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USE OF HETERODIFUNCTIONAL LIGANDS TO BRIDGE "EARLY" AND "LATE" TRANSITION METALS. CONSTRUCTION AND CHEMISTRY OF COMPLEXES CONTAINING INDIRECTLY LINKED COBALT CARBONYL AND ZIRCONOCENE UNITS

DAVID R. TUETING, SAVITHRI R. IYER *, and NEIL E. SCHORE **

Department of Chemistry, University of California, Davis, Davis, California 95616 (U.S.A.)

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Summary

Four zirconocene systems, each containing tertiary phosphine functionality indirectly linked to either or both cyclopentadienyl rings, are described. Unlike the phosphinomethylzirconocenes, in which the metal and the phosphine strongly influence each other's basic chemistry, it has been found that a variety of transformations may be carried out at either site on the more indirectly linked systems without interference from the other. Thus reduction and hydrozirconation proceed normally at the Zr center, and quaternization and complexation to a second metal may be achieved at the phosphine. Two "early-late" multimetallic systems containing Zr and Co have been prepared. Reduction and acylation at Co proceed without interference from Zr; however, attempts to generate hydrides at Zr in the bimetallic systems were unsuccessful.

Introduction

As part of our ongoing program to investigate the potential for useful and interesting chemistry of systems containing indirectly linked dissimilar transition metals, we have been investigating the chemistry of several "heterodifunctional" ligands (e.g. **1**, **2**, **3**) [1–3]. These ligands have been designed to allow for the direct, specific linkage of dissimilar metal fragments, and several complexes derived from

$(C_6H_5)_2PCH_2Li$ (**1**)

$(C_6H_5)_2P(CH_2)_nSi(CH_3)_2C_5H_4Li$ (**2**, $n = 1$; **3**, $n = 2$)

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* Formerly Savithri Sundar.

** Camille and Henry Dreyfus Teacher-Scholar, 1981–86.

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their use have already been shown to possess unusual features relative to monometallic complexes of simpler ligand systems [4].

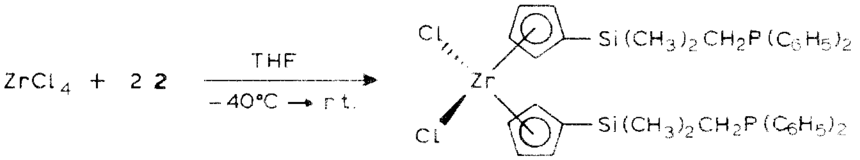
Herein we describe substituted metallocene derivatives of zirconium(IV) prepared from ligands **2** and **3**, their attachment to a second transition metal, and selective chemistry at the separate metal sites available in these complexes.

Results and discussion

Zirconocene derivatives of ligands such as **1** display a rather different spectrum of behavior at the metal center relative to the dichloride due to the fact that they are metal alkyls in addition to possessing remote phosphine functionality. In order to investigate the consequences of the remote phosphine while retaining the zirconocene dichloride moiety we have proceeded to synthesize derivatives of the latter incorporating ligands **2** and **3** as the phosphine-containing structural units in the molecules. As has been the case in all our work in this area, the ligands were synthesized as complete units before metal attachment.

Complexes derived from $(C_6H_5)_2PCH_2Si(CH_3)_2C_5H_4Li$ (ligand 2)

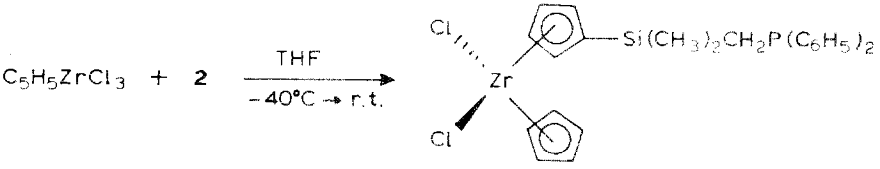
The reaction of freshly sublimed $ZrCl_4$ with two equivalents of **2** results in the formation of **4** (eq. 1).



(1)

(4)

A similar reaction of $CpZrCl_3$ with one equivalent of **2** gives **5** (eq. 2).



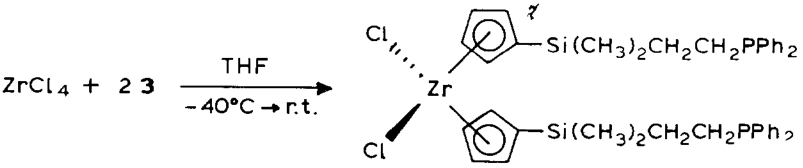
(2)

(5)

In both cases the reactions proceed rapidly, in reasonable yields, and without apparent complication from the phosphine unit. No evidence for metal–phosphine interaction is observed by NMR. Absorptions for the ligand side chain are virtually superimposable in both systems; in particular $^2J(PCH)$ is small for both compounds ($\leq$ 1 Hz). Both compounds are soluble to a significant extent in nonpolar solvents, and both may be isolated as white solids at −40°C, but monophosphine **5** melts to a viscous oil below room temperature while diphosphine **4** becomes a waxy semisolid. These latter inconvenient properties, together with the previously observed tendencies of bimetallic complexes of ligand **2** to be difficult to purify and to display complex spectroscopic properties motivated us to focus predominantly on ligand **3** as a building block for the synthesis of the desired zirconocene-based bimetallic systems. We expected that complexes of **3** would be more tractable on the basis of our experiences with the corresponding ferrocene complexes [3]. To a large measure these hopes have been successfully realized.

Complexes derived from $(C_6H_5)_2PCH_2CH_2Si(CH_3)_2C_5H_4Li$ *(ligand 3)*

Dichlorozirconocene-bis(phosphine) derivative 6. The disubstituted dichlorozirconocene derivative of ligand **3** has been prepared in ca. 35% yield by the reaction between freshly sublimed zirconium tetrachloride and **3** in a 1/2 molar ratio (eq. 3).

