cyclooctatetraene ligand⁹⁾.



The facile displacement of η^6 -bonded naphthalene.

II. NAPHTHALENE AS A BRIDGING LIGAND IN HOMO- AND HETERODINUCLEAR COMPLEXES

When naphthalene undergoes η^6 -coordination, a part of the arene ligand is left as a diene moiety which should be capable of bonding to a metal centre. Therefore it seems to be an obvious strategy to exploit mononuclear η^6 -naphthalene complexes for the construction of dinuclear complexes having bridging naphthalene ligands.

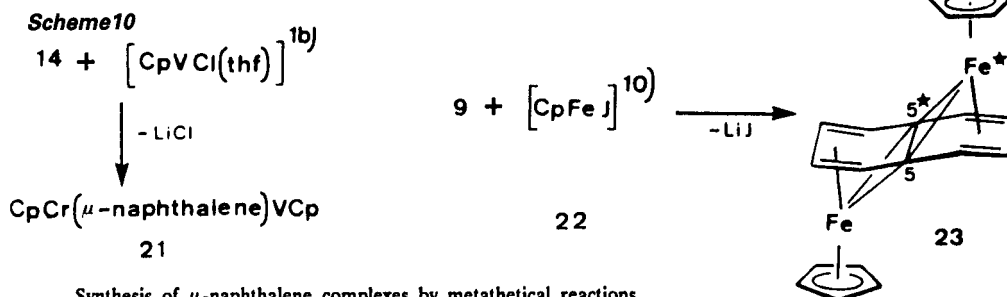


μ -Naphthalene complexes from mononuclear η^6 -naphthalene complexes.

Scheme 9 (on the left hand side) shows the result when hydrocobaltated alkylbenzene 6, used as a reagent to provide the 14e species 4, reacts with the sandwich complexes 13 or 15. The products 19 are heterodinuclear complexes having μ - η^4 : η^6 -naphthalene ligands. The vanadium cobalt compound 19 has been characterized by X-ray crystallography³⁾: the six arene carbon atoms coordinated to vanadium and the two terminal carbon atoms of the diene fragment bonded to cobalt lie in a plane which is bent away from the plane of the carbon atoms of the diene unit by 32° . In view of scheme 3 describing the reaction course of the cobalt catalyzed hydrogenation of benzene, it is not surprising that the complexes 19 readily react with hydrogen to give cobalt-free $\text{CpM}(\eta^6\text{-tetralin})$ ($\text{M} = \text{Cr, V}$) (16) and that in the presence of $\text{CpM}(\text{naphthalene})$ (13 or 15) the hydrogenation leading to the tetralin complexes 16 proceeds catalytically.

The formation of the dinuclear complexes 20 from 13 or 15 occurring thermally at elevated temperatures or by catalysis at room temperature on addition of PMe_3 is noteworthy because it shows in one reaction both chemical characteristics of η^6 -bonded naphthalene: it can be readily displaced (the familiar naphthalene ligand effect) but it is also capable of displacing other ligands from metal centres by acting as a cyclohexadiene, or more exactly, as a cyclohexadiene derivative containing a substituent with a complexed cyclopentadienyl metal fragment.

Another access to homo- or heterodinuclear μ -naphthalene complexes was found in metathetical reactions between naphthalene transition metallates and suitable ligand transition metal monohalides.



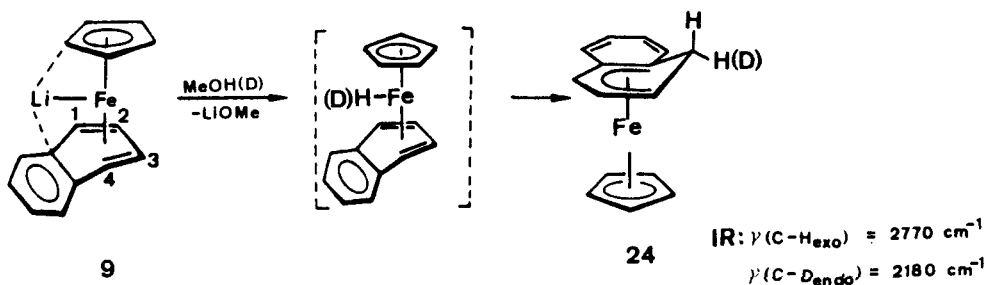
Synthesis of μ -naphthalene complexes by metathetical reactions.

