The cis configurations of the main isomers of **4b** and **5b**, isolated by recrystallization, are further attested to by the four $\nu$(CO) stretching vibrations. They appear in the infrared spectra at values close to those found for the other cis adducts (Table III).

The fact that only the cis isomer has formed even with ligand **1a** shows that its four methyl groups on the carbon $\alpha$ to the oxygen atoms do not contribute sufficiently to steric hindrance to destabilize the cis configuration in favor of a trans configuration.

While ligands having unconnected P and N donor sites have been found to behave as bidentate donors with respect to group 6 metal carbonyls,[9a,b] no evidence for the formation of adducts in which ligands **1a** or **1b** act in a bidentate fashion, either in mononuclear or in bridged species, was obtained with $M(CO)_4(nbd)$ (M = Mo, W), even though two sites were made readily available in the coordination sphere of the metal.

**Molybdenum Tricarbonyl Tris(bicycloaminophosphane) Adducts.** Trisubstituted adducts of $M(CO)_3(bcap)_3$, with M = Mo, were obtained when $M(CO)_3(mes)$[18] was allowed to react with 3 molar equiv of the ligands. Both adducts are thermally stable. No evidence for the formation of compounds having other stoichiometries such as, for example, $M(CO)_3(bcap)_2$, where one of the ligands could exhibit a bidentate behavior, was found.

Only the *fac* isomer was observed to form in both $CH_2Cl_2$ and benzene as solvents,[19] as evidenced by a single signal in the proton-decoupled $^{31}P$ NMR spectra of the crude reaction mixture with ligand **1a**. The values of the chemical shifts are close to those found in the mono- and cis disubstituted adducts, as expected, since the phosphorus atoms are comparably located trans to CO groups (Table I). The P–Mo coupling satellites confirm that coordination occurs through phosphorus ($^1J_{^{31}P-^{95,97}Mo} = 210$ Hz). The $\nu$(CO) vibrations in $CH_2Cl_2$ further establish a *fac* configuration of the adduct since they consist of two absorptions, the $A_1$ and E modes, at 1966 (s) and 1879 (vs) $cm^{-1}$, expected for $C_{3v}$ symmetry, while the *mer* configuration should give three active modes ($2 A_1 + B_1$).[17a]

Similar conclusions were reached for the isolated adduct of ligand **1b**, which consists of the most abundant of the five possible isomers expected from the various possible combinations of the two diastereoisomeric ligands on the metal.

**Characteristic Features of the Bicyclic Aminophosphanes 1 as a Ligand.** Consistent behavior of the ligand and consistent spectral characteristics of the adducts were found throughout the series of the eight $M(CO)_{6-n}(bcap)_n$ compounds we prepared. They may be summarized as follows. Both constrained aminophosphanes readily give stable zerovalent Mo and W complexes. Coordination always occurs through phosphorus. Only the cis isomers and *fac* isomers are formed when $n$ = 2 or 3, respectively. The $\nu$(CO) frequencies rank among the highest found with phosphorus ligands in such adducts.

These data are all consistent with (1) a high $\pi$-accepting capability, better, on the basis of the $\nu$(CO) infrared data, than those of $P(OCH_3)_3$, $P(OCH_2)_3CR$, or $P(CH_2CH_2CN)_3$, and (2) low steric hindrance, lower than those of these latter ligands, although the two contributions cannot be separated. Both arise from the constraints due to the bicyclic structure of the bcap ligands.

These features are further corroborated by the very short P–Fe bond length (2.105 Å) found in $(\eta^5\text{-}Cp)Fe(Ph)(CO)[\overline{P(OCH_2CH_2)_2N}]$ compared to 2.23 Å for the related $PPh_3$ adducts.[20] This shortening (0.12 Å) is significantly greater than that found in $M(CO)_5L$ (M = Cr, Mo) adducts, on progressing from $PPh_3$ to $P(CH_2CH_2CN)_3$ (0.06 Å). The latter ligand has recently been described as a good $\pi$ acceptor.[7]

**Acknowledgment.** We thank the donors of Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

**Registry No.** **2a**, 79201-51-7; **2b** ($\alpha$), 79201-52-8; **2b** ($\beta$), 79254-37-8; **3a**, 79201-53-9; **4a**, 79201-54-0; **4b** ($\alpha,\alpha$), 79215-51-3; **4b** ($\alpha,\beta$), 79201-55-1; **5b** ($\alpha,\alpha$), 79201-56-2; **6a**, 79215-50-2; **6b** ($\alpha,\alpha,\alpha$), 79215-52-4; $Mo(CO)_5(py)$, 14324-76-6; $W(CO)_5(py)$, 14586-49-3; $Mo(CO)_4(nbd)$, 12146-37-1; $W(CO)_4(nbd)$, 12129-25-8; $Mo(CO)_3(mes)$, 12089-15-5.