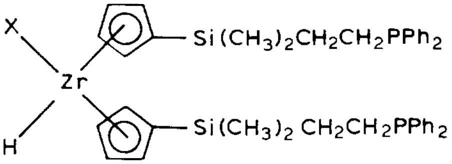


(3)

(6)

Upon addition of a cold solution of zirconium tetrachloride in THF to a well cooled solution of **3**, the proton NMR shows the replacement of the singlet due to 'Cp' protons of **3** from 5.90 ppm with a multiplet at 6.65 ppm, indicating complexation to zirconium. Zirconocene **6** is isolated as a white solid by crystallization from petroleum ether at −40°C.

Functionalization of 6 at Zr. Selective conversions of **6** to both its monohydride **7** and its dihydride **8** have been achieved. Using $LiAlH(O^tBu)_3$ as the reducing agent, we have isolated **7** as a light sensitive solid in nearly quantitative yield.

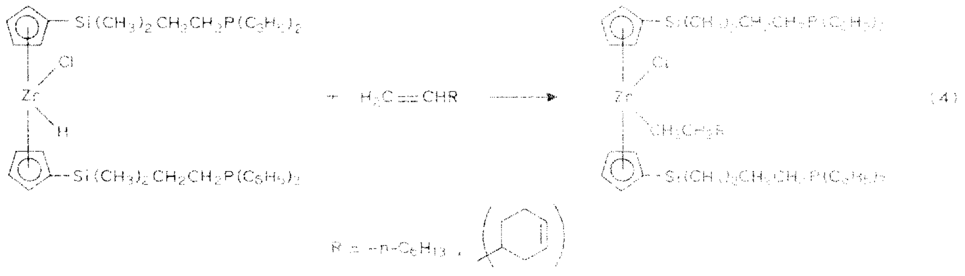


(**7** , X = Cl ;
8 , X = H)

Upon addition of $LiAlH(O^tBu)_3$, a new singlet at δ 0.20 ppm appears in the ^1H NMR, upfield to the reactant $Si(CH_3)_2$ peak at δ 0.35. Addition is stopped when $-Si(CH_3)_2$ singlet and 'Cp' resonance of the starting material are no longer seen, although addition of excess $LiAlH(O^tBu)_3$ after the conversion of **6** to **7** does not produce any further observable change in the NMR. Thus selective conversion of **6** to its monohydride has been successfully achieved.

Attempted purification of the monohydride gives a grey powder which is air, water, and light sensitive both in solution and in the solid state. The proton NMR in C_6D_6 shows the effects of chirality at the Zr center: two $Si-CH_3$ sginals are seen, and the four hydrogens on each ring are inequivalent. In THF the spectrum is simpler, presumably due to accidental chemical-shift equivalences. The hydride has not been seen in the proton NMR at 25°C. However, its presence is inferred by a broad IR absorption at 1350 cm^{-1} as well as by reaction of **7** with CH_2Cl_2 to produce a stoichiometric quantity of CH_3Cl.

A brief look at the reactivity of monohydride **7** towards simple alkenes shows that it is qualitatively similar to other chlorozirconocene hydride systems [5]. Hydrozirconations of 1-octene and 4-vinylcyclohexene take place as expected, the latter at the vinyl group only, in high yield (eq. 4). Hydrolysis forms a benzene-insoluble oxide and liberates the corresponding hydrocarbons.



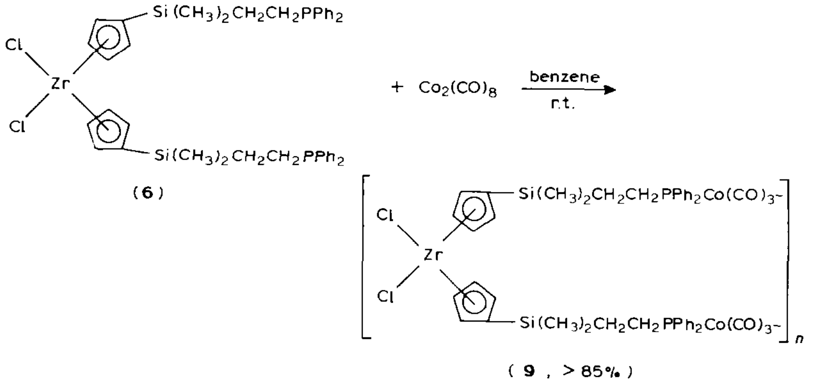
(4)

Since $LiAlH(O^tBu)_3$ was ineffective in converting **7** to its dihydride **8** we turned to $LiAlH_4$ for this purpose. Dropwise addition of a solution of $LiAlH_4$ in THF to a solution of **6** in THF results in the expected changes in the 'Cp' and $Si(CH_3)_2$ regions of the NMR. The singlet at δ 0.20 ppm due to monohydride **7** is seen immediately. With further addition of $LiAlH_4$ a new signal assigned to the $Si(CH_3)_2$ group of dihydride **8** is then observed at δ 0.28 ppm. Addition of $LiAlH_4$ is stopped when the monohydride peak disappears totally and only the peak at δ 0.28 ppm remains. Isolation of **8** is carried out in a manner similar to that used for **7**. The NMR of **8** in C_6D_6 displays very similar characteristics to that of monohydride **7**, although in THF their spectra are quite different. In this case chirality at Zr is probably aggregation induced, as has been seen by Jones and Petersen in the binuclear hydride $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$ [6]. Although elemental analysis reveals that less than 2% of the original chloride remains in the final product, NMR titration of active hydride by CH_2Cl_2 reveals a rather low 1.62 eq/Zr. This may be accounted for in several ways, including the extreme sensitivity of the isolated material, which is isolated as a black(!) solid despite precautions to avoid exposure to light. In addition, the hydride reactivity of **8** is such that some of the initially formed CH_3Cl in the NMR titration could have been further reduced to methane by unreacted **8**, thus giving an anomalously low result. This reaction does, however, regenerate dichloride **6** in quantitative yield. In spite of the analytical difficulties, the spectroscopic data appears to indicate that freshly prepared samples of **8** are of reasonable purity.

