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Synthesis, Structure, and Bonding of the Bis(phosphenium) Ion-Dicobalt Carbonyl Complex $Co_2(CO)_5(\mu\text{-}PN(CH_3)CH_2CH_2NCH_3)_2$

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The reaction of $CH_3NCH_2CH_2N(CH_3)PF$ with $NaCo(CO)_4$ in THF at 25 °C results in the formation of the metallophosphenium ion complex $Co_2(CO)_5(\mu\text{-}PN(CH_3)CH_2CH_2NCH_3)_2$. The compound has been characterized by elemental analysis, infrared and ^1H, ^{13}C, and ^{31}P NMR spectroscopies, and single-crystal X-ray diffraction analysis. The complex crystallizes in the monoclinic space group $P2_1/c$ with $a = 15.540$ (5) Å, $b = 9.779$ (3) Å, $c = 14.015$ (5) Å, $\beta = 109.15$ (3)°, $Z = 4$, $V = 2011.9$ (6) Å^3, and $\rho = 1.62$ g cm^{-3}. Least-squares refinement gave $R_F = 4.1\%$ and $R_{wF} = 6.3\%$ for 2317 independent reflections with $I \geq 2\sigma_I$. The molecule contains a $Co(2)(CO)_2$ group and a $Co(1)(CO)_3$ group with a Co–Co separation of 2.669 (1) Å. The Co atoms are asymmetrically bridged by two phosphenium ion ligands, ($PN(CH_3)CH_2CH_2NCH_3^+$), such that both phosphorus atoms are displaced toward the $Co(2)(CO)_2$ group: Co(2)–P(1) 2.051 (1) Å, Co(2)–P(2) 2.043 (1) Å, Co(1)–P(1) 2.393 (1) Å, and Co(1)–P(2) 2.426 (2) Å. The bonding in the complex has been examined by using approximate nonparameterized molecular orbital calculations. The interactions of the Co atom orbitals in $Co(CO)_2$ and $Co(CO)_3$ fragments with four molecular orbitals localized on the phosphenium ions are important in determining the final structure.

Introduction

The reactions of metal carbonyl anions with halophosphines have been found to produce several interesting cluster compounds. For example, Hayter[1] observed reactions of Ph_2PCl with $NaCo(CO)_4$ and $NaMn(CO)_5$ that led to the formation of bimetallic complexes, $Co_2(CO)_6(\mu\text{-}PPh_2)_2$ and $Mn_2(CO)_8(\mu\text{-}PPh_2)_2$, in which the phosphido ligand, Ph_2P, symmetrically bridged the two metal centers.[2] Dahl and Ryan reported a reaction of $Co_2(CO)_8$ and $PhPCl_2$ under reducing conditions, and a tetrameric metal complex $Co_4(CO)_8(\mu\text{-}CO)_2(\mu_4\text{-}PPh)_2$ was obtained.[3] Marko and co-workers[4,5] described studies of the reactions of PCl_3 and $Co(CO)_4^-$, and subsequent structural analysis of one product, $Co_2(CO)_5(PPh_3)(\mu\text{-}P_2)$, indicated that the two cobalt atoms are bonded to a symmetrically bridging P_2 ligand.[6] In a related fashion, Seyferth and Henderson[7] recently reported the formation of phosphaacetylene compounds, $Co_2(CO)_6(\mu\text{-}PCR)$, in which the P═CR ligand was suggested to bond in a side-on fashion to the two cobalt atoms. These few examples suggest that many more novel cluster species might be obtained from other combinations of metal carbonyl anions and halophosphines. In addition, it is expected that the structures and bonding patterns in these clusters should be dependent upon the character of the phosphorus ligand substituents.

We have previously reported that metal carbonyl anions induce heterolytic cleavage of phosphorus–halogen bonds in aminohalophosphines, $(R_2N)_2PX$, with the subsequent formation of metallophosphenium ion complexes.[8-10] A structure determination for the complex $Mo(\eta^5\text{-}C_5H_5)(CO)_2(PN(CH_3)CH_2CH_2NCH_3)$ revealed an unexpectedly short Mo–P bond distance.[10] A bonding analysis indicated that the aminophosphenium ion acts both as a strong σ donor and as a strong π acceptor in a manner unique to the ligand's N–P–N structural unit. Aminophosphenium ions also may act as bridging ligands as suggested in the bimetallic complex $Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}PN(CH_3)PF_2)$,[9] although the spectroscopically derived structure has not yet been verified by X-ray diffraction methods. The similarity between the synthetic methods used in our work and in the work of Hayter, Dahl, Marko, and others has led us to examine the cluster-forming potential of metallophosphenium ion complexes. We report here the synthesis of an unusual asymmetric, bimetallic complex, $Co_2(CO)_5(\mu\text{-}PN(CH_3)CH_2CH_2NCH_3)_2$, which has structural and bonding properties distinctly unlike the symmetrical butterfly-like phosphido-bridged dicobalt complexes.

Experimental Section

General Information. Standard high-vacuum and inert-atmosphere synthetic techniques were used for the manipulations of all reagents and reaction products. Infrared spectra were recorded on a Perkin-Elmer Model 621 infrared spectrometer. The samples were prepared on KBr windows, and the spectra were calibrated with polystyrene film absorptions. The ^{13}C and ^{31}P NMR spectra were recorded on a Varian XL-100 NMR spectrometer operating at 25.2 MHz (^{13}C) and 40.5 MHz (^{31}P). The data were collected in the pulse mode with use of a Nicolet TT-100 data system. Samples were contained in sealed 5-mm tubes rigidly placed in a 12-mm tube containing a deuterated lock solvent. The ^1H NMR spectra were recorded on a Varian FT-80A NMR spectrometer operating at 80 MHz. Samples were sealed in 5-mm tubes together with a deuterated internal lock solvent. Spectral standards were $(CH_3)_4Si$(^{13}C, ^1H) and 85% H_3PO_4(^{31}P).

Materials. $FPN(CH_3)CH_2CH_2NCH_3$ was prepared by literature methods.[11] $Co_2(CO)_8$ was purchased from Strem Chemicals, and $NaCo(CO)_4$ was prepared in dry THF by reduction of the dimer with sodium amalgam.[12] Each solvent was rigorously dried and degassed over an appropriate drying agent. All solvent transfers were accomplished by vacuum distillation.

Preparation of $Co_2(CO)_5(\mu\text{-}PN(CH_3)CH_2CH_2NCH_3)_2$ (1). A mixture of 3.1 mmol of $FPN(CH_3)CH_2CH_2NCH_3$, approximately 2.9 mmol of $NaCo(CO)_4$, and 50 mL of THF was stirred at 23 °C for 12 h in a previously evacuated 150-mL Schlenk flask. The contents of the flask were then frozen at −196 °C, and the evolved CO was collected and measured with a Toepler pump system; 4.1 mmol was recovered. The reaction mixture was warmed to 23 °C and filtered

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(12) Edgell, W. F.; Lyford, J. *Inorg. Chem.* **1970**, *9*, 1932. The same product is obtained by preparation of $NaCo(CO)_4$ from $Co_2(CO)_8$ and NaOH in THF.

