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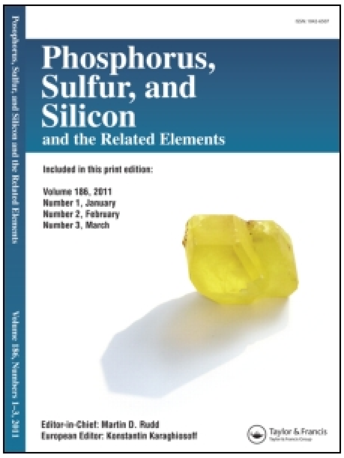

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I. -P. Lorenz[a]; C. Klasen[a]; G. Effinger[a]
[a] Institute for Inorganic Chemistry, University of Tübingen, Tubingen, FRG

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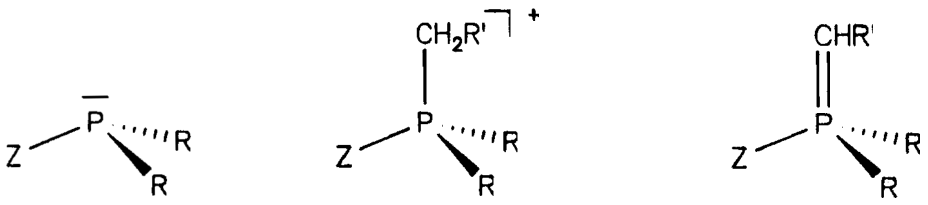
METALATED PHOSPHORUS YLIDES — ISOLOBAL WITTIG REAGENTS

INGO-PETER LORENZ, CHRISTIAN KLASEN AND GUIDO EFFINGER
Institute for Inorganic Chemistry, University of Tübingen,
Auf der Morgenstelle 18, D-7400 Tübingen (FRG)

Abstract The synthesis, structural characterization and reactivity of mono- and dimetalated phosphonium salts of the type $[\{Cp(CO)Fe(L)\}PPh_2\text{–}CH_2R']X$ or $[\{Cp(CO)_2Fe\}_2PPh\text{–}CH_2R']X$ (X = CO, P^nBu_3; X = Cl, BF_4) and of their deprotonation products, the μ_2-phosphaalkene complexes $\{Cp(CO)Fe(L)\}PPh_2{=}CHR'$ or the Wittig-analogous ferriophosphorus ylides $\{Cp(CO)_2Fe\}_2PPh{=}CHR'$ are discussed.

INTRODUCTION

Phosphonium salts of the type $[PR_3(CH_{3-x}R'_x)]BF_4$ are the standard starting materials for the *Wittig reagents* $PR_3{=}CH_{2-x}R'_x$. The analogous cationic phosphine complexes of transition metals of the type $[L_nMPR_2(CH_{3-x}R'_x)]BF_4$ may be considered as metalated phosphonium salts and therefore, they are isolobal to the phosphonium salts mentioned above. Consequently, they should be deprotonated to give metallated phosphorus ylides of the type $L_nMPR_2{=}CH_{2-x}R'_x$ (x = 0–2). Based on metalophosphines = λ^3-phosphinediyl complexes the isolobal relationship is demonstrated as follows:



Z = R (7 e-donor), ML$_n$ (17 e-donor)

RESULTS AND DISCUSSION

The synthesis of the diferriophosphonium complexes $[\{Cp(CO)_2Fe\}_2PPh\text{–}R]X$ (R = H, Ph, CH_2Ph, CH_2SiMe_3, CH_2COOEt) (**1a-e**) is successful by either the substitution reaction of $CpFe(CO)_2Cl$ with the silylphosphines $Me_3SiP(Ph)R$ and simultaneous Me_3SiCl-elimination (equation 1)[1] or by the one-pot reaction of deprotonation of $[\{Cp(CO)_2Fe\}_2PPhH]X$ (**1a**) and of the subsequent alkylation of the unstable intermediate diferriophosphine complex $\{Cp(CO)_2Fe\}_2PPh$ (**2**) (equation 2).

