material, and 65%, with no recovery. Application of this ligand exchange to the *sym*- and *unsym*-(benzoferrole)tricarbonyliron complexes yielded the analogous benzoferrametallocenes **3** and **4**.

The isolobal analogy of the ferrametallocenes to the metallocenium ions **1**, as well as to Hogeveen's pyramidal dication,[15] suggested that they might possess interesting electrochemistry and exhibit relatively low reduction potentials. Indeed, both **2a** and **2b** readily add one-electron reversibly ($E_{1/2}{}^{\mathrm{I}}$ = −1.39 and −1.76 eV, respectively),[16] although not as readily as for the isolobal complex (ferrole)tricarbonyliron **5** ($E_{1/2}{}^{\mathrm{I}}$ = −1.30 eV).[17] .

At the same time, the complexes **2a** and **2b**, similar to other metallocenes, are sufficiently electronically rich to be conveniently acylated under conventional Friedel–Crafts conditions at room temperature. Acetylation and benzoylation using the corresponding acid chloride–aluminum chloride complex in either carbon disulfide or dichloromethane occurred in 30–55% yield.[18] Consideration of ^{1}H and ^{13}C NMR chemical shift data, which often correlates with relative rates of Friedel–Crafts acylation,[19] suggested preferential electrophilic attack at the C_5-cyclopentadienyl ring. Contrary to this expectation, however, acylation occurred exclusively at the carbon adjacent to the iron in the ferracyclopentadienyl ring, i.e., presumbaly at the least electronically rich carbon atom, yielding the 2-acetyl and 2-benzoyl derivatives. In the acetylation reactions, where diacylation as well as monoacylation was observed, even the attack by the second acyl group occurred exclusively at the unsubstituted carbon adjacent to the iron, to yield the 2,5-diacetyl derivative[20] (~15% yield). Interestingly, preliminary data also suggest that the second acylation step is competitive with the first. This and additional chemistry, as well as our efforts to prepare additional mixed metallametallocenes, will be the subject of forthcoming reports.

Registry No. **2a**, 83416-31-3; **2b**, 83416-32-4; **3a**, 83416-33-5; **3b**, 83416-34-6; **4a**, 83435-71-6; **4b**, 83435-72-7; $C_5H_5Co(CO)_2$, 12078-25-0; $C_5H_5Rh(CO)_2$, 12192-97-1; $Fe_3(CO)_{12}$, 17685-52-8; $Fe(CO)_3C_4H_4Fe(CO)_3$, 50277-83-3; (benzoylcyclobutadiene)tricarbonyliron, 67612-84-4; (acetylcyclobutadiene)tricarbonyliron, 52445-09-7; 2-benzoylferracobaltocene, 83435-73-8; 3-benzoylferrocobaltocene, 83416-35-7; 2-acetylferracobaltocene, 83416-38-0; 3-acetylferracobaltocene, 83416-36-8; (benzocyclobutadiene)tricarbonyliron, 12093-06-0; thiophene, 110-02-1; (cyclobutadiene)tricarbonyliron, 12078-17-0; 2,5-diacetylferracobaltocene, 83416-37-9.

Supplementary Material Available: Tables of crystal data, thermal parameters, positional parameters, and bond angles and distances for $C_{16}H_{11}O_3CoFe$ and $C_{16}H_{11}O_3RhFe$ (9 pages). Ordering information is given on any current masthead page.

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(15) Hogeveen, H.; Kwant, P. W. *J. Am. Chem. Soc.* **1974**, *96*, 2208; *Acc. Chem. Res.* **1975**, *8*, 413.

(16) Reference electrode: Ag/AgCl, NaCl saturated aqueous electrode: Tulyathan, B.; Rieke, R.; McKennis, J. S., unpublished results, manuscript in preparation.