Table I. Experimental Data for the X-ray Diffraction Study of Crystalline $Co_2(CO)_5(\mu\text{-}PN(CH_3)CH_2CH_2NCH_3)_2$

(A) Crystal Parameters at 25 °C

crystal system: monoclinic
space group: $P2_1/c$
$a = 15.540$ (5) Å
$b = 9.779$ (3) Å
$c = 14.015$ (5) Å
$\beta = 109.15$ (3)°
$V = 2011.9$ (6) $Å^3$
$Z = 4$
mol wt = 492.2
$F(000) = 1000$
ρ(calcd) = 1.62 g/cm^3

(B) Measurement of Intensity Data

diffractometer: Syntex P3/F
radiation: Mo $K\alpha$ ($\bar{\lambda} = 0.71069$ Å)
monochromator: highly oriented graphite crystal
reflctns measd: $+h, +k, \pm l$
2θ range: 3–45°
scan type: θ–2θ
scan speed: 3.91–29.30 deg/min (in 2θ)
scan range: from $[2\theta(K\alpha_1) - 1.0]°$ to $[2\theta(K\alpha_2) + 1.0]°$
bkgd measmt: stationary crystal, stationary counter; at beginning and end of 2θ scan—each for half the time taken for 2θ scan
std reflctns: 2 measured every 48 reflections $[11\bar{7}, 212]$; no significant changes in intensity observed
reflctns collctd: 2974 total, yielding 2646 independent reflections
reflctns obsd ($I \geqslant 2\sigma_I$): 2317 (88%)
abs coeff: 19.0 cm^{-1}

under nitrogen, and the THF was vacuum evaporated. The orange solid, formed in 95% yield, coresponds to $Co_2(CO)_5(\mu\text{-}PN(CH_3)CH_2CH_2NCH_3)_2$ (**1**). The solid is air, moisture, and heat sensitive, and it is soluble in THF and benzene. The solid, when recovered by vacuum evaporation, is relatively nonvolatile and heavily solvated by THF. Recrystallization from a THF–hexane solution provides a solid product without THF solvate. Anal. Calcd for $C_{13}H_{20}N_4O_5P_2Co_2$: C, 31.7; H, 4.1; N, 11.4; O, 16.3; P, 12.6; Co, 23.9. Found: C, 31.3; H, 5.0; N, 12.0; O, 20.9; P, 13.1; Co, 17.2. Infrared spectrum (cm^{-1}) (mull; carbonyl region): 2003 m, 1979 s, 1954 s, 1937 s, 1926 s, 1918 s, and 1895 sh. Phosphorus-31 NMR (THF, 32 °C): δ 307 ($w_{1/2} \approx 550$ Hz). Carbon-13 NMR (THF, 32 °C): δ 33.06 ($^2J_{CNP} = 7.3$ Hz), 51.74 (b). Proton NMR (C_6D_6, 28 °C): δ 1.78, 2.09.

Crystal Structure Determination. Single crystals of **1** were grown from a THF/pentane solution at 0 °C. The crystal used in the structure determination (0.8 mm × 0.5 mm × 0.4 mm) was lodged in a glass capillary and sealed under dry nitrogen. The crystal was centered on a Syntex P3/F automated diffractometer, and determinations of the crystal class, the orientation matrix, and accurate unit cell parameters were performed in a standard manner.[13] The data were collected at 298 K by the $\theta/2\theta$ technique using Mo $K\alpha$ radiation, a scintillation counter, and a pulse-height analyzer. Details of the data collection are summarized in Table I. Inspection of the collected data revealed systematic absences $h = 2n + 1$ for $h0l$ and $k = 2n + 1$ for $0k0$, and the monoclinic space group $P2_1/a$ was indicated. The unit cell was transformed to the standard setting $P2_1/c$, and corrections for absorption were made on the basis of a series of ψ scans. The redundant and equivalent reflection data were averaged and converted to unscaled $|F_o|$ values following corrections for Lorentz and polarization effects.

Solution and Refinement of the Structure. All calculations were carried out on a Syntex R3/XTL structure determination system.[13] Scattering factors for Co, P, O, N, and C atoms were taken from the compilation of Cromer and Waber,[14] while those for hydrogen were taken from Stewart and co-workers.[15] Both real ($\Delta f'$) and imaginary ($\Delta f''$) components of the anomalous dispersion were included for the P and Co atoms by using the values listed by Cromer and Liberman.[16]

Table II. Positional Parameters and Their Esd's for $Co_2(CO)_5(\mu\text{-}PN(CH_3)CH_2CH_2NCH_3)_2$

atom	x/a	y/b	z/c
Co(1)	0.82794 (4)	−0.00754 (6)	0.22173 (5)
Co(2)	0.68086 (4)	0.11839 (6)	0.23764 (5)
P(1)	0.80535 (8)	0.1399 (1)	0.3477 (1)
P(2)	0.66715 (9)	−0.0195 (1)	0.1241 (1)
O(1)	0.8618 (3)	−0.2633 (4)	0.3355 (4)
O(2)	0.8433 (4)	−0.0978 (6)	0.0314 (4)
O(3)	1.0016 (3)	0.1322 (4)	0.2746 (4)
O(4)	0.6306 (4)	0.3850 (5)	0.1471 (5)
O(5)	0.5640 (4)	0.0174 (6)	0.3444 (4)
C(1)	0.8439 (4)	−0.1628 (6)	0.2920 (4)
C(2)	0.8324 (4)	−0.0597 (7)	0.1023 (5)
C(3)	0.9314 (4)	0.0827 (5)	0.2550 (4)
C(4)	0.6517 (4)	0.2809 (6)	0.1822 (5)
C(5)	0.6117 (4)	0.0551 (7)	0.3025 (5)
C(6)	0.8018 (4)	−0.0360 (7)	0.4983 (5)
C(7)	0.8780 (4)	0.3845 (5)	0.3124 (5)
C(8)	0.9093 (4)	0.1622 (7)	0.5369 (5)
C(9)	0.9400 (4)	0.2677 (6)	0.4803 (4)
C(10)	0.6220 (5)	−0.2588 (7)	0.1968 (6)
C(11)	0.6582 (5)	0.1166 (9)	−0.0479 (5)
C(12)	0.5822 (5)	−0.2220 (8)	0.0132 (7)
C(13)	0.6049 (5)	−0.1241 (9)	−0.0567 (5)
N(1)	0.8438 (3)	0.0767 (5)	0.4639 (3)
N(2)	0.8702 (3)	0.2786 (4)	0.3817 (3)
N(3)	0.6265 (3)	−0.1775 (5)	0.1135 (4)
N(4)	0.6349 (4)	0.0029 (5)	0.0016 (4)

The function minimized during the least-squares refinement[17] was $\sum w(|F_o| - |F_c|)^2$.