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# Reaction of (Chlorophosphine)iron Tetracarbonyl Complexes with Aluminum Chloride. Iron Tetracarbonyl Complexes of Two-Coordinate Phosphorus Cations

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The (chlorophosphine)iron tetracarbonyl complexes $Me_2NP(Cl)_2Fe(CO)_4$, $(Et_2N)_2P(Cl)Fe(CO)_4$, $(i\text{-}Pr_2N)_2P(Cl)Fe(CO)_4$, $[(Me_3Si)_2N]_2P(Cl)Fe(CO)_4$, and $(t\text{-}Bu)(Me_2N)P(Cl)Fe(CO)_4$ have been prepared by reaction of the corresponding phosphorus(III) chlorides with $Fe_2(CO)_9$ in hexane solution. These $Fe(CO)_4$ complexes have been characterized by elemental analysis and $^{31}P$ NMR, $^{13}C$ NMR, and IR spectroscopy. The coordinated phosphenium ions $[(Me_2N)P(Cl)Fe(CO)_4]^+$, $[(Et_2N)_2PFe(CO)_4]^+$, $[(i\text{-}Pr_2N)_2PFe(CO)_4]^+$, $[((Me_3Si)_2N)_2PFe(CO)_4]^+$, and $[(t\text{-}Bu)(Me_2N)PFe(CO)_4]^+$ have been prepared as their $AlCl_4^-$ salts by treatment of the respective precursor (chlorophosphine)iron tetracarbonyl complexes with the stoichiometric quantity of $Al_2Cl_6$ in $CH_2Cl_2$ solution. These phosphenium ion complexes have been identified by elemental analysis and $^{31}P$ NMR, $^{13}C$ NMR, and IR spectroscopy. The $\pi$-acceptor nature of phosphenium ion ligands is discussed on the basis of various spectroscopic data.

## Introduction

Recent years have witnessed an increasing concern with the chemistry of coordinatively unsaturated cations which feature main-group elements other than carbon as the central atom. At present, the best known of these species are the two-coordinate phosphorus cations of general formula $R_2P^+$ (phosphenium ions).[2] Since the six-valence-electron phosphenium

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(1) To whom correspondence should be addressed.

**Table I.** Summary of Pertinent NMR and IR Data for $(R_2PCl)Fe(CO)_4$ Complexes

| | chemical shifts, ppm$^{a,b}$ | | | IR ($\nu_{CO}$, cm$^{-1}$)$^c$ | | |
|---|---|---|---|---|---|---|
| compd | $^{31}P$ | $^{13}C$ | $J$, Hz | $A_1$ | $A_1$ | E |
| $Me_2NP(Cl)_2Fe(CO)_4$ | 192.2 | 39.69 ($NMe_2$), 211.4 (CO) | $J_{PNC} = 4.2, J_{PFeC} = 18.8$ | 2075 | 1985 | 1975, 1950 |
| $(Et_2N)_2P(Cl)Fe(CO)_4$ | 183.8 | 40.70 ($NCH_2CH_3$) 12.75 ($NCH_2CH_3$), 212.82 (CO) | $J_{PNC} = 5.1, J_{PNCC} = 3.4, J_{PFeC} = 20.5$ | 2055 | 1975 | 1955, 1940 |
| $(i\text{-}Pr_2N)_2P(Cl)Fe(CO)_4$ | 182.5 | 48.70 ($NCHMe_2$), 23.41 (NCHMe), 22.65 (NCHMe′), 212.21 (CO) | $J_{PNC} = 7.9, J_{PNCC} = 4.3, J_{PNCC'} = 3.5, J_{PFeC} = 18.9$ | | | |
| $[(Me_3Si)_2N]_2P(Cl)Fe(CO)_4$ | 268.0 | 3.88 ($Me_3Si$), 214.1 (CO) | $J_{PNSiC} = 3.1, J_{PFeC} = 17.0$ | 2060 | 2025 | 1990, 1945 |
| $(t\text{-}Bu)(Me_2N)P(Cl)Fe(CO)_4$ | 219.3 | 26.99 ($CMe_3$), 42.60 ($NMe_2$), 50.21 ($CMe_3$), 213.08 (CO) | $J_{PC} = 26.5, J_{PCC} = 5.9, J_{PFeC} = 16.2$ | 2055 | 1970 | 1945, 1935 |

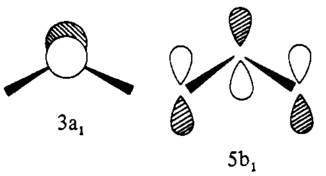
[a] See Experimental Section for statement of references used. [b] A positive value means downfield (deshielded). [c] For assignments, see text ref 4a and 16.