Phosphine chemistry of 6: complexation to cobalt

Addition of a benzene solution of **6** to a solution of $Co_2(CO)_8$ in benzene results in precipitation of a small amount of a dark solid which exhibits strong IR bands at 2010 and 1885 cm^{-1} in THF solution. These are consistent with formation of an ionic complex of the general formula $[RP(C_6H_5)_2]_2Co(CO)_3^{+}\ Co(CO)_4^{-}$ [7]. The majority of the reaction product, however, is a blackish-brown solid isolated in > 85% yield after recrystallization from a mixture of benzene and petroleum ether. Its IR in THF displays major carbonyl bands at 1945vs and 1965sh characteristic of the presence of the $\text{-}CH_2P(C_6H_5)_2Co(CO)_3Co(CO)_3P(C_6H_5)_2CH_2\text{-}$ structural unit [8]. The UV spectrum in CH_2Cl_2 shows an intense absorption at 388 nm (log ϵ =

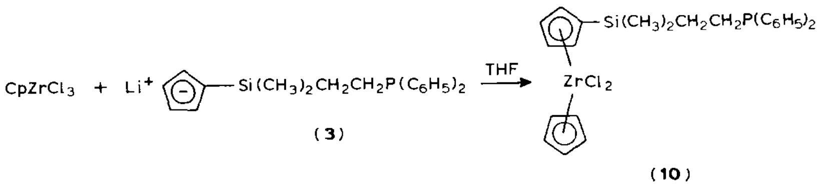
4.45) typical of this sort of complex [9]. Molecular weight determination revealed the product to be oligomeric. We therefore formulate it as **9** (eq. 5), and suspect that the same factors that resulted in the formation of bimetallic oligomers from the ferrocene counterpart of **6** are operating in this system as well [3].



(5)

*Dichlorozirconocene-mono(phosphine) derivative **10***

In order to further investigate the feasibility of chemistry at one metal center in the presence of a second, very different metal, we chose to focus on zirconocene derivative **10**, synthesized as shown (eq. 6).

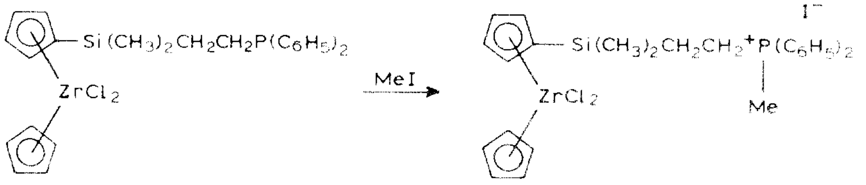


(6)

The mixed cyclopentadienyl zirconocene **10** has been successfully prepared in ca. 70% yield by the reaction, at $-60°$C, between cyclopentadienylzirconium trichloride and **3** in a 1/1 molar ratio in THF. Using a procedure similar to that employed for the isolation of the bis(phosphine) derivative **6**, **10** is obtained as a pure white solid. The ^{1}H NMR of **10** in benzene-d_6 displays two apparent triplets (J 2.5 Hz) at δ 5.87 and 6.22 ppm and a sharp singlet at δ 5.91 ppm that are assigned to the substituted and unsubstituted cyclopentadienyl rings respectively. The ^{31}P NMR in $CDCl_3$ exhibits a single, sharp peak at δ -9.15 ppm relative to external H_3PO_4. The spectroscopic data therefore supports the mixed cyclopentadienyl substitution at zirconium and indicates a free, noninteracting phosphine moiety.

*Functional chemistry of **10***

The phosphine in **10** can be characterized chemically by its reaction with methyl iodide. A white solid can be isolated in quantitative yield from the reaction between **10** and MeI in chloroform. The phosphonium salt **11** (eq. 7) is readily identified by the ^{1}H NMR in $CDCl_3$, the most distinguishing feature being the methyl doublet at δ 2.72 ppm (J 13.2 Hz).



(10) (11) (7)

The ^{31}P NMR in CDCl$_3$ displays a sharp single peak at δ + 26.3, a shift of +35.5 ppm relative to **10**, and characteristic of a quaternary phosphonium species [10].

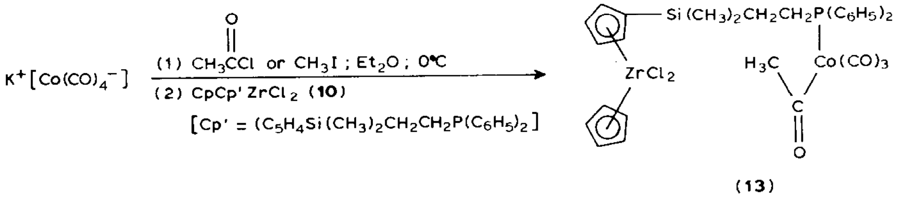
As has been found to be the case in a variety of related systems [2,11], one-electron reduction of **10** leads to a Zr^{III} species in which complexation of phosphine to metal is observed. Treatment of a THF solution of **10** with slightly greater than one equivalent of 1.5% Na/Hg results in the formation of a deep red color and the appearance of an intense set of ESR signals characteristic of a Zr^{III}-phosphine complex: $a(^{31}P)$ 19.5 G and $a(^{91}Zr)$ 23.5 G. It is not known as yet whether or not this species is monomeric, or how stable it is relative to other Zr^{III}-phosphine complexes. Efforts are underway to attempt to isolate the material in pure form for further characterization.