In the new diiron complex **23** formed by the reaction of **9** with a THF solution of CpFeI (**22**) (**22** is accessible in three steps starting from ferrocene and is only stable at low temperature¹⁰) the iron atoms are attached antifacially to different rings of a doubly folded naphthalene bridge. The magnitude of the angle of fold [13.8°; compare this with the considerably larger angles (between 30° and 40°) in the complexes **9** and **19**] and the Fe-C and C-C bond lengths as well as the ¹³C NMR data indicate that in the centrosymmetric complex **23** all naphthalene carbon atoms are iron-coordinated. The four outer atoms of each six-membered ring are complexed diene-like to a single iron atom [Fe-C distances from 2.018(2) to 2.111(2) Å], while the two junction carbon atoms are bound simultaneously to both iron atoms [Fe-C(5) = 2.457(2), Fe-C(5') = 2.466(2) Å]. The Mössbauer spectrum¹¹) shows that the two identical iron centres have an isomer shift ($\delta = 0.543 \text{ mm s}^{-1}$, $\Delta E_Q = 1.555 \text{ mm s}^{-1}$ at 290 K) which is comparable with that of ferrocene ($\delta = 0.53 \text{ mm s}^{-1}$, $\Delta E_Q = 2.37 \text{ mm s}^{-1}$), indicating that the oxidation states of the iron in both compounds are very similar.

III. IRON(II) COMPLEXES WITH BENZOCYCLOHEXADIENYL LIGANDS AS TRANSFER REAGENTS FOR CpFe-H or CpFe-D FRAGMENTS

Unlike the lithium chromium complex **14**, which on treatment with methanol affords **15** and hydrogen (Scheme 7), the reaction of the lithium iron complex **9** with the same proton source does not produce any hydrogen. Instead the η^4 -bonded naphthalene ligand gains a hydrogen atom in the α -position and is transformed into a benzocyclohexadienyl group η^5 -bonded to iron. A labeling experiment with CH₃OD has confirmed unequivocally that the deuterium atom goes into the *endo*-position, suggesting that deuteration of the iron occurs first, followed by D-migration from the metal to the arene.

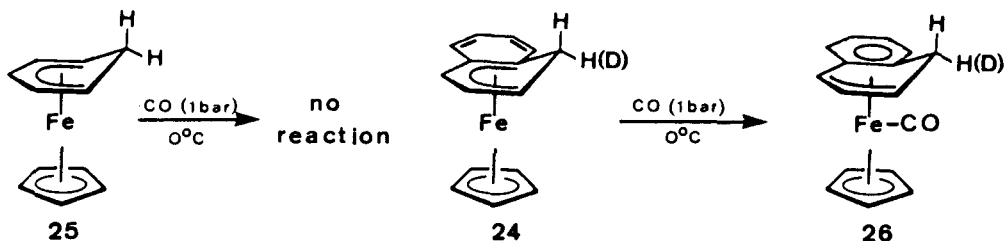
Scheme 11



Protonation or deuteration of the lithium iron complex **9**.

The new benzocyclohexadienyl iron(II) complexes **24** are considerably more reactive than the well known parent compound (η^5 -cyclopentadienyl)(η^5 -cyclohexadienyl)iron(II) [CpFe(η^5 -C₆H₇)] (**25**)¹². This is particularly clear from the reactions of **24** with substrates that do not react with **25** under the same conditions.

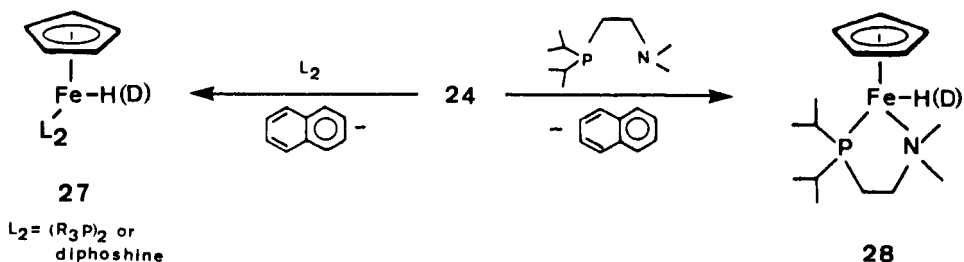
Scheme 12



Ring slippage of the benzocyclohexadienyl ligand from η^5 to η^3 .

For example, both the iron complexes **24** react rapidly with carbon monoxide (1 bar) at 0°C with addition. The products isolated are the new iron monocarbonyl complexes **26**, whose structures are unprecedented in that these complexes are the first compounds to contain η^3 -coordinated benzocyclohexadienyl ligands.

Scheme 13



The iron(II) compounds **24** as transfer reagents for CpFe-H or CpFe-D fragments.

A much more interesting reaction for preparative purposes is the *retro*-hydro- and *retro*-deuterometallation accompanied by the liberation of naphthalene, which can be achieved by treating **24** with mono- or diphosphines. These reactions proceed smoothly at 0°C leading to the formation of iron(II) half-sandwich complexes with Fe-H or Fe-D bonds. Exploiting **24** as a transfer reagent for CpFe-H or CpFe-D fragments, it was also possible to synthesize **28** containing the new phosphorus nitrogen ligand $(i\text{-C}_3\text{H}_7)_2\text{P}(\text{CH}_2)_2\text{N}(\text{CH}_3)_2$.

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