The solution and initial refinement of the structure were based on 2090 reflections ($I \geq 2\sigma_I$) without the absorption corrections. The structure was solved by direct methods with use of the program MULTAN.[18] Normalized structure factor amplitudes, $|E(hkl)|$, were generated from $|F_o(hkl)|$ values. The statistical distribution of $|E|$ values was consistent with that expected for a centrosymmetric crystal. Application of the tangent formula by MULTAN generated phases for 503 reflections with $|E| > 1.30$. Assignments of real (0 or 180°) phases to the starting reflections provided 16 solutions. An E map generated from one phase set yielded a chemically reasonable solution from which the coordinates of the two cobalt atoms could be ascertained. A structure factor calculation based on these atomic sites and assuming an overall temperature factor of 2.5 $Å^2$ gave $R_F = 47.8\%$. Subsequent Fourier syntheses revealed the locations of all remaining nonhydrogen atoms in the structure. Refinement of the positional and individual isotropic thermal parameters of the nonhydrogen atoms by means of a block-diagonal least-squares procedure using unit weights gave convergence at $R_F = 14.5\%$. The positions of the hydrogen atoms were then found by means of a difference Fourier synthesis and idealized to appropriate bond lengths and angles.

Subsequent refinement of the structure was based on the entire data set (2317 reflections with $I \geq 2\sigma(I)$) with corrections for absorption applied. Individual anisotropic thermal parameters were assumed for all nonhydrogen atoms. Refinement by means of a block-diagonalized least-squares procedure using counterweights, where $w = [\sigma_F^2 + (CF_o)^2]^{-1}$ with $C = 0.047$, gave convergence at $R_F = 4.3\%$. The coordinates of the 20 hydrogen atoms were recalculated in idealized positions, and a structure factor calculation for all 2317 significant structure factor amplitudes gave final values for R_F, R_{wF}, and GOF of 4.1%, 6.3%, and 1.1947, respectively. A final difference Fourier synthesis revealed no unusual features, with no peak greater than 0.49 e $Å^{-3}$. A table of observed and calculated structure factor amplitudes is available (Table S-1).[19] Heavy-atom positional parameters are collected in Table II. The hydrogen atoms positional

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(13) The hardware configuration for the P3/F diffractometer and the R3/XTL system has been described: Campana, C. F.; Sheppard, D. F.; Litchman, W. M. *Inorg. Chem.* **1981**, *20*, 4039. Programs used for centering reflections, autoindexing, refinement of cell parameters, axial photographs, full-matrix least-squares refinements, bond length and bond angle calculations, error analysis, least-squares plane calculations, direct-methods structure solutions, and calculation of hydrogen atom positions are those described in: "Syntex R3 Operations Manual"; R. A. Sparks, Ed.; Syntex Analytical Instruments: Cupertino, CA, 1978.

(14) Cromer, D. T.; Waber, J. T. *Acta Crystallogr., Sect. B* **1965**, *B18*, 104.

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(17) Discrepancy indices used in the text are defined as follows: R_F (%) = $[\sum||F_o| - |F_c||/\sum|F_o| \times 100$, R_{wF} (%) = $[\sum(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} \times 100$. The "goodness of fit" (GOF) is defined as GOF = $[\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$, where NO is the number of observations and NV is the number of variables.

(18) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368.

(19) Supplementary material.

parameters and all the thermal parameters are also available (Tables S-2 and S-3).[19]

MO Calculations. The computational method employed is an approximate Hartree–Fock–Roothaan SCF–LCAO molecular orbital calculation developed by Fenske and Hall[20] and modified by Campana and Ortega for the University of New Mexico IBM-360 computer system. The method is parameter-free and self-consistent and depends only on the atomic coordinates and choice of wave functions as input data. The calculations were iterated until the absolute value of the difference in the Mulliken population in each valence orbital was less than 0.001. The cobalt atomic functions were those of Richardson[21] for Co(I) with 4s and 4p exponents of 2.0 and 1.6, respectively. The carbon, nitrogen, oxygen, and phosphorus functions were the double-ζ functions of Clementi,[22] with all but the 3p orbitals reduced to single-ζ functions. An exponent of 1.16 was used for all hydrogen atoms.

The interatomic distances and angles used in the calculations were obtained from the structure determination. Symmetry-related molecular parameters were averaged so that the atomic coordinates conformed to an idealized C_s geometry. Previous calculations had provided an MO analysis for the free phosphenium ion ligand;[10,23] however, in this calculation the *N*-methyl substituent groups were replaced by N–H groups. The high-energy orbitals that are primarily metallic in character were not significantly affected by this substitution. The local Cartesian coordinate systems for the molecule were chosen as follows: (1) the *z* axis of each cobalt atom was oriented along the Co–Co bond, (2) the *z* axes of each carbonyl carbon atom and oxygen atom were directed toward the cobalt atom, (3) the *z* axes of the atoms in the phosphenium ion were oriented perpendicular to the ring plane, (4) the *y* axes of all atoms were chosen to be parallel to the plane containing the two cobalt atoms and the two phosphorus atoms, and (5) the *x* axes of all the atoms were determined by the right-hand rule.

Results and Discussion

The combination of $NaCo(CO)_4$ and $CH_3NCH_2CH_2N(CH_3)PF$ in a 1:1 reactant ratio in THF results in the formation of an orange, crystalline, air- and moisture-sensitive complex, $Co_2(CO)_5(\mu\text{-}PN(CH_3)CH_2CH_2NCH_3)_2$ (**1**), in good yield (95%). The synthesis of **1** is accompanied by the formation of NaF and CO, and the overall course of the reaction is summarized by the equation

$$2NaCo(CO)_4 + 2CH_3NCH_2CH_2N(CH_3)PF \xrightarrow[25\ °C]{THF} Co_2(CO)_5(\mu\text{-}PN(CH_3)CH_2CH_2NCH_3)_2 + 2NaF + 3CO$$

Ninety-five percent of the evolved CO predicted by this equation is recovered. No obvious intermediate species were formed in the reaction.