The ability of **10** to complex to another metal center through the free phosphine is evidenced by the reaction of **10** with $Co_2(CO)_8$ at room temperature in benzene, which gives **12** in > 70% yield as a red-brown solid. Analysis by NMR and IR support complexation of the phosphine to the cobalt metal center. The ^{1}H NMR of **12** is similar to **10**; however, downfield shifts for the methylene protons and the *ortho* phenyl protons are observed. The ^{31}P NMR displays a single sharp peak at δ +67.4, a shift of +76.5 ppm relative to **10** and in agreement with observations on related complexes of the type $Co(CO)_6(PR_3)_2$. Infrared analysis of **12** in THF displays major carbonyl bands at 1953 (vs) and 1973 (sh) cm^{-1}, again characteristic of similar $Co_2(CO)_6(PR_3)_2$ complexes [7].

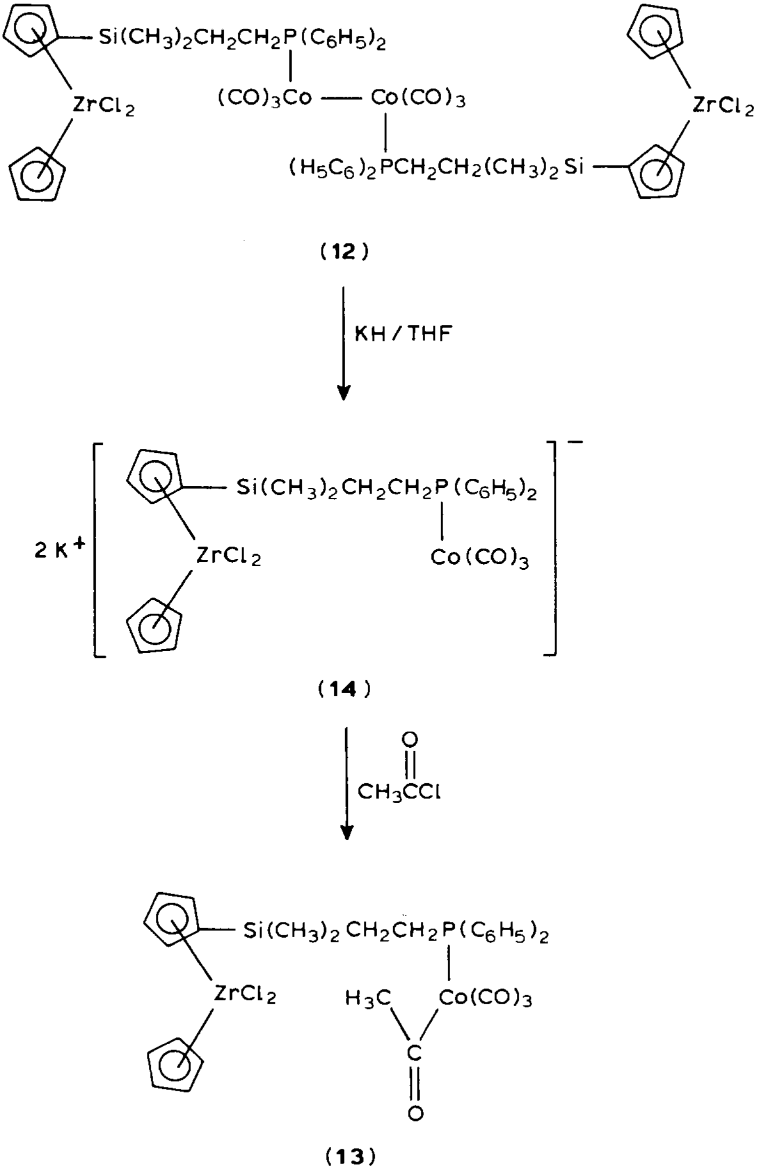
With **10** and **12** in hand, we set out to determine the feasibility of organic functionalization at zirconium both before and after complexation of the phosphine moiety to a second metal, as well as organic functionalization at cobalt in the presence of either the simple or functionalized zirconium center.

We have successfully prepared the heterobimetallic acyl derivative **13**. This complex is easily obtained as a crystalline orange solid in > 65% yield by the reaction between $K^+[Co(CO)_4]^-$ and MeI or MeC(O)Cl at 0°C in ethyl ether followed by the addition of **10** (Scheme 1). Spectroscopic data supports the presence of a cobalt acyl moiety and essentially unchanged zirconium metal center. The ^{1}H NMR in benzene-d_6 displays a sharp singlet at δ 2.67 ppm and a downfield shifted multiplet at δ 2.27 ppm for the acyl methyl and methylene (α to phosphorus) protons respectively. The ^{31}P NMR exhibits a sharp singlet at δ +49.6 ppm relative to external H_3PO_4. The IR indicates major carbonyl bands at 1953vs and 1975sh and a sharp acyl carbonyl band at 1680 cm^{-1}.

Temperature control is critical in order to avoid side product(s) when preparing **13**. As has been seen in related systems [12], at temperatures above 0°C $Co(CO)_4$ can attack **10** to form the dimer **12**. The formation of **12** is temperature dependent and can be minimized ($\leqslant$ 5%) provided the reaction temperature is kept $\leqslant$ 0°C.



SCHEME 1



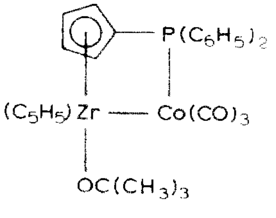
SCHEME 2

Small quantities of **12** are observed when preparing **13** regardless of choice of electrophile. Note, however, that the phosphonium salt **11** is not observed as a side product when MeI is used as the electrophile to form acyl **13**.