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(18) 2-Acetylferracobaltocene: mp 82–84 °C; IR (CS_2) 1673 (w), 1960 (vs), 1970 (vs, sh), 2035 (vs) cm^{-1}; ^{1}H NMR (CS_2) δ 2.16 (3, s, CH_3), 5.04 (5, s, Cp), 5.70 (1, "t", H_3), 5.84 (1, dd, H_2), 7.38 (1, dd, H_4); high-resolution MS, *m/e* 357.9541 (P^+) (calcd 357.9334). 2-Benzoylferracobaltocene: mp 130–131 °C; IR (CS_2) 1645 (w), 1960 (vs), 1972 (vs), 2035 (vs) cm^{-1}; ^{1}H NMR (CS_2) δ 5.14 (5, s, Cp), 5.75 (1, "t", H_3), 5.95 (1, dd, H_2), 7.24 and 7.67 (5, m, C_6H_5), 7.45 (1, dd, H_4); high-resolution MS, *m/e* 419.9481 (P^+) (calcd 419.9495).

(19) See ref 4 and references therein.

(20) 2,5-Diacetylferracobaltocene: mp 114.5–116 °C; IR (CS_2) 1675 (w), 1965 (vs), 1980 (vs), 2040 (vs)cm^{-1}; ^{1}H NMR (CS_2) δ 2.18 (6, s, CH_3), 5.18 (5, s, Cp), 5.68 (2, s, H_2H_3); high-resolution MS, *m/e* 399.9507 (P^+) (calcd 399.9444).

Two-Coordinate Phosphorus Compounds with Bis(trimethylsilyl)methyl Ligands: Phosphaalkene and Phosphide Anion†

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Received September 24, 1982

Summary: The reaction of $[(Me_3Si)_2CH]_2PCl$ with Na in *n*-hexane at 65 °C results in the formation of $[(Me_3Si)_2CH]_2PH$ (**3**) and $(Me_3Si)_2C{=}PC(H)(SiMe_3)_2$ (**4**), in addition to the phosphinyl radical $[\{(Me_3Si)_2CH\}_2P]\cdot$ (**1**) and the corresponding dimer $[(Me_3Si)_2CH]_4P_2$ (**2**). Compounds **3** and **4** have been synthesized by independent routes. The reaction of a mixture of **1** and **2** with Na in *n*-hexane produces **3** and the phosphide anion $[\{(Me_3Si)_2CH\}_2P]^-$ (**5**).

Lappert, Goldwhite, and co-workers[2] have established that stabilized phosphinyl radicals are produced when chlorophosphines bearing bulky groups are photolyzed in the presence of an electron-rich olefin. The $[\{(Me_3Si)_2CH\}_2P]\cdot$ radical, 1, which serves as a novel ligand,[3] can also be prepared by the action of Na on $[(Me_3Si)_2CH]_2PCl$ in *n*-hexane.[4,5] In the course of monitoring this reaction by $^{31}P\{^1H\}$ NMR spectroscopy, it is apparent that two further products arise in addition to the phosphinyl radical, 1, and the corresponding dimer $[(Me_3Si)_2CH]_4P_2$ (**2**).

A singlet at −72.2 ppm[6] in the 36.43 MHz $^{31}P\{^1H\}$ spectrum which becomes a doublet in a coupled spectrum (J_{PH} = 195.3 Hz) is due to the secondary phosphine, $[(Me_3Si)_2CH]_2PH$ (**3**). The identity of **3** was established via two independent routes: (i) the $LiAlH_4$ reduction of $[(Me_3Si)_2CH]_2PCl$ and (ii) reaction of the phosphinyl radical, 1, with C_6H_5SH. The yields of **3** (bp 65–75 °C at 0.04 torr) were 82% and ~100% for routes i and ii, respectively. High-resolution mass spectrum (HRMS), for **3**: calcd 350.1865; found 350.1874.

The second product exhibits a 36.43-MHz $^{31}P\{^1H\}$ chemical shift of +404 ppm,[6] thus suggesting that it is a two-coordinate phosphorus compound.[7] Identification of this material as the new phosphaalkene $(Me_3Si)_2C{=}PC(H)(SiMe_3)_2$ (**4**) is based on its independent synthesis by the following two-step procedure: (i) dehydrochlorination of $(Me_3Si)_2CHPCl_2$ with 1,4-diazabicyclo[2.2.2]octane

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† Dedicated to the memory of Rowland Pettit, whose research contributed so much to the fields of organic and organometallic chemistry.

(1) (a) University of Texas at Austin. (b) University of Edinburgh.

