as an unresolved shoulder on the PSO$^-$ peak and its mass could not be measured accurately, but an estimate by visual interpolation indicates that it is almost certainly due to PO_3^-. Azinphos methyl contains only two phosphoryl oxygen atoms; hence it cannot produce a PO_3^- ion except by reaction with the moderator gas.

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(11) The masses were measured by peak matching against a $^{79}Br^-$ reference on a ZAB/2F instrument (VG Micromass, Altrincham), using air as the reagent gas or moderator in the negative-ion chemical-ionization mode. Nominal (gauge) air pressure was 3–5 × 10^{-6} Torr; repellers and accelerator were set at 0 V and 6 kV, respectively; resolution (static) was 3500; source temperature was 200 °C; samples were introduced by unheated direct probe.

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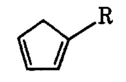
Synthesis of $(C_6H_5)_2PCH_2Si(CH_3)_2C_5H_4Li$: A Novel Heterodifunctional System for the Directed Linkage of Dissimilar Transition Metal Fragments

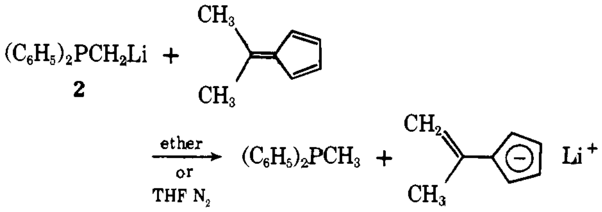
Sir:

Reports of interesting and often synthetically useful chemical processes carried out by two or more organometallic species in combination are becoming increasingly common.[1] The construction of model systems possessing two metals linked by ligand bridges, but not necessarily direct metal–metal bonds, is one approach toward probing the chemical interactions between these metal centers. Ligand bridges possessing pairs of trisubstituted phosphines (or other group 5 analogues) are of course well known;[2] far less common are reports of linked cyclopentadienide rings.[3] Both general classes of compounds are of value in the formation of bimetallic compounds possessing two identical metal centers but, not unexpectedly, are poorly suited for the construction of systems possessing very different types of metals, e.g., "early" and "late" transition metals in the same molecule. Much more versatile would be a linkage containing both phosphine and cyclopentadienide functionality. It is quite surprising, therefore, that only four such systems have been described (**1a–d**),[4] three having a direct phosphorus-ring bond, and *not a single example of such a ligand being synthesized, isolated, and attached to two different metals has ever been reported.*[5a] We report herein the initial results of our studies involving the synthesis of the first heterodifunctional compounds containing remote phosphine and cyclopentadienide functionality, and their application in the production of heterodinuclear organometallic complexes.

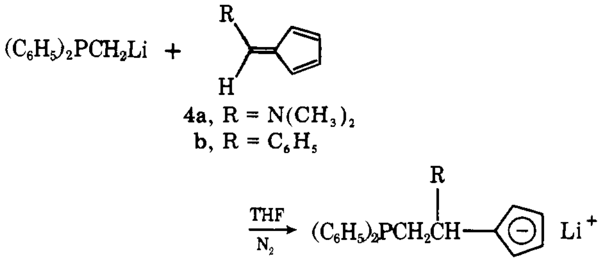


1a, R = $P(OR)_2$[4a]
b, R = PF_2[4b]
c, R = $P(C_6H_5)_2$[4c,d]
d, R = $CH_2P(C_6H_5)_2$[4e]

Both direct and stepwise routes to the desired ligands have been investigated. In the former category fall attempts to add phosphine-containing nucleophiles to fulvenes. The reaction of diphenylphosphinomethyllithium (**2**)[6] with dimethylfulvene in ether or THF leads, however, entirely to the products of proton transfer (eq 1). Although this result is not inherently surprising, it contrasts sharply with the large number of literature reports describing additions of aryl- and alkyllithiums to dimethylfulvene, none of which indicates the interference of the proton-transfer process.[7] Addition of **2** to fulvenes lacking acidic hydrogens (**4a and 4b**) does appear to take place (eq 2). In the case of **4a**, the reaction proceeds cleanly upon slow addition of solid **2**, but the product is extremely reactive and gives rise to complex chemistry when subjected to further organic transformations. The product of addition of **2** to **4b** does not form as cleanly, and, therefore, we have proceeded to develop the stepwise approach described in Scheme I.