Preliminary structural characterization of **1** was accomplished from infrared and NMR spectroscopic data. The infrared spectrum recorded from a Nujol mull revealed six distinct bands in the region 2010–1890 cm^{-1}, which must correspond to terminal cobalt–carbonyl stretching fequencies. Although vibrational mode assignments have not been accomplished, qualitative comparisons of the carbonyl band positions for **1** (2003, 1979, 1954, 1937, 1926, and 1918 cm^{-1}) with the carbonyl region in other dicobalt carbonyl complexes ($Co_2(CO)_6(PR_3)_2$, $Co_2(CO)_5(P_2)PR_3$,[24] and $Co_2(CO)_5(RC{\equiv}CR)PR_3$[25]) indicate that the frequencies for **1** are uniformly shifted to lower frequency. The absence of carbonyl frequencies in the range 1850–1700 cm^{-1} suggests that there are no bridging carbonyl ligands in **1**. A hypothetical fragment $Co_2(CO)_5^{2-}$ having C_s symmetry would be expected to have five infrared-active bands in the carbonyl stretching region. Therefore, the appearance of six bands in the carbonyl stretching region for **1** does not immediately indicate the structure eventually deduced by X-ray diffraction methods.[25]

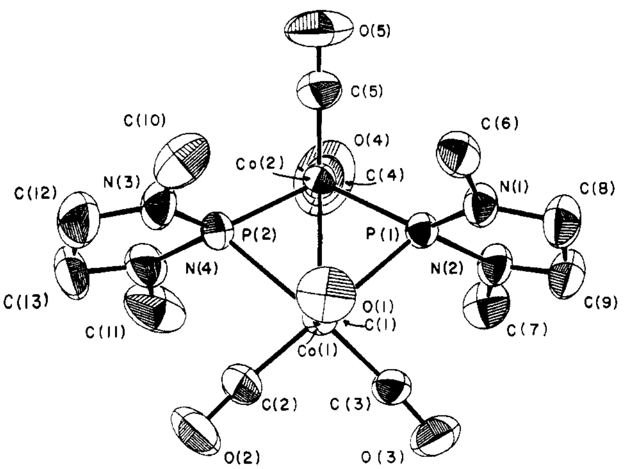

Figure 1. Molecular geometry and labeling scheme in $Co_2(CO)_5(\mu\text{-}PN(CH_3)CH_2CH_2NCH_3)_2$ (50% probability ellipsoids).

Table III. Bond Distances (Å) and Their Esd's for $Co_2(CO)_5(\mu\text{-}PN(CH_3)CH_2CH_2NCH_3)_2$

Co(1)–P(1)	2.393 (1)	Co(2)–P(1)	2.051 (1)
Co(1)–P(2)	2.426 (2)	Co(2)–P(2)	2.043 (1)
Co(1)–C(1)	1.783 (6)	Co(2)–C(4)	1.762 (6)
Co(1)–C(2)	1.773 (7)	Co(2)–C(5)	1.733 (7)
Co(1)–C(3)	1.758 (6)	C(4)–O(4)	1.131 (8)
C(1)–O(1)	1.141 (7)	C(5)–O(5)	1.147 (9)
C(2)–O(2)	1.125 (8)	Co(1)–Co(2)	2.669 (1)
C(3)–O(3)	1.141 (7)	P(2)–N(3)	1.658 (5)
P(1)–N(1)	1.659 (4)	P(2)–N(4)	1.637 (5)
P(1)–N(2)	1.664 (4)	N(3)–C(10)	1.433 (9)
N(1)–C(6)	1.443 (8)	N(4)–C(11)	1.419 (10)
N(2)–C(7)	1.452 (7)	N(3)–C(12)	1.415 (10)
N(1)–C(8)	1.448 (8)	N(4)–C(13)	1.476 (10)
N(2)–C(9)	1.455 (7)	C(12)–C(13)	1.493 (12)
C(8)–C(9)	1.473 (9)		

The ^1H NMR spectrum for **1** shows two apparent triplets centered at δ 1.78 (line spacing 6.6 Hz) and δ 2.09 (line spacing 4.0 Hz), which can be assigned to the methyl and methylene hydrogen atoms in the phosphenium ion ring. The triplets resemble those found in $[CpFe(\mu\text{-}P(CH_3)_2)CO]_2$, which displays a "deceptively simple" A_2X_2 pattern with an estimated lower limit for $J_{PP} > 13$–32 Hz.[26] By use of the same coupling conditions,[26,27] an estimated lower limit for J_{PP} in **1** can be derived, 8–22 Hz. The $^{13}C\{^1H\}$ NMR spectrum shows a doublet at δ 33.06 ($^2J_{CNP} = 7.3$ Hz) and a broad singlet at δ 51.74, which are correspondingly assigned to the methyl and methylene carbon atoms of the phosphenium ion. The $^{31}P\{^1H\}$ NMR spectrum shows a single broad resonance centered at δ 307. The absence of P–F coupling clearly indicates that the fluorine atom has been removed from the original neutral phosphine ligand, and the large downfield shift is consistent with the formation of a compound containing a phosphenium ion ligand.[28] Further unambiguous structural

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[20] Hall, M. B.; Fenske, R. F., *Inorg. Chem.* **1972**, *11*, 768. Fenske, R. F. *Pure Appl. Chem.* **1971**, *27*, 61.

[21] Richardson, J. W.; Nieuwpoort, W. C.; Powell, R. R.; Edgell, W. F. *J. Chem. Phys.* **1962**, *36*, 1057.

[22] Clementi, E. *J. Chem. Phys.* **1964**, *40*, 1944.

[23] Hutchins, L. D.; Light, R. W., Paine, R. T.; Campana, C. F., to be submitted for publication.

[24] Varadi, G.; Vizi-Orosz, A.; Vastag, S.; Palyi, G. *J. Organomet. Chem.* **1976**, *108*, 225.

[25] One infrared band in **1** probably belongs to an impurity.

[26] Hayter, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3120.

[27] The application of the coupling condition $J_{PP} > {}^1/_2 J_{HP}{}^2$ for an A_2X_2 system to **1** is not strictly correct since **1** only approximates the A_2X_2 formulation.

[28] Previous investigations have established a correlation of phosphorus chemical shifts and phosphorus coordination numbers in closely related compounds.[8–10,29,30]

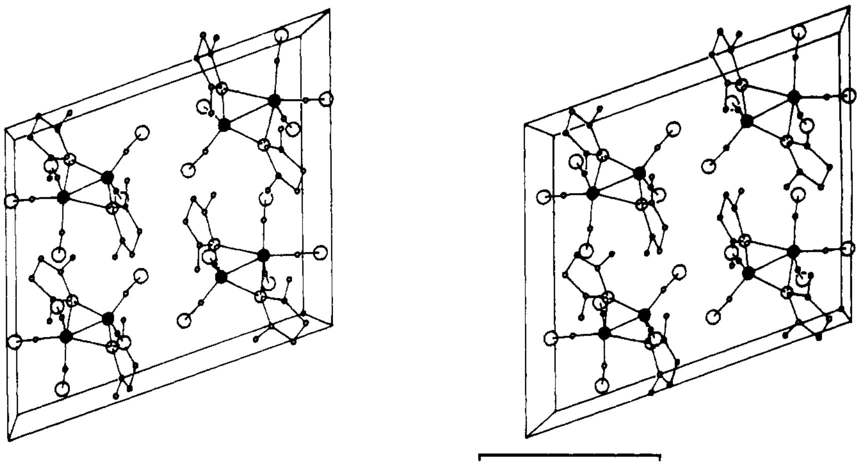

Figure 2. Stereoview of the molecular packing diagram for $Co_2(CO)_5(\mu\text{-}\overline{PN(CH_3)CH_2CH_2N}CH_3)_2$.