(2) (a) Gynane, M. J. S.; Hudson, A.; Lappert, M. F.; Power, P. P.; Goldwhite, H. *J. Chem. Soc., Chem. Commun.* **1976**, 623–624. (b) Gynane, M. J. S.; Hudson, A.; Lappert, M. F.; Power, P. P.; Goldwhite, H. *J. Chem. Soc., Dalton Trans.* **1980**, 2428–2433. (c) Cetinkaya, B.; Hudson, A.; Lappert, M. F.; Goldwhite, H. *J. Chem. Soc., Chem. Commun.* **1982**, 609–610.

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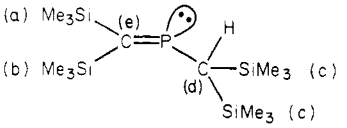
(5) This procedure was also discovered by: Power, P. P. Ph.D. Thesis, University of Sussex, 1977.

(6) Positive ^{31}P chemical shifts are in ppm downfield from external 85% H_3PO_4 and vice versa.

(7) For a summary of ^{31}P NMR data on phosphaalkenes, see: Appel, R.; Knoll, F.; Ruppert, I. *Angew. Chem., Int. Ed. Engl.* 1981, *20*, 731–744 and references therein.

0276-7333/82/2301-1720$01.25/0

(DABCO) to form $(Me_3Si)_2C{=}PCl$[8] and (ii) treatment of $(Me_3Si)_2C{=}PCl$ with $(Me_3Si)_2CHLi$[9] in hexane solution. The overall yield of 4 (bp 79 °C at 0.005 torr) starting with $(Me_3Si)_2C{=}PCl$ was 75%. HRMS for 4: calcd 348.1710, found 348.1717; NMR data for 2: ^{13}C NMR (20 MHz) (Me_4Si) Me_3Si (a) δ 2.0 (d, $J_{PCSiC} = 5.4$ Hz), Me_3Si (b) δ 4.3 (d, $J_{PCSiC} = 3.1$ Hz), Me_3Si (c) δ 3.82 (s), PC (d) δ 40.6 (d, $J_{PC} = 87.3$ Hz), PC (e) δ 191 ($J_{PC} = 89.7$ Hz).



We next address the question of the mechanisms of formation of **3** and **4**. Purification of the $[(Me_3Si)_2CH]_2PCl/Na$ reaction mixture by fractional vacuum distillation (bp 70–78 °C at 0.03 torr), followed by two recrystallizations from *n*-hexane at −20 °C, affords single crystals of the pure diphosphine $[(Me_3Si)_2CH]_4P_2$.[10] Dissolution of these crystals in *n*-hexane or toluene results in orange-red solutions which exhibit only one $^{31}P\{^1H\}$ NMR peak (+19 ppm (s)). Heating a toluene solution from +28 °C to +80 °C resulted in the gradual disappearance of the +19-ppm peak as the diphosphine **2** dissociated into the phosphinyl radical, **1**. These changes were reversible, and no new peaks appeared. Furthermore, no new ^{31}P NMR peaks were detectable upon prolonged storage of *n*-hexane solutions of **1**/**2** mixtures at 25 °C. Clearly, **3** and **4** are not produced via the phosphinyl radical, **1**, or the diphosphine, **2**. To shed more light on this question, an *n*-hexane solution of the **1**/**2** radical/diphosphine mixture was treated with an equimolar quantity of Na at 65 °C for 14 h. This resulted in the complete consumption of **1** and **2** and the formation of a 60/40 mixture of **3** and the new phosphide anion $[\{(Me_3Si)_2CH\}_2P]^-$ (**5**) (^{31}P chemical shift, −106 ppm). This experiment suggests that in the $[(Me_3Si)_2CH]_2PCl/Na$ coupling reaction, **3** arises via the phosphide anion, **5**. Interestingly, the phosphide anion, **5**, is not produced by treatment of the secondary phosphine, **3**, with *n*-BuLi, *n*-BuLi/TMEDA, MeLi, or KH, presumably because of the steric bulk of the $(Me_3Si)_2CH$ ligand.

