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The Linear $[(\text{Ph}_3\text{P})_2\text{N}]^+$ Cation. Crystal Structure of $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{V}(\text{CO})_6]^-$

Sir:

The remarkable ability of the bis(triphenylphosphine)-iminium cation to stabilize air-sensitive anions has led to its extensive use as a convenient counterion in metal carbonyl chemistry^{1,2} and has also facilitated the structure determinations of a large number of anionic metal carbonyls such as $[\text{M}_2(\text{CO})_{10}]^{2-}$ ($\text{M} = \text{Mo}, \text{W}$),³ $[\text{Cr}_2(\text{CO})_{10}]^-$,⁴ $[\text{M}_2\text{Ni}_3(\text{CO})_{16}]^{2-}$ ($\text{M} = \text{Mo}, \text{W}$),⁵ $[\text{HFe}(\text{CO})_4]^-$,⁶ $[\text{Fe}(\text{C}-\text{O})_4\text{CN}]^-$,⁷ $[\text{Fe}_2(\text{CO})_8]^{2-}$,⁸ $[\text{FeCo}(\text{CO})_8]^-$,⁸ $[\text{Co}(\text{CO})_4]^-$,⁹ and $[\text{HW}_2(\text{CO})_{10}]^-$.¹⁰ In all of these compounds, the $[(\text{Ph}_3\text{P})_2\text{N}]^+$ cation was found to have a bent geometry (as does the isoelectronic carbon analog $(\text{Ph}_3\text{P})_2\text{C}^{11}$) with rather constant molecular parameters: P-N-P bond angles in the range 134.6-141.8° and P-N bond lengths in the range 1.570-1.586 Å. We wish to report in this communication the existence of the hitherto unknown and unsuspected linear form of the $[(\text{Ph}_3\text{P})_2\text{N}]^+$ cation.¹²

$[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{V}(\text{CO})_6]^-$ was prepared by treating commercially available $[\text{Na}(\text{diglyme})_2]^+[\text{V}(\text{CO})_6]^-$ with $[(\text{Ph}_3\text{P})_2\text{N}]^+ \text{Cl}^-$.^{1a} Recrystallization *via* vapor diffusion¹³ in methylene chloride-diethyl ether afforded pale yellow, light-sensitive crystals of the compound. Crystal data: space group $R\bar{3}$ (rhombohedral); $a = 9.761$ (6) Å, $\alpha = 91.93$ (3)°, $V = 928.3$ Å³, $Z = 1$, $\rho(\text{obsd}) = 1.32$ g cm⁻³, $\rho(\text{calcd}) = 1.35$ g cm⁻³. Data were collected on an automated Nonius CAD-3 diffractometer with Mo $K\alpha$ radiation up to a 2θ maximum of 45°. The structure was solved by heavy atom methods and refined to a final R factor of 7.5% for 595 independent nonzero reflections.¹⁴

The $[\text{V}(\text{CO})_6]^-$ anion (Figure 1) is situated on a site of symmetry $\bar{3}(S_6)$ and is octahedral within experimental error. The six carbonyl groups are symmetry related to each other in such a way that there is one independent V-C distance (1.931 (9) Å), one independent C-O distance (1.146 (11) Å), and two independent C-V-C angles (90.8 (4) and 89.2 (4)°). Unlike the neutral paramagnetic $\text{V}(\text{CO})_6$, which is believed to exhibit some Jahn-Teller distortion,¹⁵ the geometry of $[\text{V}(\text{CO})_6]^-$ has long been suspected to be

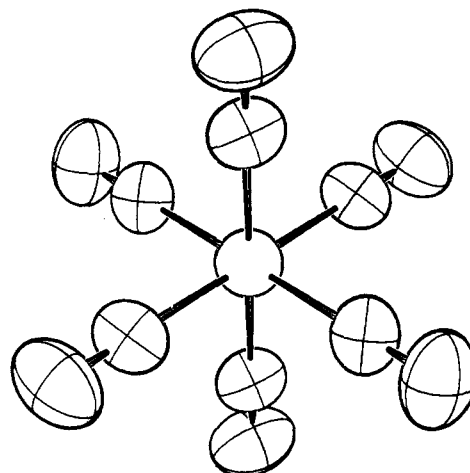


Figure 1. Geometry of $[\text{V}(\text{CO})_6]^-$, as seen down the crystallographic S_6 axis.

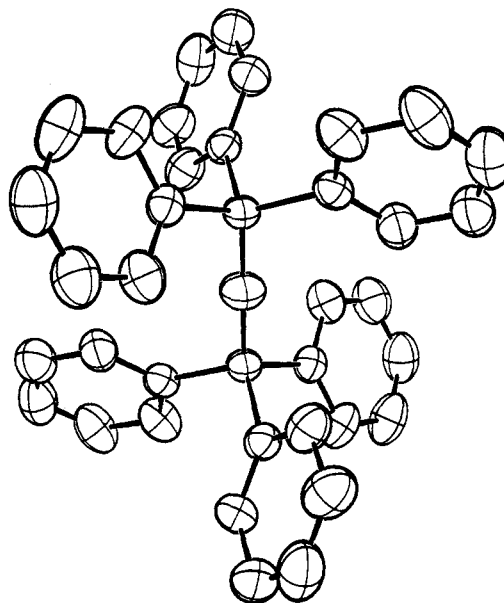
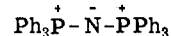


Figure 2. Geometry of the $[(\text{Ph}_3\text{P})_2\text{N}]^+$ cation in $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{V}(\text{CO})_6]^-$.

octahedral,¹⁶ but this has not been definitively proven until now. The assumption of octahedral symmetry was made in analogy to the known geometries of the isoelectronic $\text{Cr}(\text{CO})_6^{17}$ and $[\text{Mn}(\text{CO})_6]^+$.¹⁸

The $[(\text{Ph}_3\text{P})_2\text{N}]^+$ cation (Figure 2) is also situated on a site of symmetry $\bar{3}(S_6)$, with the P-N-P axis coincident with the S_6 axis. In this arrangement, the P-N-P angle is crystallographically required to be linear. Additionally, each phenyl group is symmetry related to the others, as are the two phosphorus atoms. Molecular parameters in the cation are P-N = 1.539 (2) Å, P-C = 1.788 (6) Å, N-P-C = 110.2 (2)°, and C-P-C = 108.8 (3)°.