**Table II.** Summary of Pertinent NMR and IR Data for Phosphenium Ion Complexes, $[R_2PFe(CO)_4]^+[AlCl_4]^-$

| | chemical shifts, ppm$^{a,b}$ | | | IR ($\nu_{CO}$, cm$^{-1}$)$^c$ | | |
|---|---|---|---|---|---|---|
| cation | $^{31}P$ | $^{13}C$ | $J$, Hz | $A_1$ | $A_1$ | E |
| $[Me_2NP(Cl)Fe(CO)_4]^+$ (1) | 268.8 | | | 2125 | 2060 | 2005, 1980 |
| $[(Et_2N)_2PFe(CO)_4]^+$ (2) | 307.6 | 45.64 ($NCH_2CH_3$), 13.49 ($NCH_2CH_3$) | $J_{PNC} = 3.5, J_{PNCC} = 2.8$ | 2105 | 2030 | 1965, 1940 |
| $[(i\text{-}Pr_2N)_2PFe(CO)_4]^+$ (3) | 311.3 | 56.2 ($NCHMe_2$), 24.4 ($NCHMe_2$) | $J_{PNC} = 2.8, J_{PNCC} = 3.7$ | 2090 | 2050 | 2010, 1975 |
| $[((Me_3Si)_2N)_2PFe(CO)_4]^+$ (4)$^d$ | 349.7 | 5.30 ($Me_3Si$) | | | | |
| $[(t\text{-}Bu)(Me_2N)PFe(CO)_4]^+$ (5)$^d$ | 441.5 | 28.12 ($CMe_3$), 50.75 ($NMe_2$) | | | | |

[a] See Experimental Section for statement of references used. [b] A positive value means downfield (deshielded). [c] For assignments, see text and ref 4a and 16. [d] These compounds decompose at room temperature; hence the $^{31}P$ and $^{13}C$ NMR spectra were recorded at -20 °C.

ions possess a lone pair of electrons and a formally vacant 3p orbital at the cationic center, it is clear that these ions should be capable of coordinating to transition metals. In the case of amido-substituted phosphenium ions, molecular orbital calculations[3] on the model cation, $(H_2N)_2P^+$, suggest that $\sigma$-donor behavior stems from utilization of the second occupied MO ($3a_1$) and that $\pi$ acceptance results from interaction of occupied metal nd orbitals with the $5b_1$ LUMO.



To date, two approaches have been taken[4] to the synthesis of ligated phosphenium ions: (i) the direct interaction of an $R_2P^+$ species with a neutral metal carbonyl, and, more efficiently, (ii) reaction of a precursor phosphorus fluoride, $R_2PF$, with a metal carbonyl followed by fluoride ion abstraction. In an interesting related development,[5] the coordination of neutral $R_2P$ moieties has been achieved by treatment of phosphorus(III) fluorides with organometallic anions such as $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]^-$. Since only two authentic coordinated phosphenium ions have been reported thus far, it seemed appropriate to extend the range of these novel derivatives. This paper directs itself to that end, particular emphasis being placed on the synthesis of coordinated halophosphenium ions and on increasing the steric bulk of the phosphenium ion substituents.

## Results and Discussion

**Preparation of Precursor $R_2P(Cl)Fe(CO)_4$ Complexes.** The complexes $F_2P(Cl)Fe(CO)_4$[6] and $Cl_3PFe(CO)_4$[7] are known compounds. The compounds $Me_2NP(Cl)_2Fe(CO)_4$, $(Et_2N)_2P(Cl)Fe(CO)_4$, $(i\text{-}Pr_2N)_2P(Cl)Fe(CO)_4$, $[(Me_3Si)_2N]_2P(Cl)Fe(CO)_4$, and $(t\text{-}Bu)(Me_2N)P(Cl)Fe(CO)_4$ were prepared by the reaction of the phosphorus(III) chloride with $Fe_2(CO)_9$ in hexane solution. The identities of the new $Fe(CO)_4$ complexes were established by elemental analysis and $^{31}P$ NMR, $^{13}C$ NMR, and IR spectroscopy (Table I).

**Synthesis of Coordinated Phosphenium Ion Complexes.** Since two-coordinate $PX_2$ radicals (X = F,[8] Cl[9]) are well-characterized species, it seemed obvious to attempt the synthesis of the corresponding $PX_2^+$ cations. However, Parry and co-workers[10] found that treatment of phosphorus trihalides with halide ion acceptors results in the production of adducts such as $F_3P \rightarrow AlCl_3$ rather than $PX_2^+$ salts. Inferentially, retrobonding from the halogen substituents to the cationic center is insufficient to impart thermodynamic stabilization to the $PX_2^+$ entities. Since it is widely recognized that otherwise labile species can sometimes be stabilized by incorporation into the coordination sphere of a transition metal, we decided to attempt halide ion abstraction reactions utilizing coordinated

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(3) Cowley, A. H.; Cushner, M. C.; Szobota, J. S. *J. Am. Chem. Soc.* **1978**, *100*, 7784–7786.

