# The Extent of Association of the Bis(triphenylphosphine)iminium Cation with Organometallic Anions in Tetrahydrofuran Solution

*Sir:*

The bis(triphenylphosphine)iminium cation ($PPN^+$) has gained wide-spread usage as an important counterion in organometallic chemistry due to the stabilization it affords to reactive transition metal carbonyl anions.[1-4] For example, crystallographic investigations of several metal carbonyl anions, including $HFe(CO)_4^-$,[5] $V(CO)_6^-$,[6] and $\mu$-$H[M(CO)_5]_2^-$ (M = Cr, Mo, W),[7,8] enormously air sensitive as their alkali metal derivatives, have been possible due to formation of relatively stable $PPN^+$ salts. The special stabilization is generally ascribed to a crystal packing effect with the implication being that the enhanced stability exists predominantly in solid forms of the salts. Thermal motion of anion oxygens in $Fe(CO)_4CN^-$ and $\mu$-$I[Cr(CO)_5]_2^-$ suggests that the holes created by the $PPN^+$ are quite large and from drawings of the packing structure these holes are primarily interstices between phenyl rings into which the carbonyls are oriented.[9,10] The majority of crystal structures show a bent P-N-P linkage with angles varying from 135 to 142°; with $V(CO)_6^-$ as counterion, however, the angle is 180°.[6] Charge delocalization onto the P atoms of $PPN^+$ is indicated by ESCA measurements[11] and furthermore the shift of $^1H$ NMR resonances in $PPN^+$ to 15 Hz lower than those of $PPh_3$ suggests additional delocalization of positive charge onto the phenyl rings.[12] This report presents data illustrating the extent of association of $PPN^+$ salts of metal carbonyl anions in THF solution, as well as comparisons of $Na^+HFe(CO)_4^-$ and $PPN^+HFe(CO)_4^-$ as to solution structures and solution reactivity toward $O_2$.

The salts $PPN^+HFe(CO)_4^-$,[5] $PPN^+Co(CO)_4^-$,[1] $PPN^+V(CO)_6^-$,[6] and $Et_4N^+\mu$-$H[Cr(CO)_5]_2^-$ [7] were prepared according to the literature cited. Other salts, $PPN^+\mu$-$H[Cr(CO)_5]_2^-$ and $PPN^+BPh_4^-$, were prepared and purified in a similar manner. Purity of the salts was verified by elemental analysis (Galbraith Laboratories), IR (Perkin-Elmer 521), and the consistency of conductivity measurements with repeated recrystallizations and/or preparations. The experimental approach to the conductance/concentration measurements, instrumentation, and calculations were as described previously.[13,14] All studies were carried out at 22.0 (±0.3) °C with almost total exclusion of air and moisture. Plots of equivalent conductance, $\Lambda$ vs. $c^{1/2}$ are concave, indicating a Fuoss type IV electrolyte whose ionization equilibria might be adequately described neglecting long range interionic effects.[15] Thus linear Fuoss plots ($F/\Lambda$ vs. $c\Lambda^2/F$)[15] were obtained over a $10^{-6}$-$10^{-4}$ M concentration range utilizing approximately 30 data points per study. The dissociation constant, $K_D$, $\Lambda_0$, and the center-to-center contact distance, $a$, derived fom such data are listed in Table I and represent an average of two to four complete studies with reproducibility on the order of 2-6% except for $PPN^+HFe(CO)_4^-$. The air and light sensitivity of the hydridoiron carbonylate led to a range of $K_D$ values of $4.5 \times 10^{-4}$ to $1.5 \times 10^{-4}$. The estimate of $\sim 2 \times 10^{-4}$ is an average of the three most accurate sets of measurements. Also recorded are single ion limiting conductances which were computed using the literature value of $\lambda_0^-(BPh_4^-)$,[16] and obtaining $\lambda_0^+$ for $PPN^+$ from $\Lambda_0(PPN^+BPh_4^-) - \lambda_0^-(BPh_4^-)$, i.e., Kohlrausch's law. This class of salts is particularly amenable to comparisons of solution distance parameters, as derived from conductance measurements, and solid state distance parameters since several x-ray crystal structures have been determined. Also listed in Table I are crystallographic distances taken as the distance between $N^+$ and $M^-$, the center of the cation and the center of the carbonylate.