We envisioned another route to prepare **13** involving cleavage of the cobalt–cobalt bond in dimer **12** (Scheme 2). Simple complexes of the type $Co_2(CO)_6L_2$ (L = phosphine) can be cleaved using potassium hydride [13]. Applying this reaction to **12** requires the resistance of the zirconium moiety in **10** to attack by KH. Thus, a 1 *M* solution of **10** was stirred with excess KH in THF for 36 h and the reaction monitored by NMR. No changes were observed spectroscopically and **10** was recovered unchanged from the reaction mixture. Complex **10** was, however, not inert toward Super Hydride or sodium amalgam, both of which have also been used [14,15] to cleave metal dimers such as $Co_2(CO)_8$.

Reduction of **12** using KH in THF was attempted and monitored by IR spectroscopy. After stirring for 20 h at 27°C, several additional carbonyl bands were observed in addition to the bands of unchanged **12**. The bands associated with the expected anion were noted at 1927s, 1846br and 1824sh cm^{-1}, in agreement with known species of the type $Co(CO)_3PR_3^-$. Also, a broad band at 1890 cm^{-1} due to ubiquitous $Co(CO)_4^-$ was observed (although no $Co_2(CO)_8$ was present in **12**). Continued stirring with KH for up to 48 h produced no change in the IR spectra. The reduction of **12** was not complete even when a large excess of KH was added. Dimer **12** could be completely reduced by KH in either 1/1 THF/HMPA or neat HMPA after stirring for 6 h. The bimetallic anion **14**, which exhibited a pale green-yellow color, was not isolated but reacted in situ with MeC(O)Cl giving rise to the same acyl, **13**, prepared previously.

Casey and Nief [16] have recently reported that $NaCo(CO)_4$ reacts with $(C_5H_5)[C_5H_4P(C_6H_5)_2]Zr[OC(CH_3)_3]Cl$ under photolytic conditions to give **15**, in which both Co–Zr and Co–P bonding is present. One of the possible mechanisms discussed involved initial photolysis of $Co(CO)_4^-$, leading to a species capable of Zr–Cl bond cleavage. One version of this might involve intramolecular displacement of chloride by a strongly nucleophilic $Co(CO)_3PR_3^-$ species. The stability of anion **14** with respect to possible Co–Zr bond formation casts doubt on the likelihood of this particular pathway. In this regard we have also noted that no reaction occurs between Cp_2ZrCl_2 and $Co(CO)_3P(C_6H_5)_3^-$ in THF at room temperature.



(**15**)

Functionalization at zirconium in **10** or **13** to form a zirconium hydride was attempted. We envisioned the possibility of intramolecular hydride transfer to a coordinated carbon monoxide or acyl moiety in a bimetallic complex thereby effecting a net reduction to form formyl or alkoxy type products.

After addition of $LiAlH(O^tBu)_3$ to a THF solution of **10** the NMR showed a new $Si(CH_3)_2$ singlet at δ 0.20 ppm. The expected new 'Cp' resonances were also observed: unsubstituted 'Cp' at δ 5.10 ppm (s) and substituted 'Cp' at δ 5.55 and 5.90 ppm. Addition of excess $LiAlH(O^tBu)_3$ did not affect the observed spectra and did not convert **10** to the dihydride (complexes **6** and **7** were also not converted to dihydrides using $LiAlH(O^tBu)_3$). When excess $LiAlH_4$ was used as the hydride source, it resulted in the observation of a $Si(CH_3)_2$ singlet at δ 0.25, unsubstituted 'Cp' at 5.50 (s) and substituted 'Cp' at 5.85 and 5.20 ppm as broad multiplets. This was assumed to be the dihydride of **10**.

These hydrides were found unfortunately to be thermally very unstable, and light sensitive. Consequently, attempts to isolate them were unsuccessful. The formation of the monohydride of **10** was, however, confirmed chemically by reaction with CH_2Cl_2 producing a quantitative yield of CH_3Cl, (by NMR) and regenerating **10**. Also, the hydrozirconation of 1-octene was achieved using the monohydride of **10**. The resulting alkyl derivative was both hydrolyzed to produce octane which was identified by GLC, and cleaved with iodine to liberate 1-iodooctane which was identified by GLC and NMR. The n-octyl derivative of **10** was also formed by reacting **10** with 1-octene and ^{t}BuMgCl, according to Negishi [17].

Attempts to form the hydride of **13**, however, have been unsuccessful. A variety of hydride sources were used; however, each led to the decomposition of the acyl moiety prior to formation of the zirconium hydride.

Summary

Synthetic work in the area of heterobimetallic chemistry has grown enormously in recent years, with much of the emphasis on combining "early" and "late" transition metals in order to utilize their chemical differences in activation of small molecules [1,2,11,16,18]. Both heterobimetallic complexes and their precursors, mononuclear complexes with pendant ligand sites, are essentially difunctional molecules. As such, the normal reactivity patterns at each site of functionality will be modified to a greater or lesser extent by the intramolecular disposition of the two. A full realization of the potential of these systems in application to outstanding chemical problems must include the development of selective methods for, essentially, functional group transformations in these systems. Complexes such as **10, 12**, and **13** provide useful models in which such chemistry may be explored. This study has revealed examples where current technology is adequate for selective transformation, as well as situations where more work is necessary to provide the flexibility for further synthetic manipulation. Reports of additonal efforts in these directions will be forthcoming.

Experimental

All preparations were carried out under an atmosphere of nitrogen by using either standard Schlenk techniques or a Vacuum Atmospheres Drilab. Solvents were rendered water and oxygen free by distillation from sodium benzophenone ketyl or dianion. Dicobaltoctacarbonyl was purchased from Pressure Chemical Corp. and used as received. Zirconium tetrachloride was purchased from Alfa/Ventron and was sublimed before use. Bis(cyclopentadienyl)zirconium dichloride was obtained from Aldrich and used as received. The preparations of substituted cyclopentadienides **2** and **3** have been previously described in detail [1,3]. $CpZrCl_3$ was prepared using the method of Erker, et al. [19]. All other organic reagents were distilled under nitrogen and degassed before use. Solid inorganic reagents were transferred into the drybox after being held at high vacuum for at least 12 h. Spectroscopic measurements utilized the following instrumentation. UV/visible, 8450A Hewlett–Packard; IR, Beckman IR-8; ^1H NMR, Varian A60-A, Nicolet NT-360, Varian EM390. Chemical shifts are quoted in ppm downfield from tetramethylsilane. The NMR coupling constants are expressed in Hz. Elemental analyses and molecular weight determinations were carried out by the Galbraith Microanalytical Laboratory or the U.C. Berkeley Microanalytical Laboratory.