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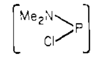
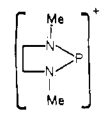
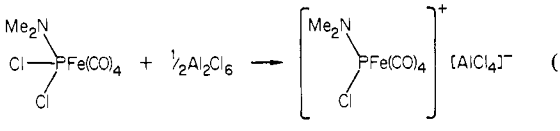
**Table III.** Comparison of $^{31}P$ NMR Data for Uncoordinated Phosphenium Ions, Coordinated Phosphenium Ions, and Precursor Chloride Complexes

| phosphenium ion | | $Fe(CO)_4$ complex | coordination chemical shift[a] | $(R_2PCl)Fe(CO)_4$ |
|---|---|---|---|---|
|  | 325[b] | 286.8 | −38.2 | 192.2 |
| $[(Me_2N)_2P]^+$ | 264 | 311[c] | +47 | 194[d] |
| $[(Et_2N)_2P]^+$ | 263 | 307.6 | +44.6 | 183.8 |
| $[(i\text{-}Pr_2N)_2P]^+$ | 313 | 311.3 | −1.7 | 182.5 |
| $[((Me_3Si)_2N)_2P]^+$ | 450.3[e] | 349.7 | −100.6 | 268.0 |
| $[(t\text{-}Bu)(Me_2N)P]^+$ | 513.2[e] | 441.5 | −71.7 | 219.3 |
|  | 264[f] | 300[c] | +36 | |
| $[(Fc)_2P]^+$[h] | 183[g] | 280[g] | +97 | 161[g] |

[a] $\delta_{complex} - \delta_{ligand}$. [b] Datum from ref 2d. [c] Data from ref 4a. [d] Datum from S. F. Sena of this laboratory. [e] Data from ref 15. [f] Datum from ref 2a. [g] Data from ref 11. [h] Fc = ferrocenyl.

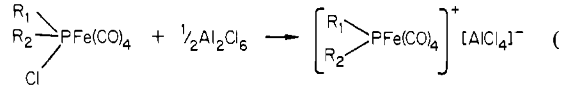
phosphorus di- and trihalides. As in the case of uncoordinated phosphenium ions,[2d] the only successful reaction of this type was that of $Me_2NP(Cl)_2Fe(CO)_4$ with $Al_2Cl_6$ in $CH_2Cl_2$ solution which proceeds according to eq 1. Compound **1** was


(1)

**1**

characterized by elemental analysis and NMR and IR spectroscopy (Table II). Other attempts to generate halophosphenium ions were unsuccessful. For example, $Me_2NP(F)_2Fe(CO)_4$ failed to react with $PF_5$, and the reaction of $Cl_3PFe(CO)_4$ or $F_2P(Cl)Fe(CO)_4$ with $Al_2Cl_6$ resulted in the production of $PCl_3$.

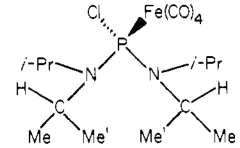
In the compounds **2–5** we were interested in the effects of


(2)

**2**, $R_1 = R_2 = Et_2N$
**3**, $R_1 = R_2 = i\text{-}Pr_2N$
**4**, $R_1 = R_2 = (Me_3Si)_2N$
**5**, $R_1 = t\text{-}Bu$, $R_2 = Me_2N$

increasing the steric bulk on the phosphenium ion stability. Compounds **2** and **3** are stable at ambient temperature and were characterized by elemental analysis, and NMR and IR spectroscopy (Table II). However, compounds **4** and **5** are not stable above −20 °C; hence their characterization is based on low-temperature $^{13}C$, $^{27}Al$, and $^{31}P$ NMR spectroscopy (Table II). The diminished thermal stability of **4** and **5** is presumably due to the steric demands of the $(Me_3Si)_2N$ and $t$-Bu substituents. The significance of $[(t\text{-}Bu)(Me_2N)PFe(CO)_4]^+$ (**5**) is that it is the first phosphenium ion complex to feature a P–C bond. Interestingly, we have subsequently been able to prepare $[(Fc)_2PFe(CO)_4]^+$ (Fc = ferrocenyl), a coordinated phosphenium ion with two P–C bonds.[11] As in the case of ferrocenyl-substituted carbocations,[12] the stabilization of this species probably originates from the delocalization of positive charge on to the ferrocenyl substitutents.