The light-sensitive diferriophosphonium compounds **1a-e** with an *open* Fe–P–Fe-skeleton very easily eliminate one CO ligand by photolysis to give the corresponding *closed* P-functionalized diferriophosphonium salts $\{Cp(CO)Fe\}_2(\mu_2\text{-}CO)(\mu_2\text{-}PPhR)$ (**3a-e**) (equation 3)[2].

The deprotonation reaction of the diferriophosphonium complexes $[\{Cp(CO)_2Fe\}_2PPh\text{–}CH_2R']X$ (R' = Ph, $SiMe_3$, COOEt) (**1c-e**) with KOH results in the formation of the unstable intermediate μ_2-P-bridged ***phosphaalkene*** complexes $\{Cp(CO)_2Fe\}_2PPh{=}CHR'$ (**4c-e**) which eliminate the dimeric iron complex $[CpFe(CO)_2]_2$ and the free, but extremely unstable ***phosphaalkene*** ligands $PhP{=}CHR'$, which dimerize to give the corresponding *1,3-diphosphetanes* (equation 4).

The monoferriophosphonium complexes $[\{Cp(CO)_2Fe\}PPh_2\text{–}CH_2R']X$ (R' = Ph, $SiMe_3$, COOEt, CN) (**5c-f**), which we have synthesized by the reaction of $[CpFe(CO)_2(H_2O)]X$ with the P-functionalized phosphines Ph_2PCH_2R' (equation 5), do not show any deprotonation reaction, but a base-like reaction (with CO_2-elimination) to give the dimeric phosphine-substituted iron complex $Cp(CO)Fe(\mu_2\text{-}CO)_2Fe(PPh_2CH_2R')Cp$ (**6c-f**) (equation 6)[3].

Finally, we succeeded in the synthesis of the P^nBu_3-substituted phosphonium complexes $[\{Cp(CO)(P^nBu_3)Fe\}PPh_2\text{–}CH_2R']X$ (R' = Ph, COOEt, CN; X = BF_4) (**7c,e,f**) — by starting with $[CpFe(CO)_2(P^nBu_3)]X$ and transferring it via $[\{Cp(CO)(P^nBu_3)Fe\}(CH_3CN)]X$ to **7c,e,f** (equation 7)[4] — and these functionalized ferriophosphonium derivatives **7c,e,f** now can be very easily deprotonated by different bases in α-position of the P-bound alkyl substituent according equation 8 to give the corresponding "metalated" phosphorus ylides $\{Cp(CO)(P^nBu_3)Fe\}PPh_2{=}CHR'$ (R' = Ph, COOEt, CN) (**8c,e,f**), a very new and interesting type of compounds which are isolobal to "organic" phosphorus ylides^4.

They have been tested as starting materials for the *Wittig-analogous* carbonyl-olefination reactions; they indeed react with benzaldehyde in a typical *Wittig-like* manner to give the corresponding alkenes^4.

Because of the complex substituent L_nM on phosphorus the new organometalated phosphorus ylides of the type **8** possess a very interesting *steric* and *electronic* potential for the desired stereoselectivity of *Wittig reactions.*

The structures of the complexes **1b**^{1}, **3b**^{2}, **6c**^{3}, **7f**^{4} (and **8e**^{4}) have been characterized by x-ray structure analysis and are shown in Figure 1.