The unanticipated linearity of the $[(\text{Ph}_3\text{P})_2\text{N}]^+$ ion in this compound¹⁹ raises some interesting questions concerning the bonding in the cation. Recent ESCA studies on $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{V}(\text{CO})_6]^-$ and other $[(\text{Ph}_3\text{P})_2\text{N}]^+$ salts²⁰ have been interpreted in favor of formalism I for the cation, implying the presence of two lone pairs on nitrogen.²¹ The bent form of the cation can be rationalized in terms of sp^2 hybridization on nitrogen, with one lone pair in an sp^2 hybrid and the other in a p orbital, the latter being free to en-



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gage in $p\pi-d\pi$ bonding with a d orbital on each phosphorus.

The linear configuration, on the other hand, is indicative of sp hybridization on nitrogen. In this case, with both lone pairs now in unhybridized p orbitals, two perpendicular sets of $P(d\pi)-N(p\pi)-P(d\pi)$ interactions are possible. The distinct shortening of the P-N bond from the bent form to the linear form (1.575 (2)²² vs. 1.539 (2) Å) could be due to enhanced $p\pi-d\pi$ bonding effects in the linear compound, although some of the contraction may also be due to the difference in covalent radius between an sp^2 nitrogen and an sp nitrogen.

The fact that salts of both linear and bent forms can be derived from a common precursor, $[(Ph_3P)_2N]^+Cl^-$, indicates that linear-bent isomerization is taking place either in solution or during crystal formation. The ease in which this conversion takes place strongly suggests that the energy difference between the linear and bent forms is not large.²³

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- (24) Fellow of the Alfred P. Sloan Foundation, 1974-1976.

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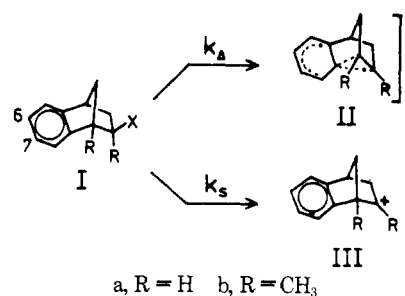
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Solvolysis of 1,2-Dimethyl-*exo*-2-benzonorbornenyl Derivatives. Direct Evidence for a Classical Carbonium Ion¹

Sir:

There seems to be general agreement that solvolytic reactions of *exo*-2-benzonorbornenyl derivatives (Ia) involve assisted ionization (k_{Δ})² to give the symmetrical bridged nonclassical ion (IIa).³ Pertinent evidence includes (a) effects of substituents in the aromatic ring on rates of solvolysis,^{2b,c,d} (b) *exo*/*endo* rate ratios,² and (c) evidently the only capturable intermediate is symmetrical.³



The situation is less clear for tertiary benzonorbornenyl systems. Electron releasing substituents at C-2 would be expected to increase k_S more than k_{Δ} and the point at which ionization changes from assisted ($k_{\Delta} > k_S$) to unassisted ($k_S > k_{\Delta}$) has been of interest for some time.⁴ On the basis of substituent effects it has been concluded that assisted ionization is involved in the 2-methyl- and 2-phenyl-*exo*-2-benzonorbornenyl systems.^{4a} In another investigation it was concluded that π participation is involved in the 6-methoxy-2-aryl-*exo*-2-benzonorbornenyl system^{4b} but not if the 6-methoxy substituent is absent.^{4c}

In earlier work⁵ we showed that solvolysis of 1,2-dimethyl-*exo*-2-norbornenyl derivatives involves the unsymmetrical classical ion and concluded that changing from the

Table I. Rate Constants for Solvolysis of Ib-Cl and Ib-OPNB^a

Compound	Temp, °C	$10^4 k_t$, min ⁻¹	$10^4 k_{\alpha}$, min ⁻¹
A. Methanol			
Ib-Cl	35.22	36.7 ± 1^b	
Ib-Cl	45.20	115 ± 3^b	$389 \pm 0.03^{c,d}$
Ib-Cl	53.48	304 ± 4	
Ib-OPNB	100.00	6.31 ± 0.01	$9.95 \pm 0.2^{a,d,e}$
Ib-OPNB	110.10	17.6 ± 0.3	$29.6 \pm 0.3^{a,d,e}$
B. 90% Acetone (v/v)			
Ib-OPNB	100.00	0.762^f	$.903 \pm 0.003^{d-f}$
Ib-OPNB	110.10	2.15^f	$2.73 \pm 0.02^{d-f}$

^a Substrate concentration 0.004 M. ^b Average of two independent experiments. ^c $[Ib-Cl] = 0.07 M$. ^d Solvent contained ~20% excess 2,6-lutidine. ^e Average of constants for rotations at four wavelengths. ^f $[Ib-OPNB] = 0.02 M$.