**NMR Spectra of Phosphenium Ion Complexes.** In all cases (**1–5**) the $AlCl_4^-$ gegenion was detected by the presence of a sharp singlet ($w_h \approx 6$ Hz, ~102 ppm)[13] in the $^{27}Al$ NMR spectra. Phosphenium ion formation was indicated by the $^{31}P$ downfield shifts of 76.6–222.2 ppm accompanying chloride ion abstraction from the precursor $R_1R_2P(Cl)Fe(CO)_4$ complexes (Tables I and II). Stereochemical evidence bearing on the question of phosphenium ion formation is provided by the $^{13}C$ NMR spectral changes which take place upon $Cl^-$ removal from $(i\text{-}Pr_2N)_2P(Cl)Fe(CO)_4$. In the chloro compound, an-



isochronous Me groups on each $i\text{-}Pr_2N$ moiety are detected in the $^{13}C\{^1H\}$ NMR spectrum. This situation arises because the phosphorus atom is effectively a chiral center in the sense that inversion at phosphorus is necessary to render the Me and Me′ environments equivalent.[14] As demonstrated by our X-ray crystal structure of $(i\text{-}Pr_2N)_2P^+$, the phosphorus atom adopts an approximately trigonal-planar geometry when the chloride ion is removed from $(i\text{-}Pr_2N)_2PCl$.[3] The coordination of an $Fe(CO)_4$ moiety to the phosphorus lone pair of $(i\text{-}Pr_2N)_2P^+$ will leave the phosphorus geometry trigonal planar; hence, the isopropyl methyl resonances are expected to be equivalent in the $^{13}C\{^1H\}$ NMR spectrum of **3**.

Another manifestation of $[R_2PFe(CO)_4]^+$ formation is provided by the fact that at ambient temperature the $^{13}C$ CO resonances are detectable in the precursor halide complexes but *not* in the corresponding coordinated phosphenium ions **1–5**. This interesting observation was made first by Bennett and Parry[4b] and attributed to rapid intermolecular CO exchange in (phosphenium)iron tetracarbonyl complexes. The $^{13}C$ CO resonances are observable on cooling providing the low-temperature solubility of the complex is sufficiently large. For example, $[(t\text{-}Bu)(Me_2N)PFe(CO)_4]^+$ (**5**) exhibits a doublet at 209.98 ppm ($J_{PNC} = 9.05$ Hz) below −20 °C. Since the (phosphenium)iron tetracarbonyl complexes involve pentacoordinate iron, they, like $Fe(CO)_5$, exhibit rapid intramolecular CO exchange even at very low temperatures.

It is interesting to compare the $^{31}P$ chemical shifts of the free phosphenium ion with those of the corresponding $Fe(CO)_4$

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(13) Akitt, J. W. *Annu. Rep. NMR Spectrosc.* **1972**, *5*, 465–556.

(14) Somewhat similar observations have been made previously. For example, $(Me_2As)_2PCF_3$ and $(i\text{-}Pr)_2PC_6H_5$ both exhibit anisochronous Me resonances at ambient temperature. See: (a) Cowley, A. H.; Dierdorf, D. S. *J. Am. Chem. Soc.* **1969**, *91*, 6609–6613. (b) McFarlane, W. *Chem. Commun.* **1968**, 229–230.

complexes (Table III). It is clear that the coordination chemical shifts, $\delta_{\text{complex}} - \delta_{\text{ligand}}$, can be either positive or negative. Such a pattern is difficult to rationalize by considering only the diamagnetic contribution to the $^{31}P$ chemical shift. It is possible, therefore, that paramagnetic terms assume an important role in these $Fe(CO)_4$ complexes. Finally, in this section we note that the $^{31}P$ chemical shift of **5** is >100 ppm larger than that of any other coordinated phosphenium ion. As in the case of the parent cation, $[(t\text{-Bu})(Me_2N)P]^+$, this deshielding is presumably caused by replacement of a $\pi$-donor dialkylamino group by a nonconjugating *tert*-butyl group.[15] It is also possible that the $Me_2N$ group in **5** is twisted out of the plane of maximum conjugation.

**Stereochemistry of (Chlorophosphine)- and (Phosphenium)iron Tetracarbonyl Compounds.** The phosphorus(III) chloride or phosphenium ion ligands could occupy an axial or equatorial site of a locally trigonal-bipyramidal geometry at iron. Qualitative group theoretical arguments indicate that axially substituted $LFe(CO)_4$ compounds ($C_{3v}$ symmetry) should exhibit three IR-active CO stretching frequencies (2 $A_1$ + E), while equatorially substituted compounds ($C_{2v}$ symmetry) should exhibit four such bands (2 $A_1 + B_1 + B_2$). However, structural assays based solely on IR data could be misleading because, as pointed out by Darensbourg et al.,[16] the E mode of axially substituted $LFe(CO)_4$ compounds is often split, thus yielding a total of four distinct $\nu_{CO}$ bands. Two X-ray crystal structures have been performed which have a bearing on the compounds of concern here. In both $Me\overline{NCH_2CH_2N(Me)P}(F)Fe(CO)_4$[17] and $(Me_2N)_3PFe(CO)_4$,[18] the aminophosphine ligand adopts an axial site in a trigonal-bipyramidal array at iron. Given the similarity of these compounds to the (chlorophosphine)iron tetracarbonyl complexes listed in Table I, it is reasonable to assume the persistence of the $C_{3v}$ skeletal geometry and to postulate that the observation of four $\nu_{CO}$ bands in the IR spectra is due to lifting the degeneracy of the E mode. Apart from some frequency shifts (vide infra), the IR spectra of the (chlorophosphine)iron tetracarbonyl compounds and the corresponding (phosphenium)iron tetracarbonyl complexes are very similar. On this basis, it is tempting to postulate that the phosphenium ion ligands also exhibit an axial site preference. If this is so, the $\nu_{CO}(E)$ modes are split in all cases as suggested in Table II.