Table IV. Selected Bond Angles (Deg) and Their Esd's for $Co_2(CO)_5(\mu\text{-}\overline{PN(CH_3)CH_2CH_2N}CH_3)_2$

Co(1)-P(1)-Co(2)	73.36 (5)	C(1)-Co(1)-Co(2)	108.3 (2)
Co(1)-P(2)-Co(2)	72.78 (5)	C(2)-Co(1)-Co(2)	120.8 (2)
P(1)-Co(1)-P(2)	94.13 (5)	C(3)-Co(1)-Co(2)	118.7 (2)
P(1)-Co(2)-P(2)	119.02 (6)	C(4)-Co(2)-Co(1)	118.9 (2)
O(1)-C(1)-Co(1)	173.5 (5)	C(5)-Co(2)-Co(1)	125.0 (2)
O(2)-C(2)-Co(1)	173.4 (6)	C(1)-Co(1)-C(2)	103.6 (3)
O(3)-C(3)-Co(1)	174.5 (5)	C(2)-Co(1)-C(3)	94.6 (3)
O(4)-C(4)-Co(2)	178.1 (6)	C(3)-Co(1)-C(1)	109.4 (3)
O(5)-C(5)-Co(2)	177.5 (6)	C(4)-Co(2)-C(5)	116.1 (3)
C(2)-Co(1)-P(2)	78.8 (2)	C(5)-Co(2)-P(2)	104.4 (2)
C(1)-Co(1)-P(2)	101.6 (2)	C(4)-Co(2)-P(2)	107.8 (2)
Co(1)-P(1)-N(1)	114.0 (2)	Co(1)-P(2)-N(3)	112.8 (2)
Co(1)-P(1)-N(2)	118.7 (2)	Co(1)-P(2)-N(4)	119.3 (2)
Co(2)-P(1)-N(1)	130.3 (2)	Co(2)-P(2)-N(3)	128.6 (2)
Co(2)-P(1)-N(2)	129.2 (2)	Co(2)-P(2)-N(4)	130.3 (2)
N(1)-P(1)-N(2)	91.9 (2)	N(3)-P(2)-N(4)	93.1 (3)
P(1)-N(1)-C(6)	123.7 (4)	P(2)-N(3)-C(10)	124.3 (4)
P(1)-N(2)-C(6)	124.5 (4)	P(2)-N(4)-C(11)	125.3 (5)
P(1)-N(1)-C(8)	115.0 (4)	P(2)-N(3)-C(12)	115.0 (5)
P(1)-N(2)-C(9)	113.9 (4)	P(2)-N(4)-C(13)	113.7 (5)
N(1)-C(8)-C(9)	107.5 (5)	N(3)-C(12)-C(13)	108.2 (6)
N(2)-C(9)-C(8)	106.9 (5)	N(4)-C(13)-C(12)	106.0 (6)
C(8)-N(1)-C(6)	119.7 (5)	C(12)-N(3)-C(10)	120.0 (6)
C(9)-N(2)-C(7)	119.3 (5)	C(13)-N(4)-C(11)	118.2 (6)

conclusions could not be obtained from these data; consequently, a single-crystal X-ray diffraction analysis for **1** was initiated.

The X-ray diffraction analysis confirmed the proposed composition of **1**. A view of the molecular unit is shown in Figure 1, and a view of the unit cell contents is shown in Figure 2. Selected interatomic bond distances and angles are summarized in Tables III and IV. A set of least-squares planes and interplanar angles are available.[19] The unit cell contains discrete dicobalt molecular units with four molecules per cell. The shortest heavy-atom intermolecular separations of 3.16 Å correspond to carbonyl O···O distances, and these large separations indicate that the molecular structure is not significantly influenced by intermolecular interactions.

The monomeric molecular unit displays C_s-*m* symmetry with a $Co(CO)_3$ fragment and a $Co(CO)_2$ fragment asymmetrically bridged by the phosphorus atoms of the two cyclic phosphenium ions. Unlike the butterfly-shaped Co_2P_2 rings in phosphido–cobalt carbonyl complexes,[1,2,4,5] the central Co_2P_2 ring in **1** is planar with the largest atomic deviation being 0.07 Å.[19] The coordination geometries for the Co(1) and Co(2) atoms are a distorted trigonal bipyramid and a distorted tetrahedron, respectively. The terminal Co(1)–CO bond distances, 1.783 (6)–1.758 (6) Å, and the Co(2)–CO bond distances, 1.762 (6) and 1.733 (7) Å, are similar to those found in a number of cobalt carbonyl complexes.[31] Likewise, the carbonyl C–O bond distances of 1.125 (8)–1.147 (9) Å fall within the range found in other metal carbonyl compounds.[31] The Co(1)–Co(2) separation, 2.669 (1) Å, is within a range of Co–Co single-bond distances found in cobalt carbonyl dimer and cluster compounds devoid of bridging carbonyl ligands.[2,3,32,33]

The nonhydrogen atoms of the individual bridging phosphenium ion ligands are planar,[19] and these ring planes are nearly perpendicular to the planes formed by Co(1), Co(2), C(1), C(4), and C(5) (82.01 and 96.46°) and Co(1), Co(2), P(1), and P(2) (86.84 and 86.75°). The small distortions indicate that both phosphenium ion ring planes are tilted slightly toward the Co(1) atom. The cobalt–phosphorus bond distances (Co(1)–P(1) 2.393 (1) Å, Co(1)–P(2) 2.426 (2) Å, Co(2)–P(1) 2.051 (1) Å, and Co(2)–P(2) 2.043 (1) Å) are uniquely and unexpectedly asymmetric. The following Co–P distances were reported for a series of cobalt–phosphido complexes: $Co_2(CO)_6(\mu\text{-}PR_2)_2$, 2.191–2.171;[2,32] $Co_4(CO)_8(\mu\text{-}CO)_2(\mu\text{-}PR)_2$, 2.244 Å.[3] The short distances in **1** suggest a strong multiple-bond character in the Co(2)–P atom overlaps. The Co–P distances associated with the Co(1) atom, on the other hand, are longer than the majority of previously reported Co–P distances[31] in phosphine-substituted organocobalt compounds. Weak phosphorus atom interactions with the $Co(CO)_3$ moiety are indicated. The gross asymmetry of the Co_2P_2 ring is also mirrored by the internal ring angles; the two Co–P–Co angles are similar, 73.36 (5) and 72.78 (5)°, while the two P–Co–P angles are quite dissimilar, 94.13 (5) and 119.02 (6)°.