Rather extensive association of the $PPN^+$ salts in THF is indicated by the ion-pair dissociation constants of the metal carbonylates which vary in the order $\mu$-$H[Cr(CO)_5]_2^- > HFe(CO)_4^- > V(CO)_6^- > Co(CO)_4^-$. The charge-to-size ratio criterion for electrostatic interaction is sufficient to explain the position of each carbonylate in the series with the exception of $HFe(CO)_4^-$. The $\lambda_0^-$ values vary according to $\mu$-$H[Cr(CO)_5]_2^- < V(CO)_6^- < Co(CO)_4^-$. This is the expected order of ion mobility based on size parameters, assuming little if any solvation of the anions. (The much smaller $\lambda_0^-$ for $HFe(CO)_4^-$ may be due to a less accurate determination or to a partial solvent shell impedance to that ion's mobility.) Indeed the small Stokes radii which may be computed from the $\lambda_0^\pm$ values ($\lambda_0^\pm = 0.819/r_\pm\eta$)[17] would support the assumption of no solvation of the carbonylates at concentrations approaching infinite dilution. In addition, the conductance derived electrostatic distance parameters, $a$, are only slightly larger than the analogous x-ray crystallographic parameters (Table I). This observation may be rationalized on the basis of either a small degree of solvent intervention, i.e., a few solvent-separated ion pairs in equilibrium with the contact ion-pairs (I ⇌ II), or on the basis of some "looseness" of the contact ion pairs, III. Thus formulation III is derived from solvent interaction external to the $PPN^+$, therein partially neutralizing the effective positive charge and concurrently the extent of electrostatic interaction. Either type of ion pair, II or III, is expected to be less associated and of greater average center-to-center distance than the closest contact exhibited by I.

$$\underset{\text{I}}{(PPN^+)(MCO^-)} + S \rightleftharpoons \underset{\text{II}}{[(PPN^+)S(MCO^-)]}$$

$$\underset{\text{III}}{(MCO^-)(PPN^+ \cdot S)}$$

With accurate interpretation $\nu(CO)$ infrared spectra may serve as convenient indicators of the extent of symmetry reduction of the metal carbonylate by virtue of cation interaction. For example, cation interaction with a carbonyl oxygen serves

**Table I.** Parameters Derived from Conductance Dependence on Concentration of Bis(triphenylphosphine)iminium Salts in THF at 22.0 °C

| Salts | $10^4 K_D$ | $\Lambda_0$ | $\lambda_0^+$ | $\lambda_0^-$ | $a$, Å[a] | crystal distance (Å)[b] |
|---|---|---|---|---|---|---|
| $PPN^+BPh_4^-$ | 1.10 | 85.2 | 44.9 | 40.3[c] | 8.9 | — |
| $PPN^+Co(CO)_4^-$ | 0.94 | 120.9 | 44.9 | 76.1 | 8.7 | 7.10 |
| $PPN^+HFe(CO)_4^-$ | ~2.0[d] | ~90 | 44.9 | ~45 | ~10.0 | 7.24 |
| $PPN^+V(CO)_6^-$ | 1.16 | 112.5 | 44.9 | 67.6 | 9.0 | 8.16 |
| $PPN^+\mu$-$H[Cr(CO)_5]_2^-$ | 2.20 | 102 | 44.9 | 57.1 | 10.2 | (7.28)[e] |
| $Et_4N^+\mu$-$H[Cr(CO)_5]_2^-$ | 0.42 | 122 | 77.9 | 57.1 | 7.6 | (7.23)[e] |

[a] The electrostatic center-to-center distance is dependent on $K_D$ and the dielectric constant of solvent: $K_D = 3000/(4\pi N a^3)\exp(-e^2/aDkT)$.[17]
[b] Minimum crystallographic distances, computed and provided by Professor R. Bau, Department of Chemistry, University of Southern California.
[c] This value is from the equal split assumption of $\Lambda_0((isoamyl)_3BuN^+BPh_4^-) = 80.6 = \lambda_0^+ + \lambda_0^- = 2\lambda_0^-$.[16] [d] Data much less reproducible.
[e] These values are for the analogous tungsten derivatives.

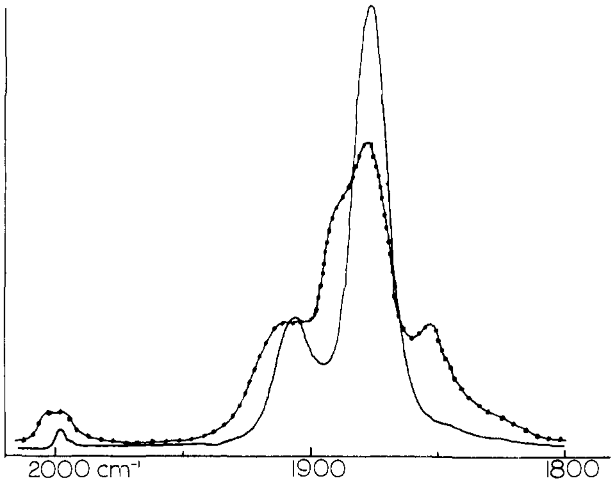
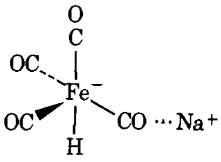