**Comments on the $\pi$-Acceptor Nature of Phosphenium Ion Ligands.** Several lines of evidence suggest that phosphenium ions behave as $\pi$ acceptors toward transition metals. In a $^{57}Fe$ Mössbauer experiment on $[(Me_2N)_2PFe(CO)_4]^+[AlCl_4]^-$, we found[11] that the isomer shift and quadrupole splitting of this cation fall in the $\pi$-acceptor region of a Collins–Pettit graph.[19] The $\pi$-acceptor nature of phosphenium ion ligands has also been inferred from interesting work by Bennett and Parry[4b] in which they demonstrated that, in contrast to the fluorophosphine precursors, $[R_2PFe(CO)_4]^+$ complexes undergo facile exchange with labeled CO. A third line of evidence stems from vibrational spectroscopy. On comparing the IR CO stretching frequencies of the coordinated phosphenium ions (Table II) with those of the precursor chlorides (Table I), it is clear that the CO stretching frequencies are up to ~85 cm$^{-1}$ larger in the phosphenium ions. Such a trend is consistent with $\pi$-acceptor behavior and has been noted previously for fluoride ion abstractions.[4a] Of course, in the case of an extremely strong $\pi$-acceptor capability, the ligand would occupy an equatorial site of a trigonal-bipyramidal $Fe(CO)_4$ moiety.[20] However, in the previous section we reasoned that the $R_2P^+$ ligand occupies an axial site.

## Experimental Section

**Materials and General Procedures.** The compounds $Me_2NPCl_2$,[21] $(Et_2N)_2PCl$,[22] $(i\text{-}Pr_2N)_2PCl$,[23] $[(Me_3Si)_2N]_2PCl$,[24] $(t\text{-Bu})(Me_2N)PCl$,[25] $F_2P(Cl)Fe(CO)_4$,[6] and $Cl_3PFe(CO)_4$[7] were synthesized and purified according to literature methods, and $Fe_2(CO)_9$ was prepared by UV irradiation of $Fe(CO)_5$ in glacial acetic acid. Commercial $Al_2Cl_6$ was purified by sublimation in vacuo, and all solvents were dried and distilled prior to use.

Virtually all the materials described herein are moisture sensitive. Accordingly, it was necessary to perform all operations in vacuo or under an inert atmosphere.

Elemental analyses were carried out by Canadian Microanalytical Services, Ltd., Vancouver, B.C., Canada.

**Spectroscopic Measurements.** The $^{13}C$ (20.0-MHz) and $^{31}P$ (36.43-MHz) NMR spectra were measured in the FT mode on Varian FT 80 and Bruker WH-90 instruments, respectively. Dichloromethane (54.2 ppm relative to $Me_4Si$) was employed as the internal reference for the $^{13}C$ spectra, and 85% $H_3PO_4$ was used as the external reference for the $^{31}P$ spectra.

IR spectra were obtained in a Perkin-Elmer 337 instrument using polystyrene as an external reference.

**Preparation of $(Me_2NPCl_2)Fe(CO)_4$.** (Dimethylamino)dichlorophosphine (8.02 g, 55.0 mmol) was syringed into a flask containing $Fe_2(CO)_9$ (17.5 g, 48.0 mmol) in 60 mL of dry, degassed hexane under a nitrogen atmosphere. The solution was either allowed to react at room temperature overnight or heated to 50 °C for 3 h. The hexane and resulting $Fe(CO)_5$ were removed by evacuation, and the resulting dark brown oil was fractionally distilled on a short-path column to yield $Me_2NPCl_2Fe(CO)_4$, bp 60 °C (0.02 torr), which solidified to a red solid, mp 34 °C. The yield of product was 6.18 g (i.e., 41%). Anal. Calcd for $C_6H_6Cl_2FeNO_4P$: C, 22.96; H, 1.93; N, 4.46; Cl, 22.59. Found: C, 22.97; H, 1.97; N, 4.52; Cl, 22.32. The foregoing procedure was employed for the synthesis of the other (chlorophosphine)iron tetracarbonyl complexes used in this work.