The bond distances and angles found in the bridging, planar phosphenium ion ligands of **1** are similar to those found in $MoCp(CO)_2(\overline{PN(CH_3)CH_2CH_2N}CH_3)$.[10] Three of the four phosphorus–nitrogen bond distances, 1.658–1.664 Å, in **1** are slightly longer than the average P–N bond distance, 1.645 Å, found in the terminal phosphenium ion of the molybdenum complex. The P(2)–N(4) distance, 1.637 (5) Å, is slightly more than 3σ shorter than the average of the other three P–N bonds, and a simple rationale for this observation is not apparent at this time. In every case, however, the P–N bond

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Table V. Percent Character and Eigenvalues of the Pertinent Molecular Orbitals and Mulliken Gross Atomic Charges for the Free Ligands

ligand	symm	orbital	eigenvalue	% orbital character	Mulliken gross atomic charges
CO	$C_{\infty v}$	5σ	−13.82	s(C), 34.5; p_z(C), 47.7; s(O), 1.0; p_z(O), 16.7	$C^{0.09-}$ $O^{0.09+}$
		2π	−0.11	p(C), 67.0; p(O), 33.0	
phosphenium ions	C_{2v}	$2b_1$	−22.84	p_z(P), 37.6; p_z(N), 2 × 27.3; p_z(C), 2 × 1.0	$P^{0.67+}$ $N^{0.15-}$
		$6a_1$	−19.65	s(P), 23.5; p_y(P), 61.8; S(N), 2 × 0.6; p(N), 2 × 4.4; s(C), 2 × 0.1; p(C), 2 × 2.0	$C^{0.10+}$ $N{-}H^{0.15+}$ $C{-}H^{0.03+}$
		$2a_2$	−18.56	p_z(P), 0.0; p_z(N), 2 × 43.1; p_z(C), 2 × 1.4	
		$3b_1$	−9.83	p_z(P), 61.7; p_z(N), 2 × 18.4	

Table VI. Percent Character and Energy of Some Pertinent Molecular Orbitals

		orbital (% character)		
orbital	energy	Co(1)	Co(2)	bridging ligand[a]
1a′	−16.10	p_z (3.6)	$d_{x^2-y^2}$ (13.3), p_z (19.2)	$6a_1$ (19.1)
1a″	−15.92	d_{yz} (1.0)	d_{yz} (7.5), p_y (19.2)	$2b_1$ (10.6), $6a_1$ (21.3)
2a′	−15.29	p_z (3.2)	$d_{x^2-y^2}$ (1.9)	$2b_1$ (38.9)
2a″	−14.98	d_{xy} (2.3), d_{yz} (9.6)	d_{yz} (2.3), p_y (2.6)	$2b_1$ (29.8), $6a_1$ (5.6), $3b_1$ (1.7)
3a″, 4a″	−12.40			$2a_2$ (96.8)[b]
3a′	−9.97	d_{z^2} (6.9), $d_{x^2-y^2}$ (14.3), d_{xy} (4.7), s (1.0), p_z (10.4)	d_{z^2}(7.3), $d_{x^2-y^2}$ (8.9)	$2b_1$ (1.5), $3b_1$ (12.1)
5a″	−9.73	d_{yz} (44.6), p_y (4.8)	p_y (7.7)	$3b_1$ (15.3)
5a′	−8.90	d_{z^2} (26.8), $d_{x^2-y^2}$ (13.9), d_{xz} (9.0), s (1.7), p_z (2.3)	d_{z^2} (27.6), $d_{x^2-y^2}$ (7.0)	$3b_1$ (3.0)
8a′	−7.32	d_{xz} (2.6)	d_{xz} (69.5), p_x (14.7)	
9a′	−4.35	d_{z^2} (17.1), s (2.6), p_z (5.9)	d_{z^2} (26.4), $d_{x^2-y^2}$ (9.9), s (1.0), p_z (11.0)	$3b_1$ (3.3)

[a] The tabulated percent orbital characters are for one ligand. The full contribution in the complex for two phosphenium ion ligands is twice the values in parentheses. [b] This percent orbital character represents the contribution to the 3a″ MO from one ligand. An identical contribution to the 4a″ MO from the second ligand also occurs.

distances in **1** are shorter than the commonly accepted P–N single-bond distance, 1.78 (3) Å,[34] and a degree of P–N multiple bonding is indicated. Lastly, the planarity of the phosphenium ion ring and the bond angles about the phosphorus and nitrogen atoms are consistent with formal sp^2 hybridization for these atoms. Taken together, the short Co–P and P–N bonds are consistent with a strong delocalization of electron density through the cobalt carbonyl–PN_2 framework.

The gross asymmetry in the Co_2P_2 ring of **1** appears to be a unique structural feature that has not been previously observed in bimetallic phosphorus-ligand complexes. However, a related yet rare geometrical distortion has been observed in several bimetallic organometal compounds containing so-called semibridging carbonyl ligands.[35] For example, Cotton and co-workers[36] have reported the crystal structure for $Cp_2V_2(CO)_5$, and the molecule is found to contain CpV(CO) and $CpV(CO)_2$ units asymmetrically bridged by two carbonyl ligands. Both bridging carbonyl ligands are displaced toward the CpV(CO) unit, V(1)–CO 1.94 (1) and 1.93 (1) Å, and away from the $CpV(CO)_2$ unit, V(2)–CO 2.40 (1) and 2.44 (1) Å. For qualitative electron-counting purposes (EAN) the molecule can be considered to contain a $CpV(CO)_3$ unit (16 electrons) and a $CpV(CO)_2$ unit (14 electrons).[35] The donation of two electrons from the $CpV(CO)_3$ fragment to the $CpV(CO)_2$ fragment through a metal–metal bond creates two 16-electron fragments but an unfavorably polar V–V bond. In response to this electronic condition it has been proposed that two carbonyls on the $CpV(CO)_3$ fragment become semibridging ligands.[35,36] Electron density from the $CpV(CO)_2$ fragment is subsequently back-donated into a π^* orbital on each of the bridging carbonyl ligands, thereby offsetting the unfavorable charge distribution in the formal unbridged representation $Cp(CO)_2V^-{-}V^+(CO)_3Cp$.

Similar formal electron-counting representations for **1** can be derived. For example, the compound can be considered to contain a $[(\text{phosphenium ion})_2Co(CO)_2{}^+]$ fragment with 18 electrons and a $[Co(CO)_3{}^-]$ fragment with 16 electrons.[37] The $Co(CO)_3{}^-$ fragment can achieve an 18-electron configuration by electron pair donation from the $[(\text{phosphenium ion})_2Co(CO)_2{}^+]$ fragment; however, an unfavorable highly polar Co–Co bond is produced. To offset the bond polarity, the two phosphenium ions take up grossly unsymmetrical semibridging ligand positions, and electron density may be formally donated from the $Co(CO)_3{}^-$ fragment to a π^* orbital on the bridging phosphenium ions.