(1)



4a, R = $N(CH_3)_2$
b, R = C_6H_5

(2)

Slow addition of a THF solution of **2** TMEDA[8] to a large excess of dichlorodimethylsilane in THF yields predominantly monoaddition product **6** if both solutions are held at −78 °C over the course of the addition. The products **5** and **6** are interesting spectroscopically because their NMR spectra display larger phosphorus–hydrogen four-bond (PCSiCH) coupling (J^4 = 0.9 and 0.7 Hz, respectively) than two-bond (PCH) coupling ($J^2 \leq 0.5$ Hz) in C_6D_6 solvent.[9,10] After removal of

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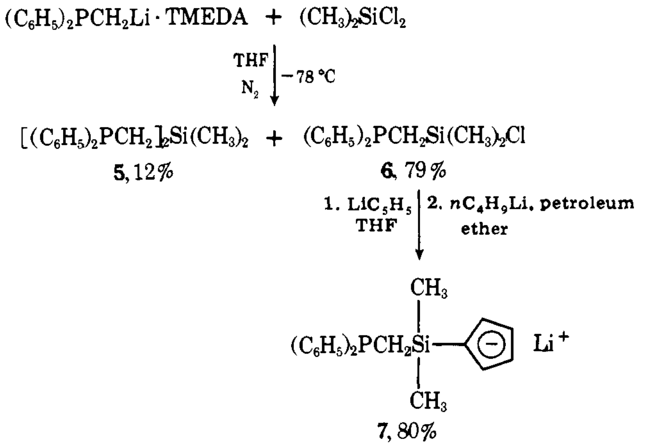
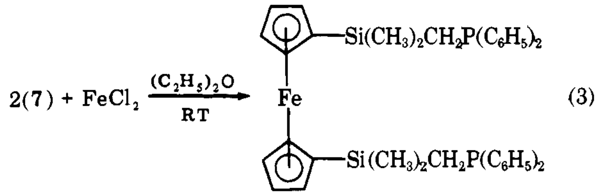
Scheme I

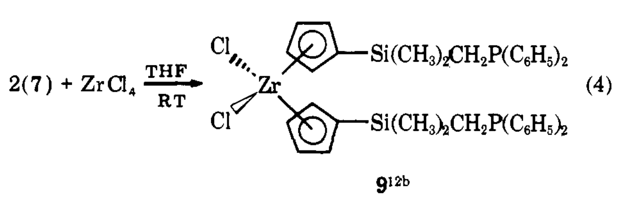


solvent, TMEDA, and LiCl by conventional means, addition of the colorless, oily mixture of **5** and **6** as a THF solution to a cold solution of LiC_5H_5 in THF instantly discharges the yellow color of the latter and generates a solution that appears to contain at least two different isomers[11] of $(C_6H_5)_2PCH_2Si(CH_3)_2C_5H_5$. Deprotonation of the crude product mixture with *n*-butyllithium in petroleum ether leads directly to the desired ligand, [dimethyl(diphenylphosphinomethyl)silyl]cyclopentadienyllithium (**7**), in 63% overall yield based on **2** TMEDA, isolated as a white, air- and moisture-sensitive solid with NMR (THF-d_8) δ 0.02 (d, J = 0.7 Hz, 6 H, Si $(CH_3)_2$), 1.55 (d, J = 2.3 Hz, 2 H, PCH_2Si), 5.97 (m, 4 H, C_5H_4Si), and 7.10–7.67 (m, 10 H, $(C_6H_5)_2P$) ppm.