Considering that the phosphaalkene **4** might be produced by dehydrochlorination of $[(Me_3Si)_2CH]_2PCl$, we treated this compound with DABCO in ether solution for 4 h at 40 °C. However, the chlorophosphine failed to react and was recovered quantitatively. Further experimentation will therefore be necessary to reveal the mechanism of phosphaalkene formation.

The coordination chemistry of the phosphide anion, **5**, is under active investigation.

Acknowledgment. We are grateful to NATO, the National Science Foundation, the Robert A. Welch Foundation, and SERC for generous financial support.

Registry No. **1**, 63429-86-7; **2**, 83436-91-3; **3**, 83436-92-4; **4**, 83436-93-5; **5**, 83436-94-6; $[(Me_3Si)_2CH]_2PCl$, 63429-87-8.

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[8] This compound was described first by Appel, R.; Westerhaus, A. *Tetrahedron Lett.* **1981**, *22*, 2159–2160.

[9] Preparation of $(Me_3Si)_2CHLi$ and thus other $(Me_3Si)_2CH$-substituted compounds is greatly facilitated by our "one-pot" synthesis of $(Me_3Si)_2CHCl$: Cowley, A. H.; Kemp, R. A. *Synth. React. Inorg. Met.-Org. Chem.* **1981**, *11*, 591–595.

[10] The structures of $[(Me_3Si)_2CH]_4P_2$ and $[\{(Me_3Si)_2CH\}_2P]\cdot$ have been determined recently by X-ray crystallography and gas-phase electron diffraction, respectively. This work will be published in a separate manuscript.

Steric Effects of Phosphido Ligands. Synthesis and Crystal Structure of Di-*tert*-butylphosphido-Bridged Dinuclear Metal–Metal Bonded Complexes of Fe(II), Co(I, II), and Ni(I)[†]

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Received June 25, 1982

Summary: Reaction of *t*-Bu_2PLi with $MCl_2(PMe_3)_2$ (M = Fe, Co, Ni) in THF at −78 °C yields $[Fe(\mu\text{-}t\text{-}Bu_2P)Cl(PMe_3)]_2$ (**1**), $Co_2(\mu\text{-}t\text{-}Bu_2P)_2Cl(PMe_3)_2$ (**2**), and $[Ni(\mu\text{-}t\text{-}Bu_2P)(PMe_3)]_2$ (**3**) whose structures have been determined by X-ray diffraction studies.

It is well-known that variation in the size of the R groups of trialkyl- or triarylphosphines (PR_3) can dramatically alter the chemical and physical properties of their transition-metal complexes.[1] However, similar studies of transition-metal phosphido complexes are not available as most of them are derivatives of diphenyl (Ph_2P^-) or dimethyl (Me_2P^-) phosphide which are not particularly bulky.[2]

As part of a program aimed at the study of steric effects in transition-metal phosphido complexes we have initially studied the chemistry of the di-*tert*-butylphosphido (*t*-Bu_2P^-) unit. At present there are only three other d-block transition-metal complexes containing this unit, and none has been structurally characterized.[3] Apart from a few phosphine-stabilized phosphido complexes of the nickel triad[2] most phosphido complexes of the transition metals have either η^5-C_5H_5, CO, or NO as ancillary ligands.[2]

We have, therefore, initially examined the reaction of the late first-row metal phosphine halides $MCl_2(PR_3)_2$ (M = Fe, Co, Ni; R = Me) with Li-*t*-Bu_2P in order to prepare a range of phosphido complexes with trialkylphosphines as stabilizing ligands.

The reaction of $MCl_2(PMe_3)_2$ (M = Fe,[4] Co,[5] Ni[6]) with 2 molar equiv of Li-*t*-Bu_2P[7] in tetrahydrofuran at −78 °C yields $[Fe(\mu\text{-}t\text{-}Bu_2P)Cl(PMe_3)]_2$ (**1**), Co_2 $(\mu\text{-}t\text{-}Bu_2P)_2Cl(PMe_3)_2$ (**2**) and $[Ni(\mu\text{-}t\text{-}Bu_2P)(PMe_3)]_2$ (**3**)[8] (Scheme I).

[†] Dedicated to the memory of Rowland G. Pettit.

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