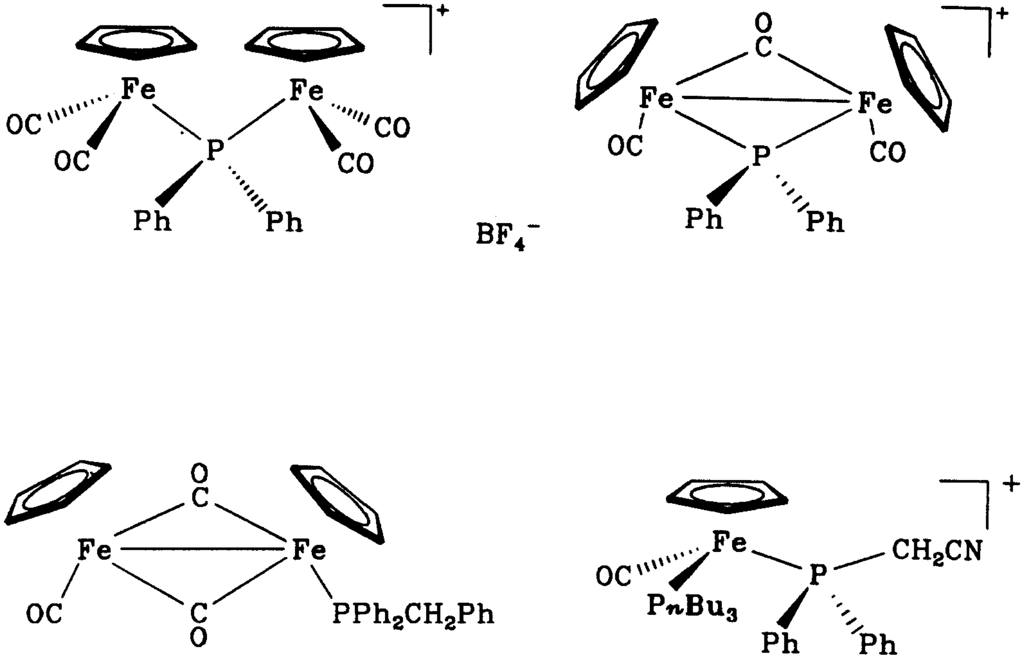


FIGURE 1 Structures of the compounds **1b**, **3b**, **6c** and **7f**

$$2\,CpFe(CO)_2Cl + Me_3SiPPhR \xrightarrow[-Me_3SiCl]{(1)} [\{Cp(CO)_2Fe\}_2PPhR]X$$

(R = H, Ph, CH_2Ph, CH_2SiMe_3, CH_2COOEt; X = Cl, I, BF_4) **1a-e**

$$\mathbf{1a} \xrightarrow[-HX]{} \{Cp(CO)_2Fe\}_2PPh \xrightarrow{+RX(2)}$$

$$[\{Cp(CO)_2Fe\}_2PPhR]X \xrightarrow[-CO]{(3)} [\{Cp(CO)Fe\}_2(\mu\text{-}CO, PPhR)]X$$

1a-e **3a-e**

$$[\{Cp(CO)_2Fe\}_2PPh\text{-}CH_2R']X \xrightarrow[-HX]{(4)} \{Cp(CO)_2Fe\}_2PPh{=}CHR'$$

1c-e **4c-e**

(R' = Ph, $SiMe_3$, COOEt) $\downarrow - [CpFe(CO)_2]_2$

$$\text{1,3-diphosphetanes} \longleftarrow \{Ph \sim P = CHR'\}$$

$$[CpFe(CO)_2(L)]X + Ph_2PCH_2R' \xrightarrow[-H_2O]{(5)} [Cp(CO)_2FePPh_2\text{-}CH_2R']X$$

(R' = Ph, $SiMe_3$, COOEt, CN; **5c-f**

X = BF_4, L= H_2O) (6) $\downarrow$ + KOH − KBF_4

$$CpCOFe(\mu\text{-}CO)_2Fe(PPh_2CH_2R')Cp$$

6c-f

$$[CpFe(CO)_2(P^nBu_3)]X \xrightarrow[-CO]{+CH_3CN} [CpFe(CO)(P^nBu_3)(CH_3CN)]X$$

(7) $\downarrow$ +PPh_2CH_2R'

$$CpFe(CO)(P^nBu_3)PPh_2{=}CHR' \xleftarrow[-HX]{+base(8)} [CpFe(CO)(P^nBu_3)PPh_2\text{-}CH_2R']X$$

8c,e,f **7c,e,f**

(R' = Ph, COOEt, CN)

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