In an effort to better understand the details of the bonding between the cobalt atoms and the bridging phosphenium ions, an approximate nonparameterized MO calculation was undertaken. So that the number of orbitals in **1** could be accommodated with the existing computational package, a substitution for the *N*-methyl groups by hydrogen on the phosphenium ion ligands was made. A careful comparison of orbital characters and eigenvalues for $(PN(H)CH_2CH_2NH^+)$ and $(PN(CH_3)CH_2CH_2NCH_3{}^+)$[38] indicated that this substitution has no significant effect upon the basic results described here. The results of the calculations are

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[37] Each cobalt(−1) atom provides ten electrons and each $CH_3NCH_2CH_2N(CH_3)P^+$ cation provides two electrons in the formal counting scheme.

[38] The calculation of the orbital characters and eigenvalues for the methyl derivative was first reported in ref 10. Full details of this work will be forthcoming.

Table VII. Mulliken Orbital Populations and Gross Atomic Charges

	d_{z^2}	$d_{x^2-y^2}$	d_{xy}	d_{xz}	d_{yz}	total 3d	s	p_x	p_y	p_z	total 4p	charge
Co(1)	1.53	1.53	1.56	1.78	1.47	7.87	0.42	0.74	0.54	0.47	1.75	0.45−
Co(2)	1.35	1.38	1.76	1.70	1.71	7.90	0.51	0.76	0.73	0.56	2.05	1.46−

	5σ	$2\pi_x$	$2\pi_y$	charge		$2b_1$	$6a_1$	$2a_2$	$3b_1$	charge
C(1)–O(1)[b]	1.34	0.28	0.25	$C^{0.31+}$, $O^{0.17-}$	phosphenium ion[a]	1.91	1.30	2.00	0.76	$P^{1.28+}$, $N^{0.45-}$, $C^{0.14+}$, $N\text{-}H^{0.15+}$, $C\text{-}H^{0.00}$
C(2)–O(2)[b]	1.31	0.31	0.29	$C^{0.31+}$, $O^{0.19-}$						
C(4)–O(4)[b]	1.31	0.31	0.28	$C^{0.37+}$, $O^{0.23-}$						

[a] The tabulated populations and charges are for one of the two symmetry equivalent ligands. [b] The tabulated populations and charges are for the three inequivalent sets of carbonyl ligands.

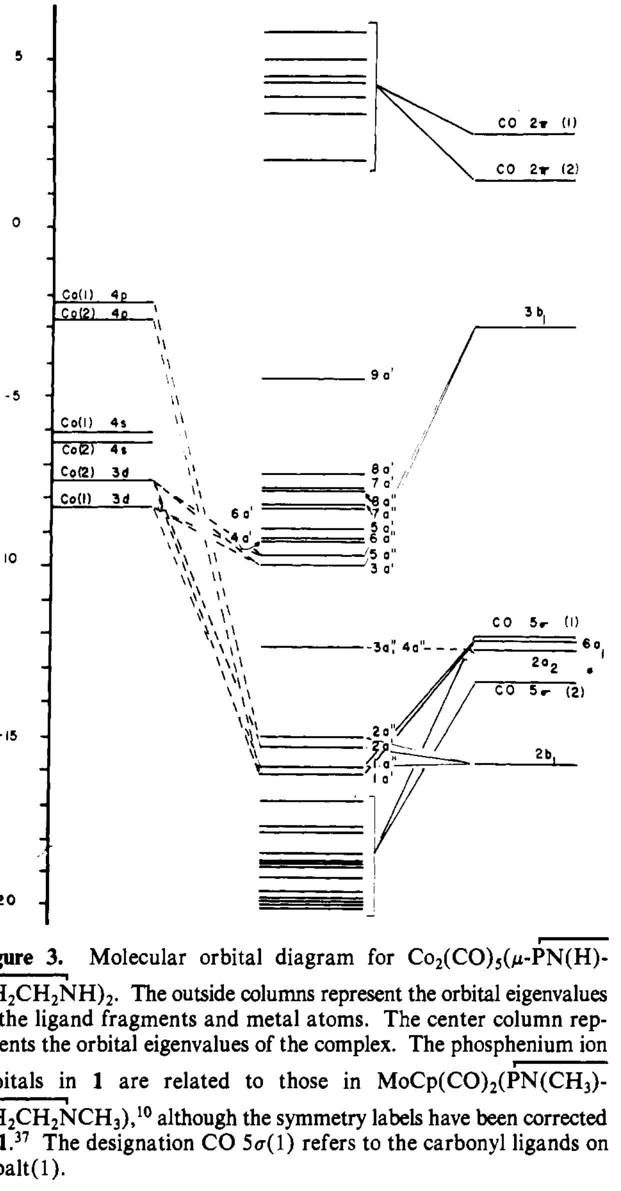

Figure 3. Molecular orbital diagram for $Co_2(CO)_5(\mu\text{-}\overline{PN(H)CH_2CH_2N}H)_2$. The outside columns represent the orbital eigenvalues of the ligand fragments and metal atoms. The center column represents the orbital eigenvalues of the complex. The phosphenium ion orbitals in **1** are related to those in $MoCp(CO)_2(\overline{PN(CH_3)CH_2CH_2N}CH_3)$,[10] although the symmetry labels have been corrected in **1**.[37] The designation CO $5\sigma(1)$ refers to the carbonyl ligands on cobalt(1).

summarized in the MO energy level diagram (Figure 3). The percent characters, eigenvalues, and Mulliken gross atomic charges for CO and $(\overline{PN(H)CH_2CH_2N}H^+)$ are presented in Table V. The percent character and energies for some pertinent molecular orbitals and the Mulliken gross atomic charges for the complex are given in Tables VI and VII.