*Dichloro-1,1'-bis[dimethyl((diphenylphosphino)methyl)silyl]zirconocene (**4**)*

A solution of 0.106 g (0.32 mmol) [[dimethyl((diphenylphosphino)methyl)silyl]cyclopentadienyl]lithium (**2**) in 2 ml THF, and a suspension of 0.040 g (0.17 mmol) $ZrCl_4$ in 2 ml THF were each prepared, cooled to −40°C, and mixed all at once. Upon warming to room temperature, the mixture became pale yellow and homogeneous, and was allowed to stir for two days. The solvent was removed in vacuo leaving a semisolid residue which was triturated with 5 ml benzene and filtered (celite). Removal of benzene left a light brown solid which was repeatedly extracted with 5 ml portions of petroleum ether which were combined, filtered, and cooled to −40°C, depositing **4** as a glassy white solid. Yield 0.060 g (46%). Although powdery when cold, **4** becomes a waxy semisolid when warmed to room temperature. NMR (C_6D_6) δ 0.43 (d, J 0.8 Hz, 12H), 1.77 (d, J 0.8 Hz, 4H), 6.03 (app t, splitting = 2.5 Hz, 4H), 6.52 (app t, splitting = 2.5 Hz, 4H), 7.07–7.35 (m, 12H), 7.44–7.82 (m, 8H). Anal. Found: C, 59.87; H, 5.64; Cl, 8.68. $C_{40}H_{44}P_2Si_2ZrCl_2$ calc: C, 59.68; H, 5.51; Cl, 8.81%.

*Dichloro-1-[dimethyl((diphenylphosphino)methyl)silyl]zirconocene (**5**)*

A solution of 0.091 g (0.33 mmol) $CpZrCl_3$ in 3 ml THF was treated, dropwise at room temperature, with a solution of 0.109 g (0.33 mmol) **2** in 3 ml THF. The mixture was stirred overnight and the solvent then removed in vacuo leaving a pale yellow semisolid. Trituration with 20 ml ether followed by cooling to −40°C removed most of the LiCl. After removal of most of the solvent the crude product was filtered in ether through a very short Florisil column. Evaporation of the ether left an oil which was taken up in ca. 20 ml petroleum ether. Cooling to −40°C precipitated a white solid which, after decantation of the cold supernatant, was found to melt well below room temperature. Yield 0.080 g (49%). NMR (C_6D_6) δ 0.42 (d, J 0.8 Hz, 6H), 1.78 (d, J 0.9 Hz, 2H), 6.00 (app t, splitting = 2.5 Hz, 2H), 6.10 (s, 5H), 6.50 (app t, splitting = 2.5 Hz, 2H), 7.11–7.36 (m, 6H), 7.43–7.80 (m, 4H). Anal. Found: C, 54.60; H, 5.11; Cl, 13.09. $C_{25}H_{27}SiPZrCl_2$ calc: C, 54.73; H, 4.96; Cl, 12.92%.

*Dichloro-1,1'-bis[(2-diphenylphosphino)ethyl)dimethylsilyl]zirconocene (**6**)*

To a cooled solution of 2.98 g (12.8 mmol) of freshly sublimed zirconium tetrachloride in 75 ml of THF was added a cold solution of 8.50 g (24.84 mmol) of [[2-(diphenylphosphino)ethyl)dimethylsilyl]cyclopentadienyl]lithium (**3**) in THF dropwise with constant stirring under nitrogen. The purple colored solution was allowed to stir for one day. Removal of THF under vacuum gave a gummy product which was stirred with petroleum ether. The filtered petroleum ether extract upon cooling to −40°C gave a white solid that weighed 3.64 g (4.40 mmol), yield 34%. NMR (C_6D_6): δ 0.40 (s, 12H), 0.70–1.20 (m, 4H), 1.90–2.30 (m, 4H), 5.95 and 6.30 (app t, splitting = 3 Hz, 8H), 7.10–7.30 (m, 12H, *m*- and *p*-Ph), 7.40–7.65 (m, 8H, *o*-Ph). Anal. Found: C, 60.61; H, 5.79; Cl, 8.45. $C_{42}H_{48}Si_2ZrP_2Cl_2$ calc: C, 60.57; H, 5.76; Cl, 8.53%.

Chlorohydro-1,1′-bis[(2-(diphenylphosphino)ethyl)dimethylsilyl]]zirconocene (7)

To a solution of 0.71 g (0.86 mmol) of **6** in 2 ml of THF was added 0.36 g (1.60 mmol) of $LiAlH(O^tBu)_3$ in 1 ml of THF dropwise using a microlitre syringe with constant stirring. The solution was allowed to stir for a period of 30 min. Removal of THF under vacuum gave a sticky solid which was extracted with pentane. The insoluble residue was removed by filtration. Evaporation of pentane under vacuum gave a black solid weighing 0.62 g (0.77 mmol), crude yield 90%. NMR (C_6D_6): δ 0.40 (s, 6H), 0.45 (s, 6H), 0.60–1.20 (m, 4H), 1.95–2.75 (m, 4H), 'Cp' peaks 4.43, 5.45, 5.60, 5.85 (br m, 8H), 7.10–8.10 (m, 20H). NMR (THF): δ 0.20 (s, 12H), 'Cp' 5.50 and 5.65 (app AA′BB′, 8H), 7.30 (br s, 20H). IR (Nujol mull): Zr–H, 1350 cm^{-1}. Anal. for hydridic H (reaction with CH_2Cl_2, NMR): 1.00 ± .05 eq. found.