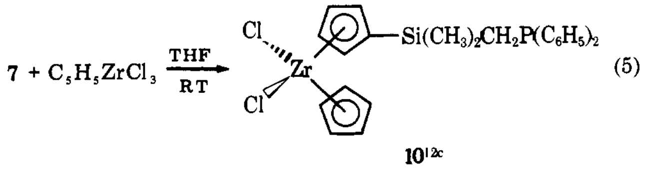
We have prepared a number of complexes of **7** with transition metals, demonstrating basically that the cyclopentadienyl and phosphine sites in this molecule are each capable of the chemistry that is characteristic of the isolated systems. Our strategy has been to make use of the reactivity difference between the two sites, attaching the cyclopentadienyl moiety to appropriate metals first, using conventional methods. Three representative preparations that we have carried out are presented (eq 3–5). The latter two reactions are the first syntheses of group 4 metallocene dihalides with free, remote phosphine functionality. In all cases the reactions proceed without apparent complication from the phosphine unit, and no evidence for metal–phosphine interaction is observed by NMR. Absorptions for the ligand side chain are virtually superimposable in all three systems and closely resemble the corresponding patterns for the free compounds described earlier; in particular, $^2J_{PCH}$ is small for all these compounds (≤1 Hz).



8[12a]

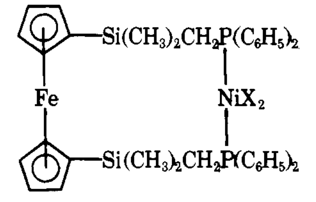


9[12b]



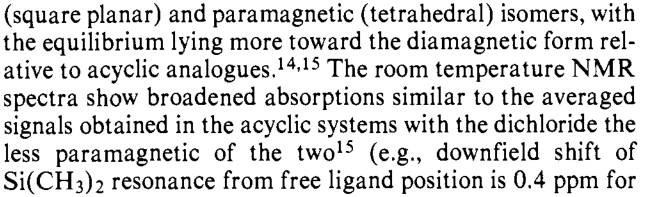
10[12c]

Complexation of the free phosphine units of these compounds to a second metal center has been achieved. Reaction of ferrocene **8** with nickel(II) salts gives rise to materials displaying properties[13] consistent with cyclic bis(alkyldiphenylphosphine)nickel dihalides **11**. In particular, these materials appear to exist in solution as mixtures of diamagnetic (square planar) and paramagnetic (tetrahedral) isomers, with the equilibrium lying more toward the diamagnetic form relative to acyclic analogues.[14,15] The room temperature NMR spectra show broadened absorptions similar to the averaged signals obtained in the acyclic systems with the dichloride the less paramagnetic of the two[15] (e.g., downfield shift of $Si(CH_3)_2$ resonance from free ligand position is 0.4 ppm for **11**, X = Cl, and 0.8 ppm for **11**, X = Br). Both display very weak electronic absorption in the 840–850-nm region, characteristic of the presence of the paramagnetic tetrahedral isomer in low concentration.



11, X = Br, Cl

In addition, attachment of the single phosphine of **10** to a second transition metal has been carried out (eq 6). The product in this case is isolated as a somewhat impure tan solid by column chromatography (Florisil/benzene–ether). Its structural features are quite evident spectroscopically: IR (THF) 1935 (vs), 1964 (m), 2058 (s) cm^{-1}; NMR (C_6D_6) δ 0.47 (br s), 2.62 (d, J = 14.5 Hz), 5.83 (t, J = 2.5 Hz), 5.97 (s), 6.36 (t, J = 2.5 Hz), 7.0–8.1 (m). The downfield shift and substantially larger PCH coupling constant displayed by the ligand methylene resonance are completely consistent with complexation with the iron center as indicated, and the IR pattern further supports the presence of an independent $Fe(CO)_4P(C_6H_5)_2R$ functional unit.



In summary, difunctional ligand **7** is a readily prepared, stable system which is capable of directed attachment to appropriate transition metal centers, yielding a variety of new, heterodinuclear complexes. Further investigations into the physical and chemical properties of these new compounds are currently underway in our laboratory. In addition, studies aimed at the preparation of analogues of **7** and their possible application in single-metal chelation as well as metal linkage have begun and will be reported on in due course.