Four phosphenium ion MO's have a significant role in determining the nature of the Co–phosphenium ion interaction, and pictorial representations of these MO's are shown in Figure 4. At the lowest energy, the $2b_1$ ligand MO is an out-of-plane three-center bonding orbital delocalized over the N–P–N unit. The $6a_1$ MO is an in-plane sp^2-type orbital that is predominantly phosphorus lone pair in character. The $2a_2$ MO is the out-of-plane ligand HOMO that is localized on the nitrogen atoms and is nonbonding with respect to the ligand. The $3b_1$ orbital is the out-of-plane three-center antibonding LUMO that is delocalized over the N–P–N fragment. The free phosphenium ion charge is set at 1.0+, and the resulting phosphorus atomic charge is 0.67+. As has been shown in many other MO calculations on metal carbonyls, the cobalt–carbonyl interactions involve the CO 5σ and 2π MO's.[39]

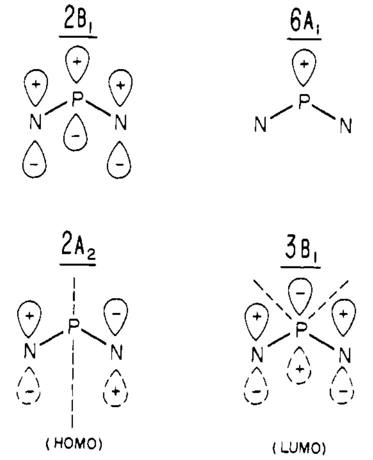

Figure 4. Orbital topology representations for the phosphenium ion ligand $(\overline{PN(H)CH_2CH_2N}H^+)$.

In **1**, the first MO's important to our discussion are labeled 1a′ and 1a″. The dominant contribution to 1a′ involves overlap of the $6a_1$ lone pair MO of each phosphenium ion with the unoccupied Co(2) $4p_z$ orbital. In addition, the $6a_1$ MO's overlap to a less efficient degree with the Co(2) $d_{x^2-y^2}$ orbital and the Co(1) $4p_z$ orbital. The contributions to the 1a″ MO in **1** involve overlap of the $6a_1$ lone pair MO's with the d_{yz} orbitals on both Co(1) and Co(2) atoms, and overlap of the $2b_1$ three-center bonding ligand MO with the unoccupied $4p_y$ orbital on Co(2). The next four MO's, 2a′, and 2a″, 3a″, and 4a″, are predominantly ligand in character and essentially nonbonding with respect to the complex. The 2a′ and 2a″ MO's contain the ligand bonding MO $2b_1$, and this orbital is weakly destabilized in the complex. The 3a″ and 4a″ MO's contain the ligand nonbonding MO $2a_2$.

The next two MO's in **1**, 3a′ and 5a″, contribute significantly to the Co–P bonding. In 3a′, the primary interaction

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(39) Teo, B. K.; Hall, M. B.; Fenske, R. F.; Dahl, L. F. *Inorg. Chem.* **1975**, *14*, 3103 and references therein. There appears to be nothing unusual involved in the Co–CO bonds in **1**, and these overlaps have not been discussed in the text.

(40) The symmetry labels for the phosphenium ion $[\overline{PN(CH_3)CH_2CH_2N}CH_3^+]$ were originally assigned[10] as $3b_2$, $3a_2$, $8a_1$, and $4b_2$. With use of the standard coordinate system on the free ligand,[23] the symmetry labels should be $3b_1$, $3a_2$, $8a_1$, and $4b_1$. These MO's correspond to $2b_1$, $2a_2$, $6a_1$, and $3b_1$ in $[\overline{PN(H)CH_2CH_2N}H^+]$.

involves back-donation of electron density from Co(1) $d_{x^2-y^2}$ and Co(2) $d_{x^2-y^2}$ orbitals into the phosphenium ion antibonding three-center MO $3b_1$. For the 5a″ MO, there is a symmetry-allowed overlap between the Co(1) and Co(2) $4p_y$ orbitals and the phosphenium ion $3b_1$ orbital. However, this overlap must provide a weak interaction since it involves the combination of formally empty metal orbitals with the empty ligand LUMO. A strong back-bonding component in the complex is derived, however, from the combination of the occupied Co(1) d_{yz} orbital and the ligand antibonding $3b_1$ orbitals. The Co(2) d_{yz} orbital, on the other hand, is antibonding with respect to the $3b_1$ ligand orbital, and no contribution to the back-bonding can be realized from this combination.

It can be concluded from the MO calculation that the major σ-bond framework in the Co_2P_2 fragment of **1** is provided by the orbital overlaps comprising the 1a′ and 1a″ MO's. The 3a′ and 5a″ MO's represent the dominant π-back-donation interactions. This picture is in accord with the simple electron-counting picture presented earlier. In addition, the assignment of the phosphenium ions as grossly unsymmetrical or semibridging ligands is consistent with the percent orbital characters, which suggest that the Co(2) fragment is more strongly involved in the acceptance of σ electron density from the phosphenium ion $6a_1$ orbitals (lone pair) while the Co(1) fragment more actively back-donates electron density to the ligand antibonding MO $3b_1$.

The 5a′ MO in **1** for the most part involves the overlap of the Co(1) d_{z^2} and $d_{x^2-y^2}$ and the Co(2) d_{z^2} and $d_{x^2-y^2}$ orbitals, respectively. These overlaps provide the major portion of the metal–metal bond. The remaining seven bonding MO's are predominantly metal in character and involve interactions between the Co atoms and the carbonyl ligands. The 8a′ MO represents the HOMO in **1** and is strongly localized on the Co(2) d_{xz} orbital. The LUMO, 9a′, is predominantly metal–metal antibonding in character. This MO lies relatively low in energy, and it may prove possible to populate this orbital by electron pair donation from a Lewis base or by chemical or electrochemical reduction.

The Mulliken population analysis (Table VII) also appears to be consistent with the qualitative electron-counting procedure outlined above. In particular, the Co(2) atom carries a greater relative negative charge than Co(1), and it might be expected that electron (base) addition would occur at Co(1). The calculated charge on the phosphorus atoms of the complex is 1.28+, which represents a charge transfer of 0.61+ away from each phosphorus atom compared to the uncoordinated ligand. This charge shift is in qualitative agreement with the observed large downfield shift of the ^{31}P NMR resonance in **1** (307 ppm) compared to that of $[CH_3NCH_2CH_2N(CH_3)P^+][PF_6^-]$ (264 ppm). By comparison, the phosphorus atom in $MoCp(CO)_2(PN(CH_3)CH_2CH_2NCH_3)$ has a phosphorus atom charge of 0.80+ and a ^{31}P δ 271.[8,10] Although there are many factors that contribute to ^{31}P chemical shifts, the dramatic downfield shifts found in metallophosphenium ion complexes seem to parallel the net charge found on the phosphorus atom.

From the results of the structural and electronic analysis of **1**, it is evident that the aminophosphenium ion $PN(CH_3)CH_2CH_2NCH_3^+$ offers a unique set of ligand qualities not found in the usual collection of tricoordinate phosphine ligands or dicoordinate alkyl or aryl phosphido ligands. The further exploitation of these ligation properties with other organometallic fragments is presently under study.

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Registry No. 1, 79391-62-1; $FPN(CH_3)CH_2CH_2NCH_3$, 33672-91-2; $NaCo(CO)_4$, 14878-28-5.

Supplementary Material Available: Listings of structure factors, hydrogen atom positional parameters, thermal parameters, and least-squares planes (13 pages). Ordering information is given on any current masthead page.