**Figure 1.** The $\nu$(CO) infrared spectrum of THF solution of $PPN^+HFe(CO)_4^-$ (—) and of a $PPN^+HFe(CO)_4$ solution to which an eightfold excess of $Na^+BPh_4^-$ has been added (-•-•-•).

to move that carbonyl group, the $M^-$—C≡O···$M'^+$, to lower frequencies and the remaining CO groups on M to higher frequencies.[13] If the cation penetrates the coordination sphere, giving rise to metal-metal bonds[18-20] or to interaction with electron density pockets such as the $Na^+$ to allylic-like C—Fe—C in $Na^+\cdot(1.5dioxane)Fe(CO)_4{}^{2-}$,[21] all CO frequencies are expected to be slightly raised with respect to the "free" anion. A symmetrical solvent or electronic environment about the anion produces a spectral pattern identical with that expected for the neutral metal carbonyl analogue. Barring some minor band width variations the spectra of all carbonylates in this study are indicative of a symmetrical field. That is, even though contact ion pairs are indicated by the conductance parameters, the charge delocalization of the cation is too great to induce any perturbation of the anion. For example, the $\nu$(CO) for $PPN^+HFe(CO)_4^-$ displays three bands at 1998 $cm^{-1}$ (w), 1905 (m), and 1876 (s), of intensity pattern expected for the distorted trigonal bipyramidal structure.[22] Upon addition of an excess of $NaBPh_4$ ($K_D$ in THF = $8.52 \times 10^{-5}$ $M^{-1}$)[16] new bands at 2003, 1910, 1890, and 1854 $cm^{-1}$ develop (Figure 1). Detailed assignments based on force constant correlations and intensity ratios will await the full report of this work; however, it is clear that the species produced is analogous to the $Na^+Ph_3PMn(CO)_4^-$ contact ion pair whose spectrum was fully analyzed previously.[13] Interaction of $Na^+$ with one of the "equatorial" carbonyl oxygens is indicated (IV).



IV

This perturbation has a dramatic effect on the reactivity of the $HFe(CO)_4^-$ toward $O_2$. The air sensitivity of cation-perturbed $HFe(CO)_4^-$, prepared by the metathesis of $PPN^+HFe(CO)_4^-$, may be quantitatively compared with that of the symmetrical $HFe(CO)_4^-$. Rigorously excluding air, THF solutions of $PPN^+HFe(CO)_4^-$ and $NaBPh_4$/$PPN^+HFe(CO)_4^-$ are stable under $N_2$ over extended periods. Upon introducing identical quantities of air, presumably saturating the solutions, a smooth decomposition of the carbonylate is observed, showing a first-order rate dependence on $HFe(CO)_4^-$. The half-lives of decomposition at 22 °C are 105 min for $PPN^+HFe(CO)_4^-$ and only 4.8 min for $NaBPh_4$/$PPN^+HFe(CO)_4^-$ (4:1 ratio, species IV clearly observable by IR).

It is possible that the asymmetric $PPN^+$ exercises a physical, covering type of protection toward its associated anion, even in solution. Preliminary results on studies of the air-sensitivity of $Et_4N^+HFe(CO)_4^-$, i.e., the counterion of $HFe(CO)_4^-$ here is a large symmetrical cation, incapable of either a "covering" effect or perturbation, lead us to suggest that the instability of $Na^+HFe(CO)_4^-$ results from cation distortion, producing steric and/or electronic sites more susceptible to reaction.

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## Metalation and Carboxylation of Activated Carbon–Hydrogen Bonds by Complexes of Iridium and Rhodium

*Sir:*

Metalation of carbon–hydrogen bonds has been of interest as a means of activating these bonds for subsequent reactions.[1] Recent activity in $CO_2$ coordination chemistry has afforded examples of adduct formation[2] and of $CO_2$ insertion reactions.[3] We report both metalation and carboxylation reactions of activated hydrocarbons (A-H) such as acetonitrile, acrylonitrile, and phenylacetylene, by the complexes $ML_4^+$, M = Rh, Ir; L = trialkylphosphine or -arsine (eq 1 and 2).

$$M(L)_4^+ + A\text{-}H \overset{K_1}{\rightleftharpoons} M(A)(H)(L)_4^+ \tag{1}$$

$$M(L)_4^+ + A\text{-}H + CO_2 \overset{K_2}{\rightleftharpoons} M(O_2CA)(H)(L)_4^+ \tag{2}$$

$\{Ir[(C_2H_5)_2PCH_2CH_2P(C_2H_5)_2]_2\}Cl$ ($[Ir(depe)_2]Cl$, **1**) was