Hydrozirconation of 4-vinyl-1-cyclohexene by 7

To a solution of 0.61 g (0.77 mmol) of **7** in 4 ml benzene was added 0.82 g (0.76 mmol) of 4-vinyl-1-cyclohexene dropwise using a microlitre syringe and the reaction was allowed to stir under nitrogen at room temperature for one day. Removal of benzene and unreacted 4-vinyl-1-cyclohexene under vacuum gave a brown pasty mass which was shown by NMR to contain 1,1′-bis[(2-(diphenylphosphino)ethyl)dimethylsilyl](2-(4-cyclohexenyl)ethyl)zirconocene chloride. Crude yield 0.52 g (0.57 mmol), yield 75%. NMR (C_6D_6): δ 0.20 (s, 12H), 0.3–2.5 (m, 11H), 5.3–6.4 (m, 8H), 5.80 (app d, 2H), 7.30 (m, 20H). Treatment of this product with water liberated 4-ethylcyclohexane in quantitative yield, identified by comparison with an authentic sample (GLC, NMR).

Dihydro-1,1′-bis[(2-(diphenylphosphino)ethyl)dimethylsilyl]zirconocene (8)

To a solution of 0.10 g (0.12 mmol) of **6** in 2 ml of THF was added 0.01 g (0.24 mmol) of $LiAlH_4$ in 1 ml of THF in drops using a microlitre syringe. The solution was allowed to stir for a period of 30 min. Removal of THF under vacuum gave a sticky solid which was extracted with pentane. The insoluble solid residue was removed by filtration. Pentane was removed under high vacuum to give a black solid weighing 0.05 g (0.07 mmol), crude yield 55%. NMR (C_6D_6): δ 0.40 (s, 6H), 0.45 (s, 6H), 0.60–1.20 (m, 4H), 1.95–2.75 (m, 4H), 'Cp' peaks 4.43, 5.45, 5.60, 5.85 (br m, 8H), 7.10–8.10 (m, 20H). NMR (THF): δ 0.28 (s, 12H), 'Cp' 5.30 and 5.90 (app t, 8H), 7.30 (br s, 20H). Anal. Found: C, 61.24; H, 6.46; Cl, 0.12. $C_{42}H_{50}Si_2P_2Zr$ calc: C, 66.18; H, 6.56; Cl, 0.00%. Anal. for hydridic H (reaction with CH_2Cl_2, NMR): 1.62 ± .05 eq. found. No further efforts at purification of **7** or **8** were made.

Dichloro-1,1′-bis(2-(diphenylphosphino)ethyl)dimethylsilyl]zirconocenehexacarbonyldicobalt (9)

To a solution of 0.21 g (0.56 mmol) of dicobaltoctacarbonyl in 40 ml of benzene was added a solution of 0.41 g (0.49 mmol) of **6** in 40 ml of benzene in drops with constant stirring under nitrogen. The solution was allowed to stir for a period of one day. The small amount of black solid formed was removed by filtration and was discarded. Removal of benzene under vacuum gave a brown solid that was recrystallized from a mixture of benzene and petroleum ether. The brown recrystallized material weighed 0.46 g (0.42 mmol), yield 85%. IR (THF): 1945vs, 1965sh cm^{-1}. UV (CH_2Cl_2): λ_{max} 388 nm, log ϵ (4.45). ^1H NMR (C_6D_6): δ 0.33 (s, 12H), 0.85 (m, 4H), 1.16 (m, 4H), 5.95 (br s, 4H), 6.28 (br s, 4H), 6.87–7.78 (m, 20H). ^{31}P NMR ($CDCl_3$): δ +67.2. Anal. Found: C, 50.31, 54.13; H, 4.60, 5.03; Cl, 7.09. $C_{48}H_{48}Si_2P_2Co_2O_6Cl_2Zr$ calc: C, 51.52; H, 4.30; Cl, 6.40%. Note, however, that NMR data indicate that samples of **9** as isolated above are $\geqslant$ 98% pure with respect to either proton- or phosphorus-containing species. Molecular weight (DMF, osmometric). Calc for monomer: 1118. Found: 3034.

*Dichloro-1-[(2-(diphenylphosphino)ethyl)dimethylsilyl]zirconocene (**10**)*

A clear, colorless solution of 3.38 g (12.9 mmol) $CpZrCl_3$ in 300 ml THF was cooled to −60°C using a $MeOH/H_2O/CO_2$ slush bath. To the cold solution was added dropwise 5.00 g (14.8 mmol) **3** in 100 ml THF over a 2-h interval. The resultant purple solution was stirred at −60°C for 3 h, allowed to warm to 25°C and stirred for 16 h. The clear, gold solution was taken to dryness in vacuo to obtain a tan/white solid. The solid was extracted several times with ether (3 × 100 ml) and n-hexane (2 × 100 ml). The extracts were combined, concentrated in vacuo to 150 ml and the pale yellow solution cooled to −25°C for 48 h. The precipitated white microcrystalline solid was collected by filtration, rinsed with cold n-hexane (2 × 15 ml) and dried in vacuo. A white powder was isolated in a yield of 5.16 g (9.16 mmol; 71%). ^1H NMR (C_6D_6) δ 0.30 (s, 6H), 0.82–0.91 (m, 2H), 1.98–2.13 (m, 2H), 5.87 (app t, splitting = 2.5 Hz, 2H), 5.91 (s, 5H), 6.22 (app t, splitting = 2.5 Hz, 2H), 7.03–7.12 (m, 4H), 7.41–7.47 (m, 6H). ^1H NMR ($CDCl_3$) δ 0.33 (s, 6H), 0.73–0.81 (m, 2H), 1.90–1.96 (m, 2H), 6.41 (s, 5H), 6.53 (app t, splitting = 2.5 Hz, 2H), 6.64 (app t, splitting = 2.5 Hz, 2H), 7.29–7.38 (m, 10H). ^{31}P NMR ($CDCl_3$) δ −9.15 Anal. Found: C, 56.15; H, 5.40; Cl, 12.24. $C_{28}H_{30}SiPZrCl_2$ calc: C, 55.51; H, 5.16; Cl, 12.60%.