**$(Et_2N)_2P(Cl)Fe(CO)_4$:** yellow-orange liquid, bp 118–120 °C (0.05 torr), prepared in 28% yield. Anal. Calcd for $C_{12}H_{20}ClFeN_2O_4P$: C, 38.1; H, 5.3; N, 7.4. Found: C, 38.8, H, 5.8; N, 8.0.

**$(i\text{-}Pr_2N)_2P(Cl)Fe(CO)_4$.** Upon attempted distillation of the crude compound, decomposition was noted to occur; the only identifiable phosphorus containing compound was $(i\text{-}Pr_2N)_2PCl$, which sublimed into the neck of the distillation head. However, even without distillation the brown liquid product was found to be quite pure on the basis on NMR spectroscopy (Table I).

**$[(Me_3Si)_2N]_2P(Cl)Fe(CO)_4$:** dark red liquid, bp 88–95 °C (0.03 torr), prepared in 30% yield. Anal. Calcd for $C_{16}H_{36}ClFeN_2O_4PSi_4$: C, 34.6; H, 6.5; N, 5.1. Found: C, 34.8; H, 6.3; N, 5.3.

**$(t\text{-Bu})(Me_2N)P(Cl)Fe(CO)_4$:** reddish brown liquid (which solidified slowly on standing), bp 80–85 °C (0.01 torr), prepared in 66% yield. Anal. Calcd for $C_{10}H_{15}FeNO_4P$: C, 35.80; H, 4.51; N, 4.17. Found: C, 36.19; H, 4.76; N, 4.34.

**Preparation of (Phosphenium)iron Tetracarbonyl Compounds. $[Me_2NP(Cl)Fe(CO)_4]^+[AlCl_4]^-$ (1).** In a typical reaction, 0.398 g (1.49 mmol) of freshly sublimed $Al_2Cl_6$ was added slowly to a solution of $Me_2NP(Cl)_2Fe(CO)_4$ (0.936 g, 2.98 mmol) in 8 mL of $CH_2Cl_2$ at −78 °C under a nitrogen atmosphere. The reaction mixture was allowed to warm slowly to room temperature, during which time it assumed a blood red color. Prolonged cooling of the reaction mixture

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to -20 °C produced an orange crystalline solid. Removal of the $CH_2Cl_2$ followed by drying afforded $[Me_2NP(Cl)Fe(CO)_4]^+[AlCl_4]^-$ in virtually quantitative yield (1.29 g, 2.89 mmol). Anal. Calcd for $C_6H_6AlCl_5FeNO_4P$: C, 16.11; H, 1.36; N, 3.13. Found: C, 15.77; H, 1.73; N, 3.00.

The following compounds were prepared in virtually quantitative yields by an analogous procedure.

$[(Et_2N)_2PFe(CO)_4]^+[AlCl_4]^-$ **(2)**: orange solid. Anal. Calcd for $C_{12}H_{20}AlCl_4FeN_2O_4P$: C, 28.41; H, 4.19; N, 5.45. Found: C, 28.15; H, 3.95; H, 5.47.

$[(i\text{-}Pr_2N)_2PFe(CO)_4]^+[AlCl_4]^-$ **(3)**: orange solid. Anal. Calcd for $C_{16}H_{28}AlCl_4FeN_2O_4P$: C, 33.83; H, 4.98; N, 4.93. Found: C, 33.27; H, 4.80; N, 5.10.

The compounds $[((Me_3Si)_2N)_2PFe(CO)_4]^+[AlCl_4]^-$ (**4**) and $[(t\text{-}Bu)(Me_2N)PFe(CO)_4]^+[AlCl_4]^-$ (**5**) were not stable above -20 °C; hence it was necessary to identify them by means of low-temperature NMR spectroscopy (see Table II and text).

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**Registry No.** **1**, 78939-84-1; **2**, 78939-86-3; **3**, 78939-88-5; **4**, 78939-90-9; **5**, 78939-92-1; $(Me_2NPCl_2)Fe(CO)_4$, 78939-93-2; $(Et_2N)_2P(Cl)Fe(CO)_4$, 78939-94-3; $(i\text{-}Pr_2N)_2P(Cl)Fe(CO)_4$, 78939-95-4; $[(Me_3Si)_2N]_2P(Cl)Fe(CO)_4$, 78939-96-5; $(t\text{-}Bu)(Me_2N)P(Cl)Fe(CO)_4$, 78939-97-6; $Fe_2(CO)_9$, 15321-51-4.