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(5) (a) This, of course, excludes bimetallic systems prepared by functionalization of an already metal-bonded cyclopentadienyl ring, e.g., metalations of $(C_5H_5)_2Fe$:[5b] (b) Rosenblum, M. "Chemistry of the Iron Group Metallocenes: Ferrocene, Ruthenocene, Osmocene"; Interscience: New York. 1965.

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(9) (a) Conformational and solvent effects commonly lead to small two-bond phosphorus–hydrogen coupling constants,[9b,c] although larger four-bond than two-bond couplings are unusual: the related molecule $(CH_3)_2PCH_2Si(CH_3)_2Cl$ has $^2J = 1.3$ and $^4J = 0.5$ Hz.[9d] (b) Horn, H.-G.; Sommer, K. *Spectrochim. Acta, Part A* **1971,** *27*, 1049. (c) Grim, S. O.; Mitchell, J. D. *Inorg. Chem.* **1977,** *16*, 1762, 1770. (d) Grobe, J.; Heyer, G. *J. Organomet. Chem.* **1973,** *61*, 133.

(10) NMR of **6**: δ 0.42 (d, $J = 0.9$ Hz, 6 H, $Si(CH_3)_2$), 1.82 (br s, 2 H, PCH_2Si), 7.2–7.9 (m, 10 H, $(C_6H_5)_2P$) ppm; NMR of **5**: δ 0.15 (t, $J = 0.7$ Hz, 6 H), 1.52 (br s, 4 H), 7.2–7.9 (m, 20 H) ppm.

(11) Crude mixture displays NMR signals (THF) at δ 0.07 (d, $J = 0.8$ Hz) and −0.16 (d, $J = 0.9$ Hz) ppm. In THF, **6** shows δ 0.28 (d, $J = 0.9$ Hz) ppm.

(12) (a) **8** was isolated as a red-orange liquid (benzene/alumina(I) chromatography). Calcd for $C_{40}H_{44}P_2Si_2Fe$: C, 68.76; H, 6.35; Si, 8.04; Fe, 7.99. Found: C, 68.69; H, 6.46; Si, 7.97; Fe, 8.13. NMR (benzene-d_6): δ 4.12 and 4.32 (apparent t, 'J' = 1.8 Hz, C_5H_4). (b) **9** was isolated as a white solid from petroleum ether at −40 °C, melting below room temperature. Calcd for $C_{40}H_{44}Cl_2P_2Si_2Zr$: C, 59.68; H, 5.51; Cl, 8.81. Found: C, 59.87; H, 5.64; Cl, 8.68. NMR (benzene-d_6): δ 6.03 and 6.52 (apparent t, 'J' = 2.5 Hz). (c) **10** was isolated as was **9**. Calcd for $C_{25}H_{27}Cl_2PSiZr$: C, 54.73; H, 4.96; Cl, 12.92. Found: C, 54.60; H, 5.11; Cl, 13.09. NMR (benzene-d_6): δ 6.10 (s, C_5H_5), 6.00 and 6.50 (apparent t, 'J' = 2.5 Hz, C_5H_4).

(13) (a) X = Br, brown solid (precipitates from benzene/petroleum ether at 25 °C), darkens above 115 °C: mp 138–142 °C dec; visible (benzene) λ_{max} 411, 507, 845 nm; NMR (benzene-d_6) δ 1.15, 4.15, 4.30, 5.95, 9.50 (all broad; latter three are averaged positions for para, ortho, and meta protons of phenyl rings). (b) X = Cl, red solid (from ethanol): mp 63–66 °C dec; visible (benzene) λ_{max} 484, 838 nm; NMR (benzene-d_6) δ 0.75, 4.15, 4.30, 7.60 (all broad).

(14) (a) The dibromonickel(II) complex of 1,2-bis(diphenylphosphino)ethane is diamagnetic and that of 1,3-bis(diphenylphosphino)propane is ~50% diamagnetic in solution.[14b] (b) Van Hecke, G. R.; Horrocks, W. D. *Inorg. Chem.* **1966,** *5*, 1968.