*Quaternization product of **10** with iodomethane: Formation of **11***

To a clear, colorless solution of 130 mg (0.23 mmol) **10** in 5 ml chloroform was added 16 μl (0.25 mmol) CH_3I by syringe. The reaction was stirred at 27°C for 6 h. Proton NMR analysis indicated the reaction had gone to completion as no starting material remained. Solvent removal in vacuo yielded 150 mg (0.21 mmol, 93%) of a white microcrystalline solid. The salt is soluble in $CHCl_3$, THF, and DME; it is insoluble in Et_2O, benzene, or hexane. ^1H NMR ($CDCl_3$) δ 0.43 (s, 6H), 0.92–1.00 (m, 2H), 2.72 (d, *J* 13.2 Hz, 3H), 3.07–3.16 (m, 2H), 6.49 (s, 5H), 6.62 (app t, splitting = 2.5 Hz, 2H), 6.86 (app t, splitting = 2.5 Hz, 2H), 7.62–7.81 (m, 10H). ^{31}P NMR ($CDCl_3$) δ +26.3. Anal. Found: C, 44.72; H, 4.27. $C_{27}H_{32}SiPZrCl_2I$ calc: C, 46.02; H, 4.54%. NMR data show no detectable (< 2%) impurities.

*Bis[dichloro-1-[2-(diphenylphosphino)ethyl)dimethylsilyl]zirconocene]hexacarbonyldicobalt (**12**)*

To a dark red solution of 188 mg (0.55 mmol) $Co_2(CO)_8$ in 30 ml benzene was added dropwise 562 mg (1.00 mmol) of **10** in 20 ml benzene. The dark solution was stirred at 27°C for 18 h, filtered, and the filtrate taken to dryness in vacuo to obtain a red, oily solid. The solid was dissolved in 20 ml benzene and then carefully layered with 80 ml n-hexane. The solvents were allowed to slowly mix by diffusion. The resultant red/brown microcrystals were isolated by filtration, rinsed with 20 ml n-hexane and dried in vacuo. Yield 470 mg (0.33 mmol, 67%). ^{1}H NMR (C_6D_6) δ 0.30 (s, 6H), 1.18–1.25 (m, 2H), 2.43–2.49 (m, 2H), 5.94 (br s, 7H), 6.33 (app t, splitting = 2.5 Hz, 2H), 6.92–7.03 (m, 12H), 7.64–7.70 (m, 8H). ^{31}P NMR ($CDCl_3$) δ +67.4. IR (THF) 1953vs, 1973sh cm^{-1}. UV (CH_2Cl_2) λ_{max} 386 nm (log ϵ 4.18). Anal. Found: C, 49.66; H, 4.38; Cl, 9.83. $C_{58}H_{58}Si_2P_2Zr_2Cl_4Co_2O_6$ calc: C, 49.38; H, 4.11; Cl, 10.06%.

*Acetyltricarbonyl[dichloro-1-[((2-diphenylphosphino)ethyl)dimethyisilyl]zirconocene-P]cobalt (**13**)*

a. Using CH_3I. To a solution of 210 mg (1.0 mmol) $K^+[Co(CO)_4^-]$ in 15 ml ether, cooled to 0°C, was added at once 700 mg (1.25 mmol) **10** in 3 ml THF. To the resulting pale yellow solution was immediately added 2.0 ml (570 mg, 4.0 mmol) of a 2 *M* MeI solution in ether dropwise by syringe. The yellow solution was stirred at 0°C for 3 h, followed by solvent removal in vacuo to obtain a yellow oil. Extraction with 30 ml ether, filtration and solvent removal yielded an orange solid. Recrystallization from THF/n-hexane at −78°C yielded 520 mg (0.69 mmol, 69%) of an orange solid.

b. Using CH_3COCl. To a solution of 145 mg (0.69 mmol) $K^+[Co(CO)_4^-]$ in 10 ml ether, cooled to 0°C, was added dropwise 0.76 ml (0.76 mmol) of a 1 *M* acetyl chloride solution in ether. The colorless solution gradually turned yellow as the mixture was stirred at 0°C for 4 h. To the solution was then added 427 mg (0.76 mmol) of **10** in 2 ml THF by syringe. The mixture immediately turned orange and an orange solid precipitated from solution. Stirring at 0°C for 2 h followed by solvent removal in vacuo yielded an orange oily solid. Extraction with 30 ml ether, filtration and solvent removal resulted in a feathery orange solid. Recrystallization from THF/n-hexane at −78°C yielded 283 mg (0.38 mmol, 55%) of an orange solid. ^{1}H NMR (C_6D_6) δ 0.28 (s, 6H), 0.94–1.02 (m, 2H), 2.24–2.31 (m, 2H), 2.67 (s, 3H), 5.88 (app t, splitting = 2.5 Hz, 2H), 5.92 (s, 5H), 6.25 (app t, splitting = 2.5 Hz, 2H), 6.97–7.06 (m, 6H), 7.40–7.47 (m, 4H). ^{31}P NMR (C_6D_6) δ +49.6. IR (C_6D_6) 1975sh, 1953br, 1680 cm^{-1}. Anal. Found: C, 50.14; H, 4.49. $C_{31}H_{32}SiPZrCl_2CoO_4$ calc: C, 49.73; H, 4.28%.

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