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Contribution from the Chemistry Departments, University of Tasmania, Hobart, Tasmania, Australia 7001,
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# Coordination Chemistry of Methylmercury(II). Complexes of Aromatic Nitrogen Donor Tripod Ligands Involving New Coordination Geometries for $MeHg^{II}$

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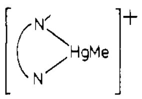
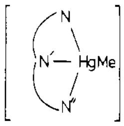
Complexes $[MeHgL]NO_3$ {L = diphenyl(2-pyridyl)methane ($pyCHPh_2$), bis(2-pyridyl)phenylmethane [$(py)_2CHPh$], and the tripod ligands tris(2-pyridyl)carbinol [$(py)_3COH$] and bis(2-pyridyl)(*N*-methyl-2-imidazolyl)carbinol [$(py)_2$(*N*-MeIm)COH]} are obtained from addition reactions in acetone. The ligand $(py)_2CHPh$ is formed on reaction of (2-benzylpyridyl)lithium with 2-bromopyridine. $^1H$ NMR spectra indicate that $(py)_2CHPh$ and $(py)_2$(*N*-MeIm)COH are present as bidentates in methanol solutions of their complexes, with the latter coordinated via the imidazolyl ring and one pyridyl ring. Spectra are consistent with the presence of weak $\pi$ interactions between mercury and phenyl rings in the $(py)CHPh_2$ and $(py)_2CHPh$ complexes and the uncoordinated pyridyl ring in the $(py)_2$(*N*-MeIm)COH complex. In complexes $[MeHgL]NO_3$ (L = $(py)_3COH$, $(py)_3CH$) the ligands are present as tridentates in methanol. Crystalline $[MeHgL]NO_3$ [L = $(py)_3COH$, $(py)_2$(*N*-MeIm)COH] have the tripod ligands coordinating as tridentates, with irregular coordination geometries based on a dominant C–Hg–N′ moiety [Hg–N′ = 2.28 (1) Å, C–Hg–N′ = 150 (1)° ($(py)_3COH$) and 2.13 (1) Å, 170 (0)° ($(py)_2$(*N*-MeIm)COH)] with weaker Hg–N,N″ bonds [2.45 (1), 2.53 (1) ($(py)_3COH$) and 2.66 (1), 2.71 (1) Å ($(py)_2$(*N*-MeIm)COH)]. For [MeHg($(py)_2$(*N*-MeIm)COH)] the coordination geometry resembles a trigonal bipyramid lacking one equatorial donor and with axial direction C–Hg–N′ [crystal data: [MeHg($(py)_3COH$)]$NO_3$ space group $P\bar{1}$, $Z = 2$, $a = 10.216$ (4) Å, $b = 12.628$ (5) Å, $c = 9.614$ (3) Å, $\alpha = 103.71$ (2)°, $\beta = 129.67$ (2)°, $\gamma = 91.86$ (3)°, $R = 0.044$ for 2107 reflections having $I \geq 3\sigma(I)$; [MeHg($(py)_2$(*N*-MeIm)COH)]$NO_3$ space group $P\bar{1}$, $Z = 2$, $a = 11.739$ (6) Å, $b = 9.689$ (2) Å, $c = 8.182$ (2) Å, $\alpha = 94.70$ (4)°, $\beta = 95.58$ (2)°, $\gamma = 97.00$ (2)°, $R = 0.042$ for 2652 reflections having $I \geq 3\sigma(I)$].

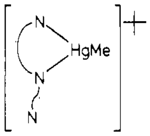
Methylmercury(II) is regarded as an essentially unifunctional cation to give coordination number 2 for mercury,[3] although three-coordination is now well established in a series of complexes $[MeHgL]NO_3$ for both the solid state and solution where L are potentially uni- or bidentate ligands, e.g., 2,2′-bipyridyls,[4,5] bis(2-pyridyl)methanes,[6,7] and bis(*N*-pyrazolyl)methane (I).[8] In addition, 2,2′:6′,2″-terpyridyls act as tridentates in the solid state (II) but as bidentates in methanol (III).[6,7] The coordination geometry for mercury in these complexes involves a dominant C–Hg–N group close to linearity [C–Hg–N = 164 (1)–179 (1)°, Hg–N = 2.16 (1)–2.26 (2) Å] with weaker bonding to additional nitrogen atoms [2.43 (3)–2.96 (2) Å], consistent with essentially sp hybridization for mercury with weaker bonding via interaction of nitrogen lone pairs with one empty 6p orbital of mercury.



I

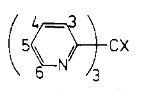


II

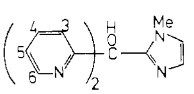


III

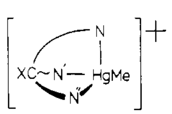
With this simplified bonding model as a guide "tripod" ligands such as IV and V may also be expected to encourage



$py_3CX(X{=}H,OH)$
IV



$py_2(NMeIm)COH$
V



VI

coordination number 4 with a novel coordination geometry involving bonding of N and N″ to *both* empty 6p orbitals of mercury (VI). Also, ligands of this type satisfy two primary requirements followed in our earlier studies: they are flexible

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