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Reaction between Chlorophosphoranes and Benzyltri-*n*-butylammonium or Trimethylsilyl Azides. Direct Observation of Hexacoordinate Intermediates in Displacement Reactions at Pentacoordinate Phosphorus

Sir:

The number of hexacoordinate phosphorus compounds that has been prepared is relatively small. They are formed either from nucleophilic anions and neutral pentacoordinate phosphoranes[1,2]

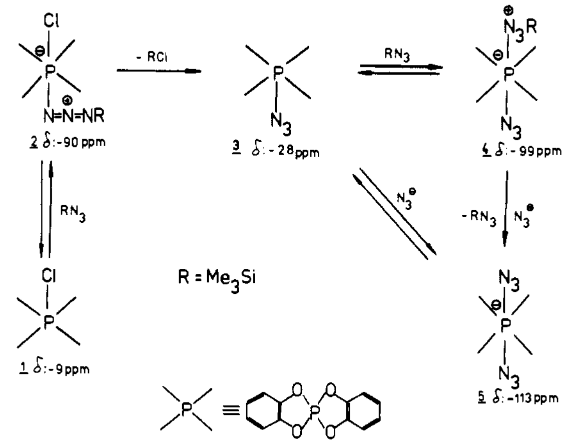
$$R_5P + Nu^- \rightarrow R_5P^-\text{-}Nu$$

or from phosphoranes and amines.

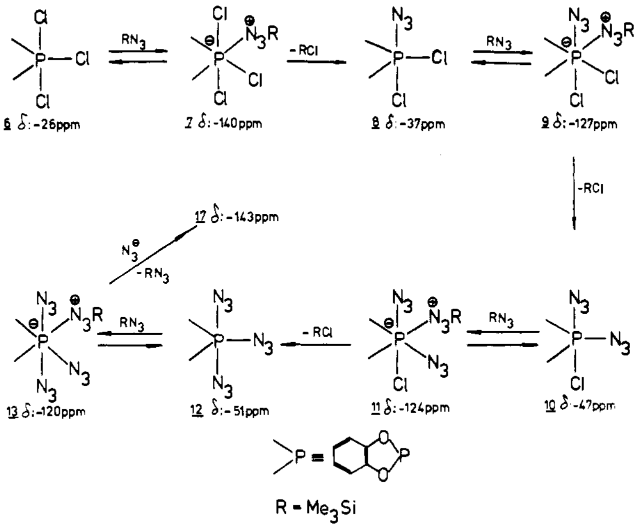
$$R_5P + NR_3' \rightarrow R_5P^-\text{-}N^+R_3'$$

In the latter case they have the charge distribution of a zwitterion.[2,3] There is growing realization that hexacoordinate phosphorus species may play an important role in organophosphorus chemistry and biochemistry. Ramirez and his collaborators have postulated hexacoordinate intermediates from the observations of base catalysis in the hydrolysis of cyclic phosphoranes.[4]

Scheme I



Scheme II



Archie and Westheimer have provided strong support for the hypothesis that hydrolysis of some acyclic phosphoranes proceeds via hexacoordinate phosphorus intermediates or transition states.[5] There remains the intriguing problem of the extent to which the hexacoordinate compounds are involved as intermediates in the substitution at the pentacoordinate phosphorus atom.[6] We describe herein results which reveal that such hexacoordinate phosphorus complexes are indeed formed as observable species in the reaction between chlorophosphoranes containing single or double catechol bidentate ligands with benzyltri-*n*-butylammonium and trimethylsilyl azides.

The reactions of chlorophosphoranes **1** and **6** with trimethylsilyl or benzyltri-*n*-butylammonium azides were performed under the following conditions. To a solution of the chlorophosphorane in ethyl chloride or nitropropane was added the azide at the temperature of liquid nitrogen. The mixture was then warmed gradually and the changes in species present were observed by FT proton-decoupled ^{31}P NMR spectroscopy. The experimental results together with the structural assignments for intermediates and final products are given in Schemes I-III.

Reaction between bis(*O*-phenylene)chlorophosphorane **1** and 1 molar equiv of trimethylsilyl azide at −100 °C in ni-

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